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# ANALYSIS OF THE TRACE VOLATILE ORGANIC COMPOUNDS IN LANDFILL GAS USING AUTOMATED THERMAL DESORPTION GAS CHROMATOGRAPHY-MASS SPECTROMETRY

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A method is presented for the determination of trace volatile organics in landfill gas using automated thermal desorption—gas chromatography—mass spectrometry. The method includes preconcentration of the trace volatiles using sample tubes containing a sandwich of three adsorbents, Tenax TA, Chromosorb 102 and Carbosieve SIII. Breakthrough and recovery measurements were carried out on the sample tubes for landfill gas volumes of up to 1 litre. Breakthrough was not observed on any of the samples taken and recovery for all the components was found to be approximately 100%. Over 125 VOCs were identified in the landfill gas.

**KEY WORDS:** Municipal waste, landfill gas, volatile organic compounds (VOCs), thermal desorption, gas chromatography.

## INTRODUCTION

Landfill as a final disposal method has a low priority in the EC hierarchy of waste management options, with waste minimisation being the preferred method. Landfill is, however, by far the most widely used disposal route in the UK, accounting for approx. 90% of controlled waste. Household and other similar wastes contain substantial amounts of organic carbon which is used as a nutrient source by micro-organisms during the process of decomposition. Initially the metabolism of refuse components is dominated by aerobic processes and involves a range of organisms including invertebrates, such as mites, which ingest organic material, together with fungi, bacteria and actinomycetes<sup>1</sup>. As the oxygen becomes depleted anaerobic processes commence, the most important being methanogenesis. The predominant gases released during methanogenesis are typically carbon dioxide (30–35%) and methane (60–65%) together with a large number of trace gas components. The resulting mixture is assigned the general description of 'landfill gas'.

Although monitoring of the carbon dioxide and methane levels in landfill gas is routinely carried out by the site operators on a daily basis, the trace components present are generally overlooked. The main reason for this is that at the present time there are no legislative requirements for landfill operators to monitor trace gases.

Identification and quantification of the trace components is, however, important for several reasons. Firstly, a number of studies have identified components which could be hazardous to the landfill worker's health and affect local and, in some cases, global air quality<sup>2-16</sup>. Secondly, the information acquired from sites of differing ages may provide a valuable insight into waste decomposition processes. Thirdly, an increasing number of landfill sites are using landfill gas to fuel modified diesel engines for electricity generation. Gases containing chlorinated compounds react with oxygen and water during the combustion process forming HCl, which contributes to the corrosion of surfaces within the combustion chamber<sup>2</sup>. Analysis of the trace volatiles can identify the presence of chlorinated compounds and zones of landfills where the gas is considered unsuitable can be isolated accordingly.

The objective of this study was to develop a fast, convenient and robust method for the determination of all the trace volatile organics in landfill gas. This poses a number of problems for the analytical chemist. The concentrations present are typically of the order 0–150 mg m<sup>-3</sup>, therefore, preconcentration of the individual components must take place prior to analysis. One method of achieving this is to pass the gas through a sampling tube containing a suitable adsorbent which retains the analytes of interest and not the bulk matrix gases. The adsorbed analytes can then be extracted by either solvent or thermal desorption.

A number of sorbent tube sampling techniques for the analysis of landfill gases have been reported. Brooks and Young<sup>3</sup> use a dual-tube system, one containing Tenax GC and the second containing Porapak Q. In order to prevent breakthrough of the lighter components, the second half of the Porapak Q tube was cooled to –80°C using solid carbon dioxide. Assmuth and Kalevi<sup>4</sup> and Harkov *et al.*<sup>5</sup> both used a single Tenax tube and restricted their investigations to the higher-molecular-weight trace components. The approach outlined in this paper offers a number of advantages over the aforementioned methods. Firstly, all the trace volatile organic components present in landfill gas are trapped on a single tube without the need for sub-ambient cooling. Secondly, sampling can be carried out by site personnel, which reduces analysis costs. Thirdly, as all the trace components are trapped on one tube, analysis times are greatly reduced.

### *Study site*

The site used for the initial studies was a containment site with only the lower 15% of the waste being saturated with leachate. Waste has been deposited since 1985 and completed areas progressively restored. The existing gas extraction system consists of a series of vertical wells and gas transmission lines that convey landfill gas to a blower. The extracted landfill gas is being used to fuel an electricity generation system.

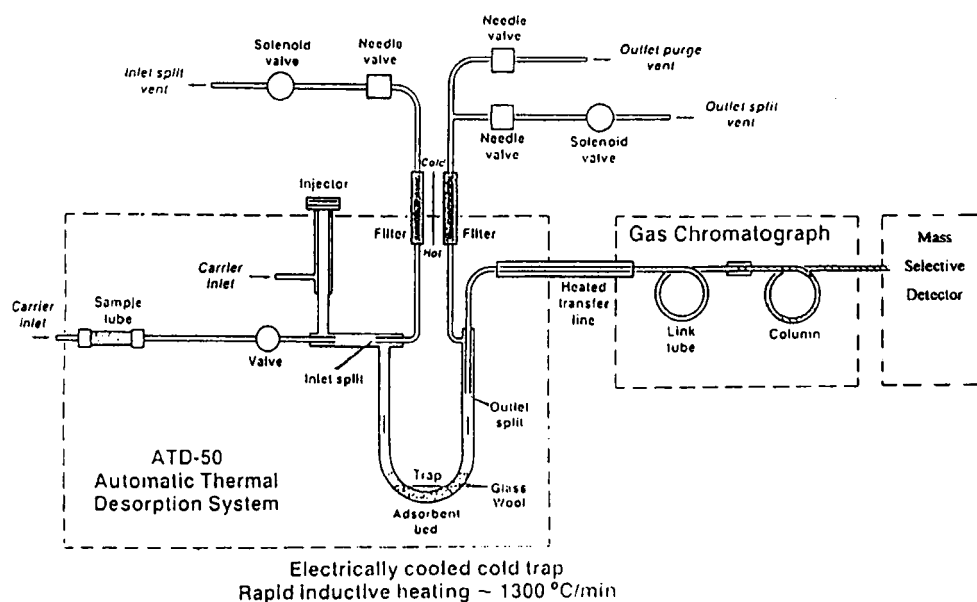
## EXPERIMENTAL METHODOLOGY

### *ATD-GC-MS*

The technique developed for the analysis of the landfill gas samples was Automated Thermal Desorption-Gas Chromatography-Mass Spectrometry. The thermal desorber can be considered as an automated injector for the gas chromatograph. As with any

chromatographic injector, the aim is to introduce as much of the analytes onto the column in as short a time interval as possible so that chromatographic performance is not compromised. This is achieved by two-stage desorption. The aim of the first desorption stage is to obtain 100% elution of the components of interest from the ATD sampling tube, and, depending on whether the instrument is operating in split or splitless mode, simultaneously transfer 100% of these components onto a cold trap at  $-30^{\circ}\text{C}$ . The aim of the second desorption stage is to achieve 100% elution of the retained components from the cold trap in as short a time interval as possible, so that they are transferred to the analytical column as a narrow band of vapour. The instrument used for the work presented in this paper was a Perkin Elmer ATD50, a schematic diagram of which is shown in Figure 1. The ATD50 was fitted with a multiple splitter accessory which enables the flow of carrier/sample gas to be reduced prior to the cold trap (inlet splitting), after the cold trap (outlet splitting) or a combination of both (multiple splitting). As the landfill gas samples contained relatively high concentrations of volatile organic compounds, the splitter accessory was operated in the multiple splitting mode.

The instrumentation used for the separation and detection of the trace components was a Hewlett Packard 5890 gas chromatograph connected to a Hewlett Packard 5970 mass selective detector. The above system was controlled with a Hewlett Packard 9000 workstation running HP MS-Chemstation software under UNIX. The mass range used for all the analyses was 20–250 amu. A lower limit of 20 amu was selected to exclude interference from water vapour. Fragmentation pattern identification was achieved by software comparison with the Wiley/NBS database of mass spectra. The main benefit of this system is that it allows direct identification of the majority of unknown components without the use of external reference compounds.



**Figure 1** Schematic diagram of a Perkin Elmer ATD50 (reproduced by kind permission of Perkin-Elmer Ltd).

### *Sampling tubes*

The use of sorbent tubes requires careful consideration of the adsorbent-adsorbate system<sup>17-32</sup>. For example, if a strong adsorbent such as graphitised carbon is used it may prove difficult to extract higher-molecular-weight components such as the substituted aromatics. Conversely if a relatively weak adsorbent such as Tenax TA is used, lighter components such as propane, butane or the chlorofluorocarbons would only be partially adsorbed or not adsorbed at all. As the volatile organics present in the gas were expected to have a wide range of boiling points, the first problem to address was the choice of adsorbent. This was overcome by using a sandwich of adsorbents, with each layer having different adsorptive characteristics. They were prepared by filling 6.4 mm I.D. × 89.0 mm stainless-steel tubes with a 1:1:1 ratio by volume of the following adsorbents packed in series: Tenax TA (80/100 mesh)/Chromosorb 102 (80/100 mesh)/Carbosieve S111 (60/80 mesh).

A summary of the physical properties of the adsorbents is given in Table 1. The adsorbents were arranged in order of increasing adsorptive properties and stainless-steel gauzes placed between the adsorbent layers to reduce back diffusion. A blank run was carried out on each adsorption tube prior to sampling or calibration. Each sampling tube was then immediately sealed with Swagelok® end-caps fitted with PTFE ferrules.

### *Sampling procedure*

Gas samples were taken directly from the gas extraction array which had been installed to pipe the landfill gas from active areas of the site to the generator. 500 ml of landfill gas was drawn through the sampling tubes at 50 ml/min using a Gilian® Personal Air Sampler fitted with a constant-low-flow module. Gilian® pumps were selected because they automatically compensate for any changes in backpressure which may occur during the sampling process to an accuracy of ± 5%. The tubes were then immediately capped and stored at 4°C until analysed.

### *Calibration procedure*

Quantitation was achieved by an external standard method. Twelve components, all of which were liquids at room temperature, were selected such that most of the compounds identified in landfill gas were either in the standard mixture or were

**Table 1** Physical characteristics of selected adsorbents.

<i>Physical properties</i>	<i>Tenax TA</i>	<i>Chromosorb 102</i>	<i>Carbosieve S111</i>
Type	POP*	STY-DVB**	Carbon molecular sieve
Polarity	Low polarity	Slightly polar	Low polarity
Water affinity	Low	Low	Low
Surface area (m <sup>2</sup> /g)	20–35	300–400	ca. 800
Temperature limit (°C)	375	250	400
Boiling-point range of adsorbed analytes (°C)	100–350	30–180	–30–80

\*POP: Phenylphenylene oxide polymer.

\*\*STY-DVB: Styrene-divinylbenzene copolymer.

isomers of one of the standards. A list of the components used is given in Table 3. Stock mixtures containing 0.5 ml of each calibrant were prepared on a daily basis using high-purity HPLC-grade chemicals obtained from Fisons. Initially, the calibration mixtures were prepared by diluting known volumes of the stock mixture in methanol. However, it was found that the methanol interfered with the adsorption process which resulted in a loss of precision. This problem was overcome by injecting the neat stock mixture onto the sampling tubes and increasing the overall split ratio on the ATD50 from 100:1 to 200:1. The calibrated tubes were prepared as follows; the tubes were clamped in an upright position with a plug of silanised glass wool inserted into the top. The Gilian® pumps were then used to draw a 50 ml/min flow of clean air through the tubes for a period of 10 min. Immediately after switching the pump on, a known volume (0.05, 0.20, 0.35 and 0.50 µl) of the neat 12-component mixture was injected onto the silanised glass wool, taking care not to push the needle into the bed of packing. Two sets of standards were analysed, one before the landfill gas samples and one after.

## RESULTS AND DISCUSSION

A summary of the optimised analytical conditions is given in Table 2. It is important to note that in developing these conditions a large number of inter-related factors had to be taken into account. An example of this is the choice of column. Initial work was carried out using a 25 m BP5 Ultra 2 column, with 0.25 µm film thickness. Although this was adequate for site screening purposes, the column produced poor

**Table 2** Instrumental Set-up.

<i>Perkin elmer ATD50</i>	<i>Hewlett packard 5890</i>
<b>Mode</b> Two-stage desorption	<b>Injector temperature</b> 250°C
<b>Inlet split</b> 27 ml min <sup>-1</sup>	<b>Detector</b> HP5970B
<b>Outlet split</b> 17 ml min <sup>-1</sup>	<b>Detector temperature</b> 250°C
<b>Overall split ratio</b> 200:1	<b>Detector mass range</b> 20–250 amu
<b>Cold trap low</b> –30°C	<b>GC column</b> RTX®-1; 60 m; 0.32 mm ID; 1.5 µm d <sub>f</sub> .
<b>Cold trap high</b> 300°C	<b>Oven temperature programme</b> 35°C for 5 min, then ramp at 5°C per min to 180°C
<b>Trap adsorbent</b> Tenax TA	<b>Carrier gas</b> Helium
<b>Desorption temperature</b> 250°C	<b>Linear velocity</b> 21 cm sec <sup>-1</sup> (1 ml min <sup>-1</sup> flow rate)
<b>Desorption time</b> 15 min	

**Table 3** Data from analysis of calibration standards.

Compound	Detection limit (mg m <sup>-3</sup> )	Retention time (min)	Weight on tube (µg)	Precision (n = 6) (%RSD)	Correlation Coefficient (R <sup>2</sup> )
Ethanol	0.06	5.99	3.29–32.88	5.1–1.6	0.996
Dichloromethane	0.08	8.15	5.53–55.29	4.6–1.1	0.989
Hexane	0.03	11.57	2.75–27.54	6.0–1.2	0.993
Benzene	0.04	14.16	3.65–36.52	4.4–2.2	0.985
Cyclohexane	0.03	14.64	3.25–32.49	4.7–0.6	0.990
Heptane	0.03	16.48	2.85–28.49	3.8–1.0	0.992
Toluene	0.04	19.42	3.61–36.12	4.8–2.8	0.979
p-Xylene	0.04	24.31	3.58–35.83	6.8–2.4	0.977
Nonane	0.03	25.79	2.99–29.90	6.9–2.4	0.985
n-Decane	0.02	29.88	3.04–30.42	7.8–1.7	0.977
l-Limonene	0.03	31.24	3.51–35.08	6.2–1.0	0.982
n-Dodecane	0.02	37.43	3.12–31.19	5.5–1.6	0.983

resolution of early eluting peaks; benzene and cyclohexane coeluted and the retention times were not reproducible. It was thought that the varying retention times were due to the percentage levels of methane affecting the partitioning of the VOCs between the mobile and stationary phase. Methane is partially adsorbed by the carbosieve and consequently introduced into the GC along with the VOCs. These problems were largely overcome by using a 60 m Restek RTX®-1 (100% dimethyl polysiloxane) column, 1.5 µm film thickness, supplied by Thames Chromatography. The lower phase ratio and increase in sample capacity of the RTX®-1 column enabled reproducible retention times to be obtained. Also the combination of lower phase ratio, decrease in stationary phase polarity and, to a lesser extent, increased column length, greatly improved the separation of the early eluting peaks and allowed the separation of benzene and cyclohexane to be achieved. The use of thick-film capillary columns at elevated temperatures can lead to unacceptable stationary phase bleed. However, column bleed only became significant above 250°C and was minimal in the temperature range used for the VOCs analyses (35–180°C). Column performance was checked periodically by calculating the resolution of benzene and cyclohexane. For a new column, the R<sub>s</sub> value was typically about 2.2. If the R<sub>s</sub> value fell below 1.5 (approximate baseline separation), the column was replaced.

A typical chromatogram of a calibration standard is given in Figure 2. Although the thermal desorber purges the sample tubes with helium prior to desorption of the volatile organics, air trapped within the carbosieve structure is not completely removed (Peak 1). Peak 11 on the chromatogram is an impurity from the 1-limonene stock solution. The results from statistical analysis of the calibration procedure are tabulated in Table 3. Preliminary studies had suggested that it was not possible to obtain an RSD of less than 10% by thermal desorption. The reason for this was found to be related to the desorption cycle programme. The tubes are automatically elevated into the desorption position and held adjacent to the desorption oven at a temperature of 250°C. Desorption of the VOCs does not occur until the GC oven has cooled down to the initial temperature. The ATD then receives a trigger signal from the GC and continues the desorption cycle. It was found that during the delay between the tube being elevated into the desorption position and the ATD starting the desorption cycle, the adsorbed VOCs were slowly being lost. This was overcome by extending the sample delay on the ATD to include the time for

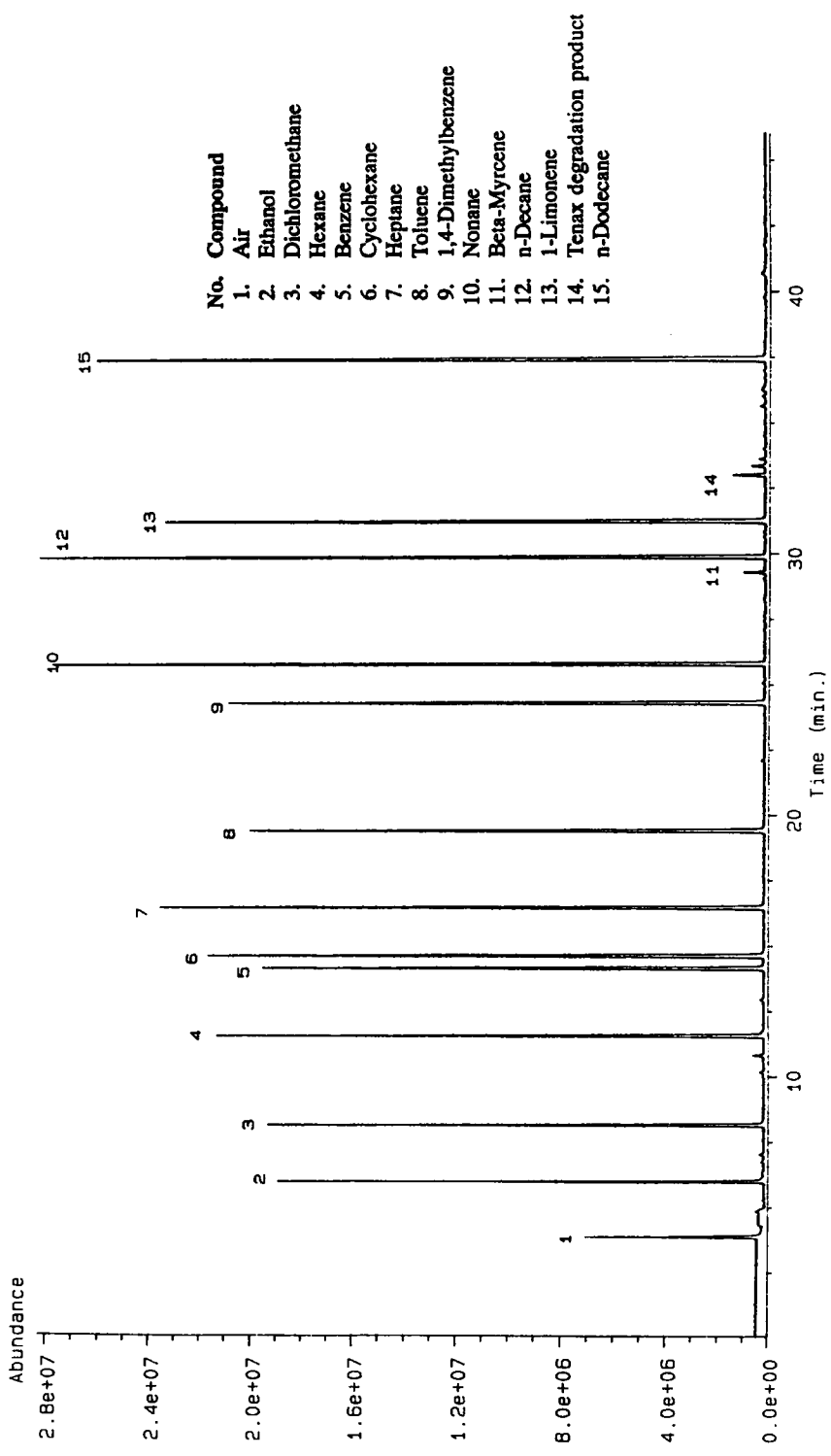


Figure 2 Annotated chromatogram of a calibration standard.



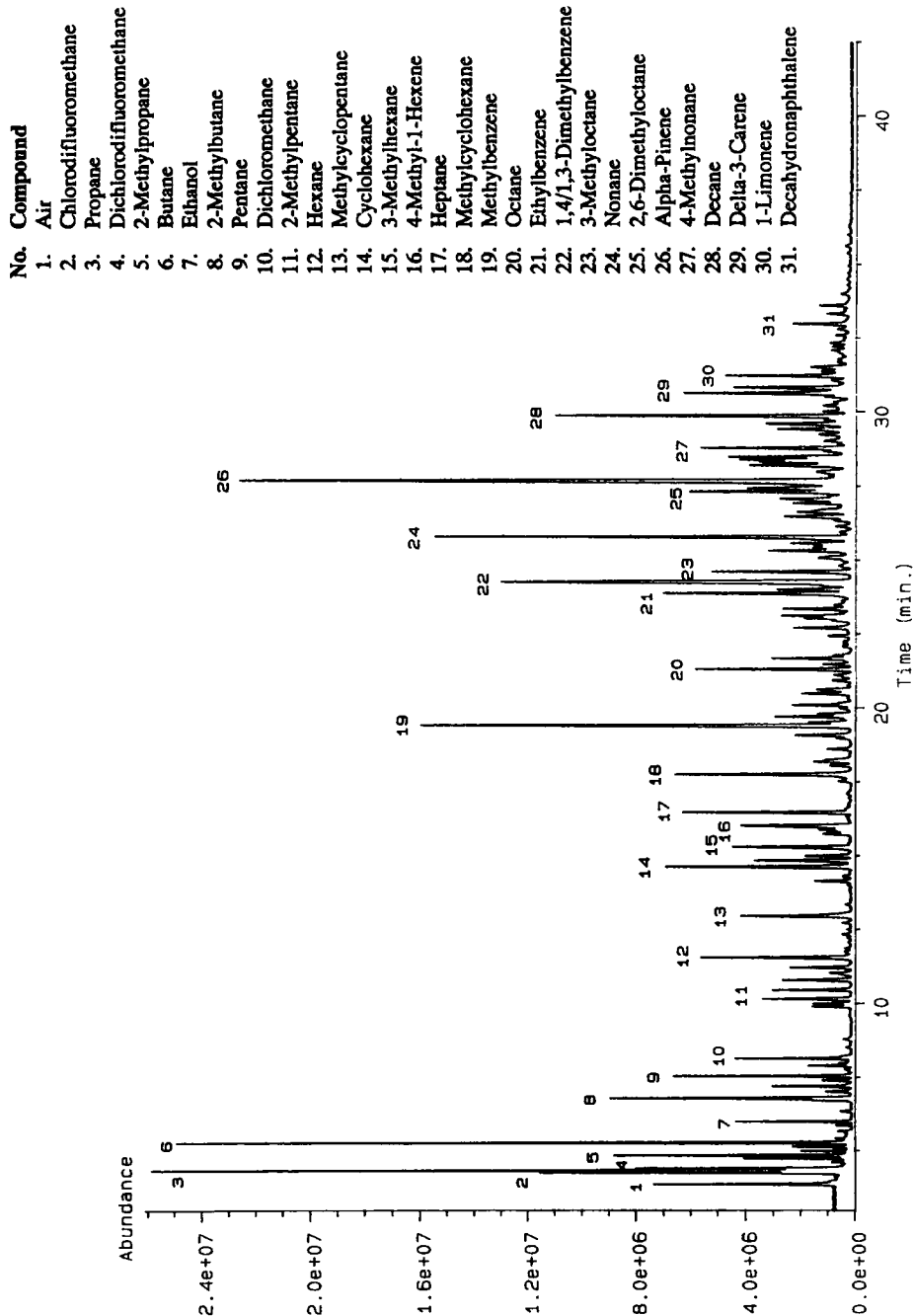


Figure 3 Annotated chromatogram of VOCs in a landfill gas.

the GC oven to cool. A marked improvement in the RSD values was observed with the highest being below 8%. The detection limits quoted in Table 3 relate to a 500 ml sample of landfill gas analysed under the instrumental conditions given in Table 2. Clearly increased sensitivity can be achieved by increasing the volume of landfill gas sampled or decreasing the split ratio on the ATD50.

Breakthrough and recovery measurements were carried out on the sampling tubes for landfill gas volumes of up to 1 litre. Breakthrough was assessed by placing a second sample tube in series with the first and recovery by carrying out a second analysis of the first sample tube. Breakthrough was not observed for any of the samples taken and recovery for all the components was found to be approx. 100%. An example of a chromatogram obtained from the analysis of a landfill gas is given in Figure 3 together with a list of the major trace components. Over 125 components have been identified. A summary of the typical levels observed at the study site is tabulated in Table 4. The results obtained are consistent with those reported by other authors<sup>3,12</sup>.

## CONCLUSION

In this study, we have demonstrated that ATD-GC-MS can be used for the rapid analysis of the trace volatile organic components in landfill gas. Sampling can be carried out by untrained personnel and the total analysis time is less than 90 min. There are areas, however, which require further investigation. The first of these is the calibration

**Table 4** Principal components identified in a landfill gas and summary of total concentrations of VOCs detected.

<i>Compound</i>	<i>Concentration (mg m<sup>-3</sup>)</i>	<i>Compound</i>	<i>Concentration (mg m<sup>-3</sup>)</i>
Chlorodifluoromethane	25	Heptane	8
Propane	34	Methylcyclohexane	13
Dichlorodifluoromethane	22	Methylbenzene	35
2-Methylpropane	12	Octane	8
Butane	29	Ethylbenzene	14
Ethanol	8	1,4/1,3-Dimethylbenzene	36
2-Methylbutane	16	3-Methyloctane	7
Pentane	9	Nonane	22
Dichloromethane	15	2,6-Dimethyloctane	10
2-Methylpentane	5	α-Pinene	55
Hexane	9	4-Methylnonane	5
Methylcyclopentane	8	Decane	14
Cyclohexane	12	δ-3-Carene	12
3-Methylhexane	7	1-Limonene	9
4-Methyl-1-hexane	8	Decahydronaphthalene	3
Total alkanes and alkenes	258	Total pinenes	88
Total aromatics	110	Total alcohols and ketones	17
Total chlorinated compounds	111	Total cyclic compounds	93

procedure. Components identified in landfill gas range from 1,1,2,2-tetrafluoroethane to dodecane. Clearly a single calibration mixture cannot be used to cover such a wide range of boiling points and physical properties. The solution to this problem may be to use detector response factors for components which are not directly quantified. The second area which requires further investigation is the choice of adsorbents. There is very little information on breakthrough volumes, particularly with regard to samples with high humidity levels, such as landfill gas. We are currently undertaking a programme of research to address these problems.

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