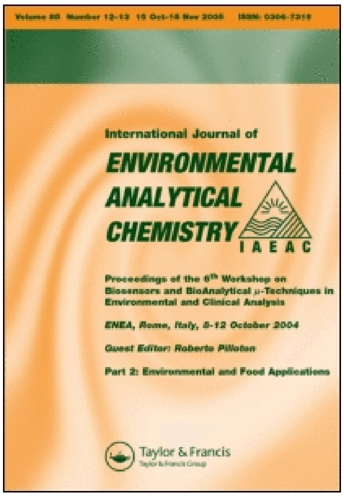

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Junyapoon, Suwannee , Bartle, Keith D. , Ross, Andrew B. , Cooke, Michael and Smethurst, Brian F.(2000) 'Programmed Temperature Vaporization Injection (PTV) in the Analysis by Gas Chromatography-Mass Spectrometry (GC-MS) of the Constituents of Landfill Gas', International Journal of Environmental Analytical Chemistry, 77: 4, 337 — 348

To link to this Article: DOI: 10.1080/03067310008032701

URL: http://dx.doi.org/10.1080/03067310008032701

Intern. J. Environ. Anal. Chem., Vol. 77(4), pp. 337-348
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PROGRAMMED TEMPERATURE VAPORIZATION INJECTION (PTV) IN THE ANALYSIS BY GAS CHROMATOGRAPHY-MASS SPECTROMETRY (GC-MS) OF THE CONSTITUENTS OF LANDFILL GAS

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(Received 6 March 2000; In final form 13 May 2000)

Trace volatile compounds emitted from both domestic and industrial landfills have been identified by programmed temperature vaporization injection (PTV) coupled to gas chromatography with detection by ion-trap mass spectrometry (GC-ITD/MS). The PTV injection system has been developed using a combination of two six-port valves to achieve problems of interference in GC-MS while loading sample. A large volume of landfill gas was re-concentrated onto a sorbent trap, then rapidly liberated into the GC-ITD/MS system by programmed thermal desorption. Using this method, trace volatile compounds in gases from both domestic and industrial landfills such as aromatic hydrocarbons, terpenes, chlorinated hydrocarbons, and sulfur compounds can be identified and quantified.

Keywords: Programmed temperature vaporization (PTV); GC-ITD/MS; trace volatile compounds; landfill gas

INTRODUCTION

Almost all solid waste, both domestic and industrial, is disposed of in landfills [1] since this is the most economic form of disposal. Although the EC Landfill Directive [2] is aimed at reducing the amount of biodegradable municipal waste disposed of in landfills, the impacts of old and current landfills on the environment will remain for the foreseeable future. Landfill gas is inevitably generated

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from the decomposition of organic compounds by micro-organisms. Variations between landfill gases are dependent on the composition of solid wastes, age of landfills, climatic conditions and landfill operation [1]. As landfill gas has various impacts on the environment such as unpleasant odours, poor air quality, and human health problems [1, 3–4], its composition has been widely studied. The increase in combustion of landfill gas also makes a detailed breakdown, more important, as trace impurities can often have a bearing on emission profiles [5]. The level of carbon dioxide and methane in landfill gas is monitored routinely by the site operators, but trace volatile compounds are not normally studied because there are no current legislative requirements. Some volatile organic compounds (VOCs) emitted from landfills are potentially mutagenic or carcinogenic e.g. vinyl chloride, and many studies of these trace volatile compounds have been reported [4, 6–10]. Although there are several reports concerning the composition of VOCs in landfill gases, there have been only a few studies of organosulfur compounds [9–10], and there is no work identifying trace volatile compounds in industrial landfill gases. Brookes and Young [9] detected volatile compounds emitted from landfills using concentration tubes containing Tenax GC and Porapak Q, and a condensate trap, with a cryogenic injection system. Non-polar species, trapped onto Tenax GC, were analysed by using a non-polar capillary GC column coupled to a mass spectrometer, whilst low molecular weight compounds were adsorbed onto Porapak Q, and water-soluble compounds were condensed in the cold trap. Final analysis was performed using a packed GC column coupled to a mass spectrometer. Both techniques required long analysis times. Wilkins and Larsen [10] identified sulfur compounds and volatile organic compounds in headspace gases produced by household waste collected by refuse trucks. Similar experiments were carried out on gases generated by micro-organisms from household waste and building materials in nylon bags. The sample gases were concentrated on a Tenax TA tube, then desorbed using an automated thermal desorption (ATD)-GC-MS with a cold trap operating at temperatures between −30 °C and 300 °C. Methanethiol and dimethyl sulfide could not be analysed using this technique because of the limitations of the Tenax TA adsorbent. Allen *et al.* [7] also analysed volatile hydrocarbon and chlorinated compounds in landfill gas, using the same technique. The gas samples were collected into sorbent tubes containing a series of adsorbents, Tenax TA, Chromosorb 102 and Carbosieve SIII. The sorbent tubes were immediately capped with Swagelok caps with PTFE ferrules at both ends and brought back to the laboratory for analysis. However, even with this precaution, gas samples may still be lost before analysis. This sampling method also requires a sorbent tube for each individual gas sample.

The aim of this work was to apply a simple sampling and analysis technique originally developed for air analysis [11] to landfill gas analysis and to develop

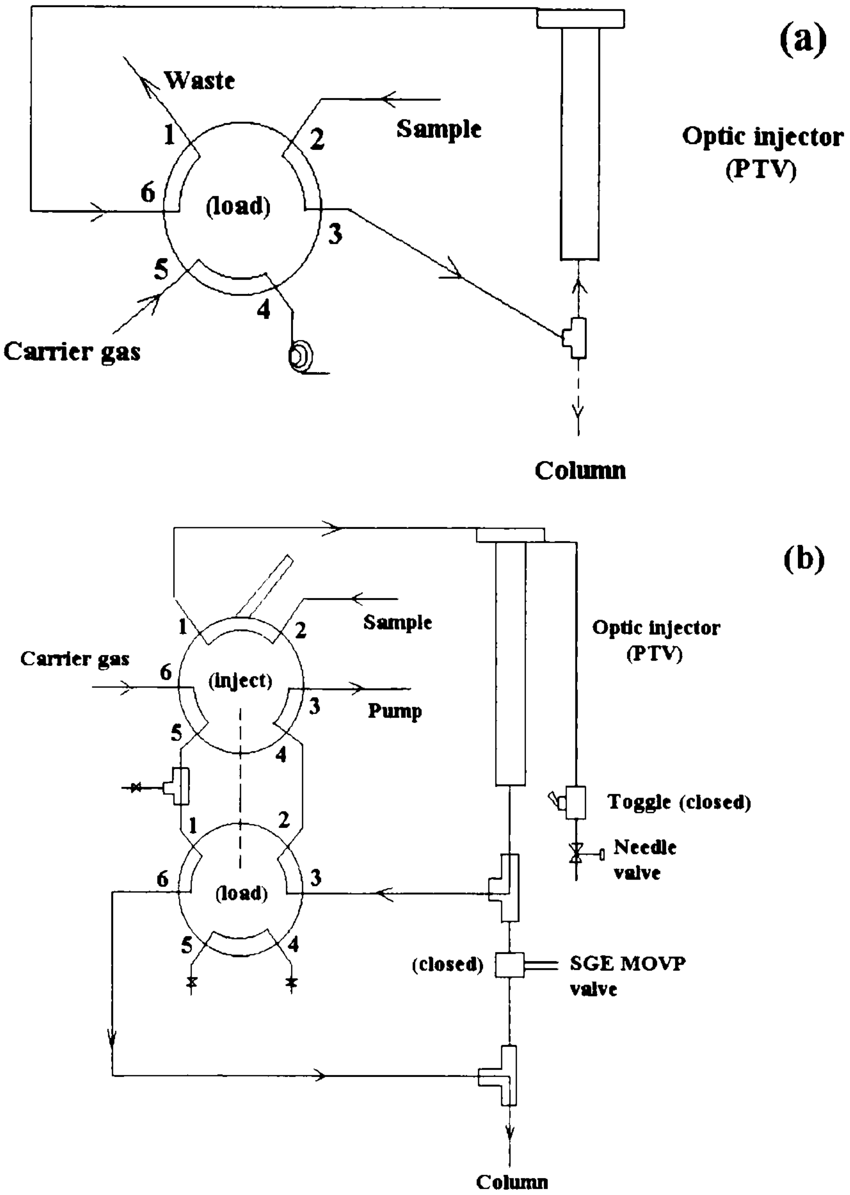


FIGURE 1 Schematic of two injection systems, (a) single valve injection system, and (b) dual valve injection system

the valve configuration for linkage to a mass spectrometer. The system consists of a programmed temperature vaporization injection (PTV) coupled to a gas chromatograph with an ion trap mass spectrometer as detector (GC-ITD/MS). Characterisation of trace volatile compounds in both domestic and industrial landfill gases has been performed. Samples of landfill gases were collected in evacuated canisters from various landfill sites and brought back to the laboratory for analysis. A large volume of each gas sample (up to 600 ml) was passed through a sorbent tube containing Tenax GC which was then heated rapidly to transfer the analytes onto the GC column. The valving configuration linking the PTV to the chromatographic column has been developed further from previous work [12] ensuring all sample gas passes through the sorbent trap, unlike in the single valve method where escape onto the column is possible. This procedure eliminates any effect of increasing pressure and also contamination of the GC column during loading of the gas sample (Figure 1). The developed system has considerable advantages over previously employed sampling methods. Primarily, the instrument maybe operated continuously on-site, requiring little operator interaction. For off-line laboratory analysis, it also has the following four advantages. Firstly, gas samples are taken easily into an evacuated canister without a requirement of a sampling pump. The stability of VOCs and sulfur compounds stored in a Silcosteel canister has previously been studied [13]. Secondly, only one sorbent trap is used, which can be re-used after each analytical run. Thirdly, a wide range of compounds can be analysed within one analysis; this can reduce analysis time. Finally, it eliminates the requirement of a cryogenic injection system so that water vapour is not retained by the injection process, and is not introduced into the chromatographic column. The coupling of mass spectrometry provides increased sensitivity and selectivity.

The application of the developed PTV-GC-ITD/MS to landfill gas has been demonstrated by characterising trace volatile compounds from different landfill sites containing different types of waste and landfill age. We have previously detected a range of sulfur containing compounds in household landfill gas using PTV-GC-AED [12]. These, and others have now been identified by using both retention time of standards and library matching by PTV-GC-ITD/MS.

EXPERIMENTAL

Materials and instruments

A Finnigan MAT ITS-40 ™ ion trap mass spectrometer was coupled to a Varian gas chromatograph fitted with a programmed temperature vaporization injection

(PTV) (AI-Cambridge, ATAS, UK). The GC column was a DB 1701 fused silica capillary, coated with 1 µm film thickness, 14% cyanopropyl phenyl silicone, 30 m × 0.25 mm i.d. (J&W Scientific Incorporated). The PTV injection system used a combination of two six-port Rheodyne valves (model 7010), assembled with stainless steel and VESPEL rotor seal (Supelco), and stainless steel tubes, 1.63 mm o.d., as the connection as shown in Figure 1 (b). These valves were held at room temperature during operation. 60–80 mesh Tenax GC (Thames-Restek, UK) was used as the sorbent trap. The PTV injector was programmed from 30 °C (initial temperature) to 210 °C at 16 °C min^{-1}, holding at 210 °C for 1 min. The GC oven was programmed from 40 °C (initial temperature), holding at 40 °C for 5 min, to 75 °C at 5 °C min^{-1}, holding at 75 °C for 5 min, then increased from 75 °C to 110 °C at 3 °C min^{-1}, and then increased from 110 °C to 220 °C at 20 °C min^{-1}. Helium was used as the carrier gas at a flow rate of 1 ml min^{-1}. The transfer line between the GC and ITS-40 was operated at 250 °C. The ion trap MS was operated in electron impact (EI) mode with a mass range 35–400 amu, scan speed 1 second and a filament/ multiplier delay of 30 seconds. After each analytical run, the sorbent trap was cleaned with the transfer valve in the inject mode and the split valve open, to remove contamination from the trap. The trap was purged with helium gas while the PTV injection was heated from 30 °C to 240 °C holding at 240 °C for 30 minutes. A blank was run after each cleaning. Previous tests have been shown the compounds of interest to be desorbed quantitatively from the sorbent trap. The cleaning cycle ensures that high molecular weight residues contained in the trap do not pass through to the GC column.

Landfill sites

Samples of gas emitted from two domestic landfills (sites A and B) and one industrial landfill (site C) were studied. To assess the effect of landfill age on the constituents of evolved gas, two different domestic landfills, sites A and B, were studied. Landfill site A contained primarily domestic wastes but also received some chemical waste in limited volume. It was situated on an old quarrying site with a lining system and had been covered for about two years. Landfill site B contained similar waste to site A, but had been covered for some five years. Landfill gases from different sampling points on landfill site B were compared. Site B-1 is situated about 200 metres from site B-2. Industrial landfill site C was still active and was composed of industrial wastes such as general factory refuse, both special and controlled waste, filter cake, gypsum, demolition waste, ash, laboratory waste, and asbestos.

TABLE I Trace volatile compounds identified in both domestic (sites A and B) and industrial (site C) landfill gas (see chromatograms in Figure 2 (a), (b), and (c), respectively)

Site A		*Site B*		*Site C*	
Compound (Peak No.)		*Compound (Peak No.)*		*Compound (Peak No.)*	
Sulfur compounds					
Dimethyl sulfide	**(2)**	Dimethyl sulfide	**(1)**	Dimethyl sulfide	**(1)**
		Dimethyl disulfide	**(3)**	Ethyl methyl sulfide	**(2)**
		3-Thiophenethiol	**(5)**	Dimethyl disulfide	**(5)**
Aromatic hydrocarbons / Hydrocarbons					
Benzene	**(5)**	Benzene	**(2)**	Benzene	**(3)**
Toluene	**(7)**	Toluene	**(4)**	Toluene	**(6)**
Nonane	**(9)**	Nonane	**(6)**	Nonane	**(8)**
Ethyl benzene	**(10)**	Ethyl benzene	**(7)**	Ethyl benzene	**(9)**
1,4/1,3-Dimethyl benzene	**(11)**	1,4/1,3-Dimethyl benzene	**(8)**	1,4/1,3-Dimethyl benzene	**(10)**
1,2-Dimethyl benzene	**(12)**	1,2-Dimethyl benzene	**(9)**	1,2-Dimethyl benzene	**(11)**
1,2,4-Trimethyl benzene	**(13)**	1,2,4-Trimethyl benzene	**(11)**	1,2,4-Trimethyl benzene	**(12)**
1,3,5-Trimethyl benzene	**(14)**	1,3,5-Trimethyl benzene	**(12)**	1,3,5-Trimethyl benzene	**(13)**
1,2,3-Trimethyl benzene	**(16)**	1,2,3-Trimethyl benzene	**(14)**	1,2,3-Trimethyl benzene	**(15)**
		1-Methyl-3-propyl benzene	**(15)**	1,1-Dimethyl ethyl benzene	**(17)**
				1-Nitroethyl benzene	**(19)**
Chlorinated compounds					
1,2-Dichloroethene	**(1)**	Cyclohexane methyl dichloroacetate	**(10)**	Trichloroethylene	**(4)**
1,1-Dichloroethane	**(3)**			Tetrachloroethylene	**(7)**
1,1-Dichloroethene	**(4)**				
Trichloroethylene	**(6)**				
Tetrachloroethylene	**(8)**				
Terpenes					
3-Carene	**(15)**	3-Carene	**(13)**	3-Carene	**(14)**
				Limonene	**(16)**
				α – Pinene	**(18)**

Sample preparation

Standard preparation

In view of the wide range of volatilities of the compounds investigated, only semi-quantitative determinations were possible, and these were based on detection responses determined as follows.

10 µl of each liquid sulfur standard, dimethyl sulfide, ethyl methyl sulfide, diethyl methyl sulfide, dimethyl disulfide, dially sulfide, propyl sulfide, diethyl disulfide, methyl propyl disulfide, and propyl disulfide (Aldrich), were mixed in a two-litre flask sealed with a SUBA seal, previously flushed with nitrogen gas. 0.1 ml of the flask contents was injected into the sorbent trap, using a gas tight syringe, and a split ratio of 30 ml min^{-1} and then desorbed into the GC-ITD/MS by programmed thermal desorption. 15 µl of a number of liquid hydrocarbon (benzene, toluene, nonane, α-pinene), chlorinated hydrocarbon (dichloromethane, chloroform, trichloroethylene, tetrachloroethylene, chlorobenzene), and oxygen containing standards (ethanol, propan-1-ol, methyl ethyl ketone, methyl isobutyl ketone)(Aldrich), were mixed in a 250 ml flask sealed with a SUBA seal, previously flushed with nitrogen gas. As above, 0.1 ml of the flask contents was injected into the sorbent tube and analysed with the same analytical parameters as mentioned above. All standards were prepared at room temperature.

Landfill gas samples

Landfill gases were taken either directly from ducts (domestic) or from wells (industrails) through a 1 m long Teflon tube (1.63 mm o.d.) into evacuated canisters (3.2 1 Silcosteel canisters, Thames-Restek, UK). All samples were collected at room temperature. The filled canisters were brought back to the laboratory and pressurised with helium gas to two bar, measured with a pressure gauge. 200 ml of sample gases from landfill sites A and B-1, 500 ml of sample gas from landfill site B-2, and 600 ml of sample gas from landfill site C (measured at atmospheric pressure) were passed through the sorbent trap and injected into the GC-ITD/MS by programmed thermal desorption.

RESULTS AND DISCUSSION

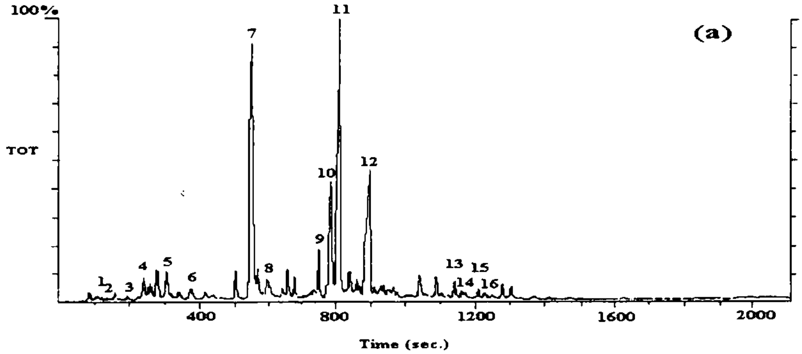
The total ion-current chromatograms of gases from domestic landfill sites A and B, and the industrial landfill site C are shown in Figure 2. The method was found to be repeatable. Aromatic and aliphatic hydrocarbons, terpenes and chlorinated hydrocarbons were identified (Table I) in all the emissions from all three sites by means of the retention times of standards and mass spectra. Toluene and C_2-substituted benzenes were the compounds present at highest concentration in both domestic and industrial landfill gases. The VOCs identified were similar to those found in previous work [4, 9–10]. The results of semi-quantitative determinations of sulfur compounds, aromatic hydrocarbons, and chlorinated compounds, derived from peak areas of mass spectra of standards and samples, from the three different landfill sites are shown in Table II. Because of the different methods of sample collection at each landfill site, it is difficult to compare the concentrations of trace compounds. This can be seen from the concentrations of constituents in the gas from landfill site C, which were apparently low because the gas sample was diluted with air during sampling. The older domestic landfill site (Figure 2(b)) was found to release more higher molecular weight compounds than the newer one (Figure 2(a)), a result consistent with the more rapid decomposition of smaller molecules by micro-organisms.

TABLE II Concentrations of compounds detected in landfill gases

Compound	*Concentrations of compounds detected in landfill gases* ($\mu g\ l^{-1}$)			
	Site A	*Site B-1*	*Site B-2*	*Site C*
	(200 ml)	*(200 ml)*	*(500 ml)*	*(600 ml)*
Dimethyl sulfide	a	a	a	a
Ethyl methyl sulfide	ND	ND	ND	< 1
Dimethyl disulfide	ND	20	5	< 1
Benzene	15	a	1	< 1
Toluene	250	140	50	10
Nonane	60	140	40	< 1
Trichloroethylene	20	ND	ND	< 1
Tetrachloroethylene	40	ND	ND	< 1

Remark: a = detected but the concentration was too low to quantitate
ND = not detected

The constituents of gases emitted from different sampling points of the same landfill site (site B) were similar but their concentrations greatly differed (Table II). Sulfur compounds found in landfill gas in previous work [12] by GC with sulfur selective (181 nm emission line) atomic emission detection were identified by PTV-GC-ITD/MS. Dimethyl sulfide, dimethyl disulfide, and 3-thi-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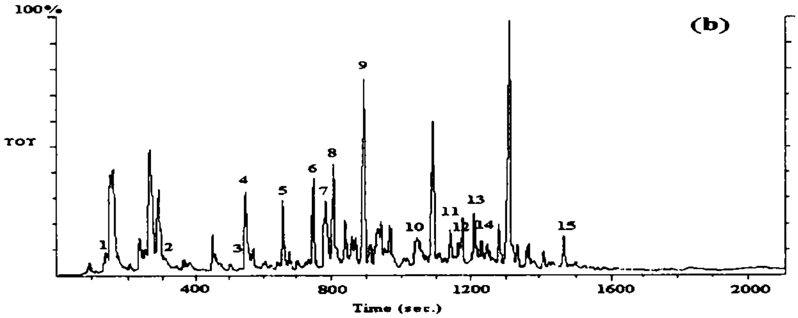
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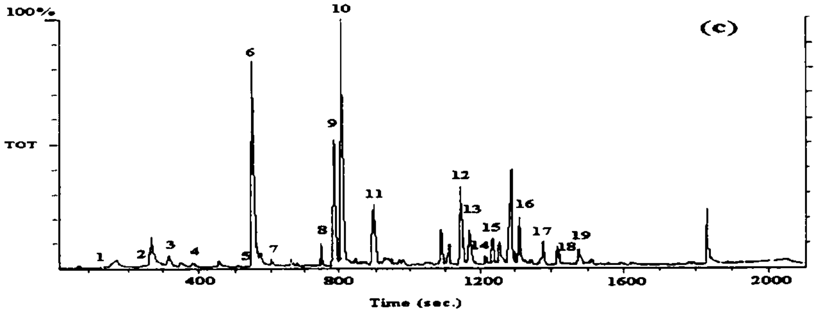
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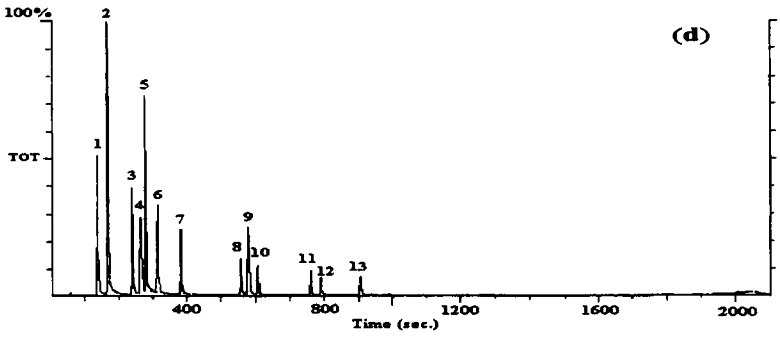

FIGURE 2 (a), (b), and (c) Mass chromatograms of 200 ml-600 ml of domestic landfill gas site A, B, and of industrial landfill gas site C injected via PTV. Peak identities were confirmed using retention times of constituents of standard mixture (see chromatogram in d). The identification of chromatograms in (a), (b), and (c) is shown in Table I. Peak identifications of standard mixture in (d): 1, ethanol; 2, dichloromethane; 3, methyl ethyl ketone; 4, propan-1-ol; 5, chloroform; 6, benzene; 7, trichloroethylene; 8, toluene; 9, methyl isobutyl ketone; 10, tetrachloroethylene; 11, nonane; 12, chlorobenzene; 13, α-pinene

ophenethiol were identified in the domestic landfill, whilst dimethyl sulfide, ethyl methyl sulfide, dimethyl disulfide, were identified in the industrial landfill (Table I). Mass spectra of these sulfur compounds are shown in Figure 3. The alkyl sulfide compounds most likely result from transformation of sulfur compounds by micro-organisms in landfills. A similar methylated sulfur compound, dimethyl sulfide, has also been found in an anaerobic peat [14]. These results are consistent with biomethylation reactions. This work demonstrates the application of the developed PTV injection system coupled to GC-MS for environmental monitoring work.

CONCLUSIONS

The direct coupling of PTV to GC-MS permits the application of gas sample analysis. The methodology presented may prove particularly useful for the types of trace level gas analysis encountered in occupational health and environmental disciplines. Volatile organic compounds emitted from both domestic and industrial landfills can be simply analysed using the direct coupling of PTV to GC-ITD/MS. With this large volume injection system operating without cryogenic injection, sulfur compounds, aliphatic and aromatic hydrocarbons, chlorinated compounds, and terpenes were identified and semi-quantified in both

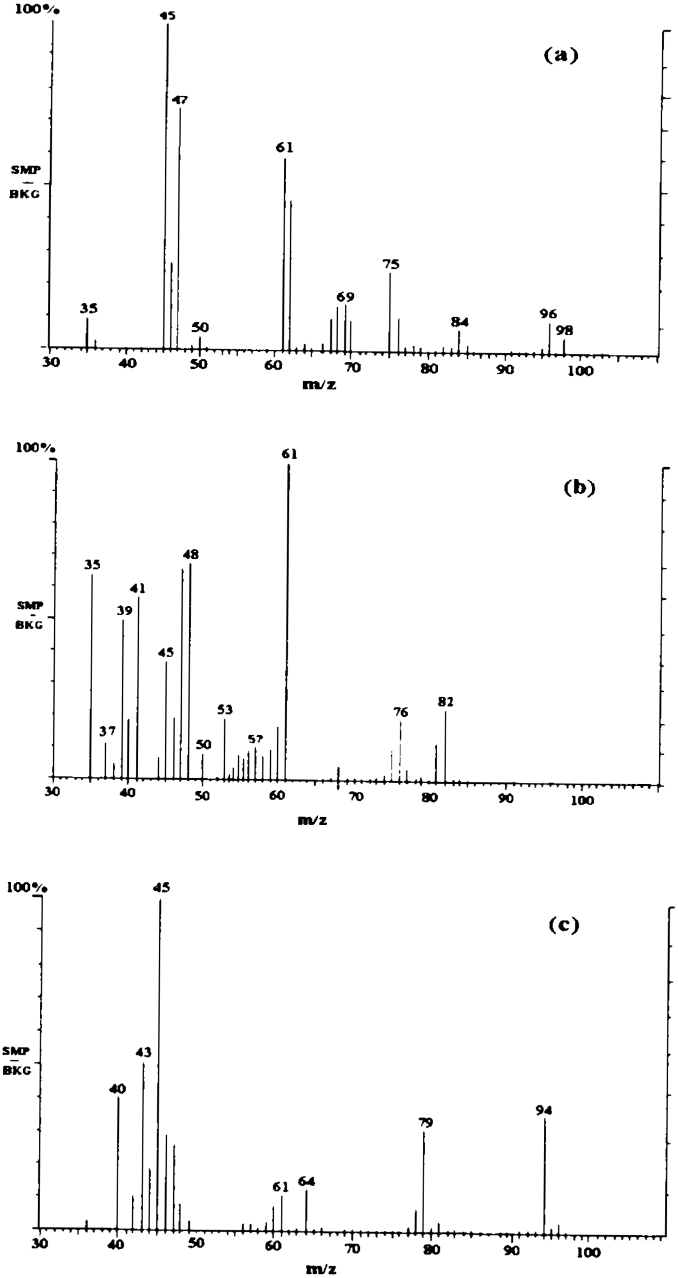

FIGURE 3 Mass spectra shown in (a), (b), and (c) confirmed the identification of peak 1, dimethyl sulfide; peak 2, ethyl methyl sulfide; and peak 5, dimethyl disulfide in Figure 2 (c)

domestic and industrial landfills. The age and the waste type present in the landfill affect the constituents and their concentrations. In addition, different points of the same landfill site release different concentrations of similar gas species. The technique can be used for on-line monitoring of trace gas composition.

Acknowledgements

The authors are grateful to the Government of Thailand for support of this work through a studentship (SJ) and also thank Mr Bernard Frere, and the staffs of the landfill sites for their assistance.

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