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THERMAL DESORPTION TECHNIQUES FOR THE ANALYSIS OF TRACE LEVEL VOC'S IN LANDFILL GAS

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ABSTRACT

Landfill gas is a product of the natural biological decomposition of organic material contained in waste deposited in landfills. The predominant gases released during the decomposition processes are carbon dioxide (30-35%) and methane (60-65%) together with a large number of trace volatile organic compounds. The resulting mixture is assigned the generic description of "Landfill Gas". The aim of the work described in this thesis was to develop a method for the analysis of all of the VOC's present in landfill gas, then briefly assess the environmental implications of their release into the atmosphere.

The method developed utilised automated thermal desorption - gas chromatography - mass spectrometry. Preconcentration of the trace VOC's was achieved by using a sandwich of three adsorbents, Tenax TA, Chromosorb 102 and Carbosieve SIII. The latter adsorbents were selected on the basis of breakthrough volume measurements conducted for twelve compounds representative of the trace VOC's identified in landfill gas. Field trials of the developed method were conducted at seven UK landfill sites. Over 140 compounds were detected, of which more than 90 were common to all seven sites. The groups of compounds and concentrations observed were alkanes (302-1543mgm^{-3}), aromatic compounds (94-1906mgm^{-3}), cycloalkanes (80-487mgm^{-3}), terpenes (35-652mgm^{-3}), alcohols and ketones (2-2096mgm^{-3}) and halogenated compounds (327-1239mgm^{-3}). The observed variations in landfill gas composition were largely attributed to differences in the waste composition and the stage reached in the decomposition processes at each of the sites. Three sites were found to have total chlorine concentrations, derived from the organochlorine compounds in the gas, of above 250mgm^{-3}. Chlorine contents of this level were considered to be potentially damaging to gas fuelled engines used for electricity generation. Chloroethene (<0.1-87mgm^{-3}) was identified as being the most abundant toxic component. Chloroethene levels in the landfill gases sampled from two of the sites studied were found to be in excess of the UK maximum exposure limit by a factor of five and three. Total VOC's emissions from four of the seven sites was estimated to be of the order 10^4 kg/year. An analytical system for remote monitoring of the VOC's utilising thermal desorption - FTPAS is proposed and the relative advantages and disadvantages discussed.

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CONTENTS

Page

Chapter 1 Landfill Gas

Chapter 2 Theoretical Aspects of the Sampling and Analysis of Trace Levels of Volatile Organic Compounds

Chapter 3 Adsorbent Selection

Chapter 4 Optimisation of the Sampling and Analytical Procedures

Chapter 5 A Study of the Trace Volatile Organic Compounds in Landfill Gas at Seven UK Landfill Sites

Chapter 6 Remote Monitoring of the Trace Volatile Organic Compounds in Landfill Gas

Chapter 1

Landfill Gas

1.1 Introduction

At present, the UK produces approximately 120-130 million tonnes of controlled (industrial, commercial and domestic) waste per year, of which 18-20 million tonnes is household refuse.[1] The majority of this waste (>90%) is disposed of in landfills. The term "landfill" broadly describes any controlled operation where waste is deposited on land.[2] Landfill Gas is evolved from the decomposition of the biodegradable waste in a landfill. In order to understand the evolution of landfill gas and its potential impact on the environment, it is first necessary to appreciate the need for landfills and the regulations which govern their design and operation. The following chapter provides a brief history of waste management legislation in the UK, a discussion of landfill design, landfill gas production and utilisation, and finally a literature review of the origin and significance of the trace volatile organic compounds (VOC's) in landfill gas. Although the majority of the information within this chapter is presented from the UK perspective, the underlying principles are consistent with those of other industrialised countries.

1.2 Legislative History of Waste Management in the UK

Prior to 1972 there was little or no regulation of the disposal of wastes. As a result of incidents of pollution, most notably involving cyanide in the West Midlands, the government introduced the 1972 Deposit of Poisonous Waste Act.[3] The aim of the act was to control disposal through a notification procedure and make it illegal to deposit waste in a manner which was likely to cause hazard to health or the environment. The 1972 Act was superseded by the Control of Pollution Act (COPA) in 1974, which was subsequently updated in 1980. Under COPA, waste disposal licences were conceived.[4] The latter point is central to the improvement in landfilling practices as the licence, which can be revoked or modified, sets out the conditions within which the landfill operation will be conducted. Part 1 of the Control of Pollution Act has now been replaced by the 1990 Environmental Protection Act (EPA).[5] The EPA has further increased the controls on waste disposal operations and has introduced a "duty of care" on both the producers and handlers of waste in the private and public sector. The overall effect of all the aforementioned legislation is that the landfilling of waste has evolved from a routine disposal method into a technology in its own right.

1.3 Future Trends in UK Waste Management

There is increasing pressure for change within the waste management industry with the favoured alternatives being waste minimisation and, wherever possible, recycling of reusable resources.[6] The recycling of waste, however, has technical and market limitations, & becomes increasingly expensive as the percentage of the waste recycled increases and also has an adverse environmental impact.[7] In addition, not all waste can be recycled and other recyclable wastes may become contaminated. Consequently, alternative disposal options will continue to be required. It is also clear that Britain, as a member of the European Community (EC), will increasingly be controlled by EC derived legislation. The proposal for a directive on landfill was approved by the EC in April 1991 and is now subject to consultation in its draft form. Although this will not affect the fundamental design and operation of landfills, currently recommended by the UK Department of the Environment, the volume and types of waste presently accepted at some of the sites may change. It is clear, however, that whichever waste disposal option is selected or new legislation introduced, the landfilling of waste will continue to play an important role in future waste management strategies.

1.4 Landfill Design

The principal hazards to the environment arising from the landfilling of wastes are the production of leachate and landfill gas. Leachate is formed by the percolation of water through the landfill dissolving the water soluble products formed during the degradation of the waste. The resulting liquor can have total organic carbon concentrations in excess of 20000mg/l.[8] The effect of high organic content leachates on natural groundwaters is long lasting due to the low amount of oxygen available to degrade them at depth and the low rates of dispersion.[9]

In order to safeguard groundwater quality, landfill designs were based on two general principals, "disperse and attenuate" and "containment". In practice the division of landfill sites into these two discrete categories is only a generalisation and many sites will, at least in the short term, provide an element of containment. Conversely, in the long term, the majority of containment sites will allow the slow release of leachate. The concept of disperse and attenuate relies upon the capacity of natural materials to alter the composition of leachate passing through it, reducing its potential for environmental damage. This approach has largely been phased out in the UK with the emphasis now being placed on engineered containment.[10] Containment sites are designed to minimise the accumulation of leachate and prevent any leachate which does accumulate from leaving the site. This is achieved in three ways. Firstly, the production of leachate is reduced by infilling in a series of cells followed by progressive capping and restoration as each cell is infilled to its final level. The landfill capping usually consists of a low permeability layer, which minimises the ingress of rainwater, followed by successive layers of sub-soil and top-soil. The second design feature ensures that any leachate that is produced can be removed easily from the site. This is accomplished by lining the base of the landfill with a blanket of free draining material with a perforated drainage pipework system incorporated within it. Leachate can then be extracted, treated and discharged to a public sewer. The final design feature is the landfill liner, which prevents the leachate accumulated at the base of the landfill from migrating into the adjacent strata. Materials currently in use include clay and colliery shale, compacted to a permeability of no greater than $10^{-9}ms^{-1}$, and composite systems, so called because they combine natural materials, such as clay, with polymeric membranes. The structure of a typical containment site is illustrated overleaf in Figure 1.1.

1.5 Landfill Gas

Landfill gas as an environmental hazard is largely a recent phenomenon which has in part arisen because of changes in landfilling practices. The use of impermeable linings and caps to reduce the formation and migration of leachate, prevents the escape of gas through the landfill surface and instead encourages lateral migration. The significance of this problem was dramatically illustrated at Loscoe in Derbyshire where, in March 1986, a house was completely destroyed by a methane gas explosion.[11] The source of the methane was found to be an adjacent landfill site.

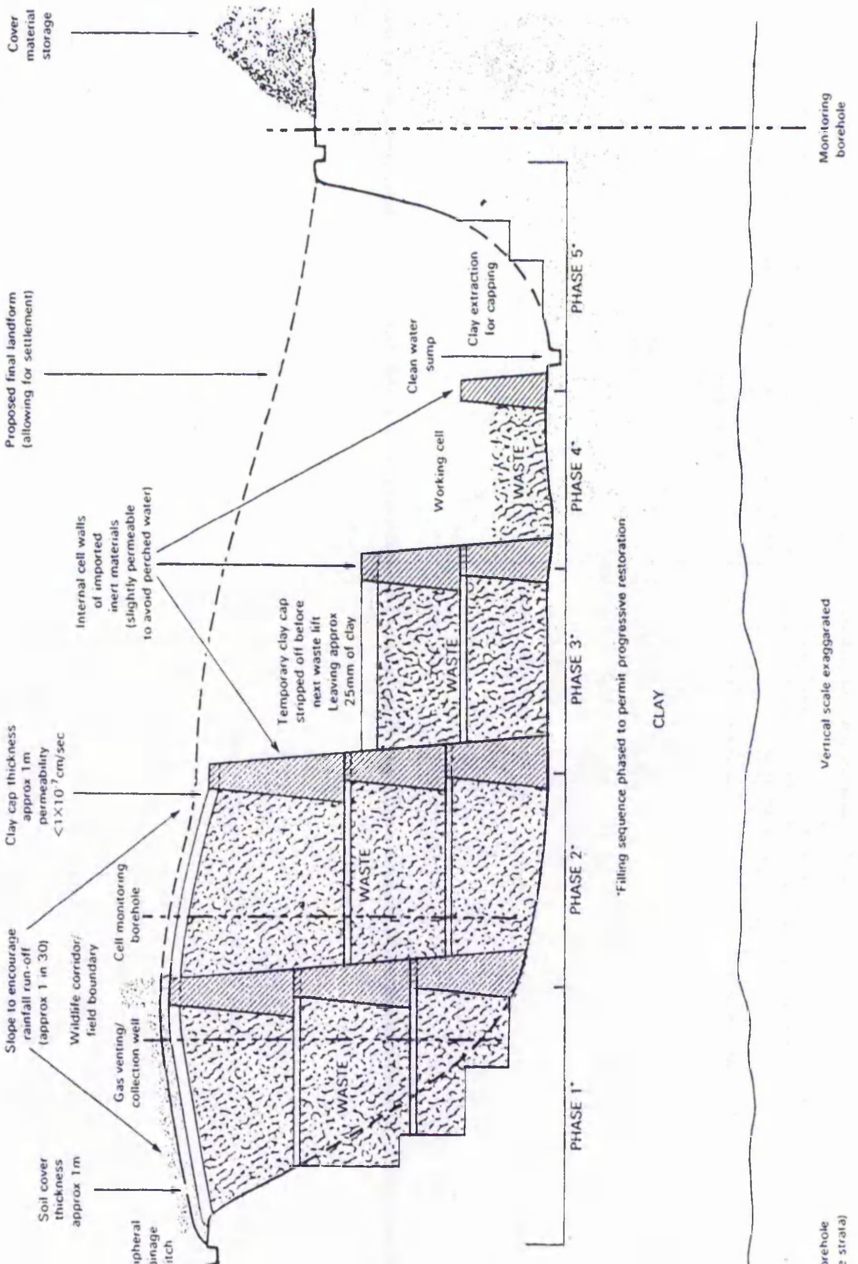


Figure 1.1 Cross-section through a Typical Containment Site

(As from Waste Management Paper 26)

1.5.1 Evolution

Landfill gas is a product of the natural biological decomposition of organic material contained in wastes deposited in landfills. The latter includes paper, animal and vegetable matter and garden wastes such as hedge clippings, shrubs and trees. The production of the principal landfill gas components (methane and carbon dioxide) is thought to essentially occur in five more or less sequential phases.[12] The first of these is the initial adjustment or aerobic phase, which requires the presence of oxygen. In the majority of cases, the aerobic phase is limited to the period during waste deposition and continues until there is insufficient free oxygen to sustain the process. The main decomposition products are water and carbon dioxide. As the oxygen becomes depleted and anaerobic conditions develop, the next phase in the decomposition process commences, the transition phase. The transition phase is characterised by a drop in the oxidation/reduction potential of the liquids held within the waste. At about -50 to -100mV, nitrate and sulphate contained within the waste can act as electron acceptors in biological conversion reactions and are often reduced to nitrogen and hydrogen sulphide respectively.[12] As the oxidation/reduction potential continues to fall, a number of different microbiological processes, responsible for the conversion of the organic material in the waste to methane and carbon dioxide, are activated. The third phase, known as the acid phase, is characterised by an acceleration of the bacterial activity initiated in the second phase. Initially celluloses, fats, proteins and carbohydrates undergo hydrolysis and fermentation to produce fatty acids and alcohols together with carbon dioxide and hydrogen. Subsequent breakdown of the fatty acids and alcohols provides substrates for the methanogenic bacteria, which convert acetate to methane and carbon dioxide in a ratio of 3:2.[13] The latter mixture, which characterises the fourth phase in landfill gas production, forms the bulk of the gases evolved and is thus assigned the general description of "landfill gas". The final phase, known as the maturation phase, occurs after the readily available biodegradable organic material has been converted to methane and carbon dioxide in Phase IV. As moisture continues to migrate through the waste, areas of the biodegradable material that were previously unavailable will be converted. However, the rate of landfill gas generation in Phase V is significantly reduced as the majority of the available nutrients have been removed and the substrates that remain in the landfill are only slowly biodegradable. The decomposition pathway of organic materials contained in domestic waste is summarised in Figure 1.2. Figure 1.3 illustrates a typical landfill gas production profile.

1.5.2 Environmental Impact

Methane is a colourless, odourless, flammable gas, is lighter than air and is a greenhouse gas. Methane forms an explosive mixture with air at concentrations between 5% and 15% by volume.[16] Carbon dioxide is also a colourless, odourless gas but is heavier than air. Unlike methane, carbon dioxide is non-combustible. It is, however, classed as a highly toxic chemical.[14] As a result of its high solubility, carbon dioxide is able to rapidly diffuse into the blood stream and consequently its effects are almost instantaneous. At concentrations of 3% by volume, shortness of breath and headache occur, becoming severe at 5-6% by volume. Concentrations of 22% by volume or above, are likely to be fatal.[14] The implementation of rigorous operational procedures have minimised the risk of fires, asphyxiation and explosions at landfill sites. Without appropriate control measures, however, landfill gas is able to migrate both within and beyond the site boundary.

Figure 1.2 Decomposition Pathway of Materials Present in Domestic Refuse

(As from Waste Management Paper 26)

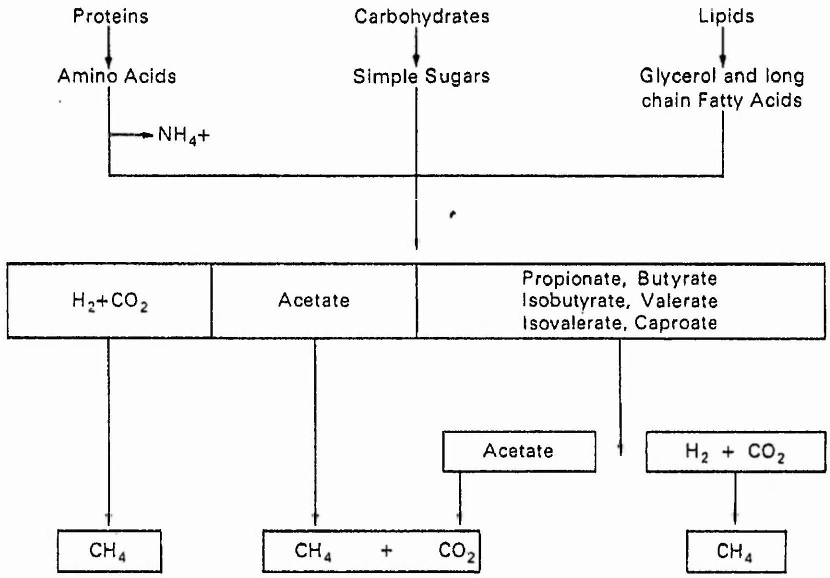
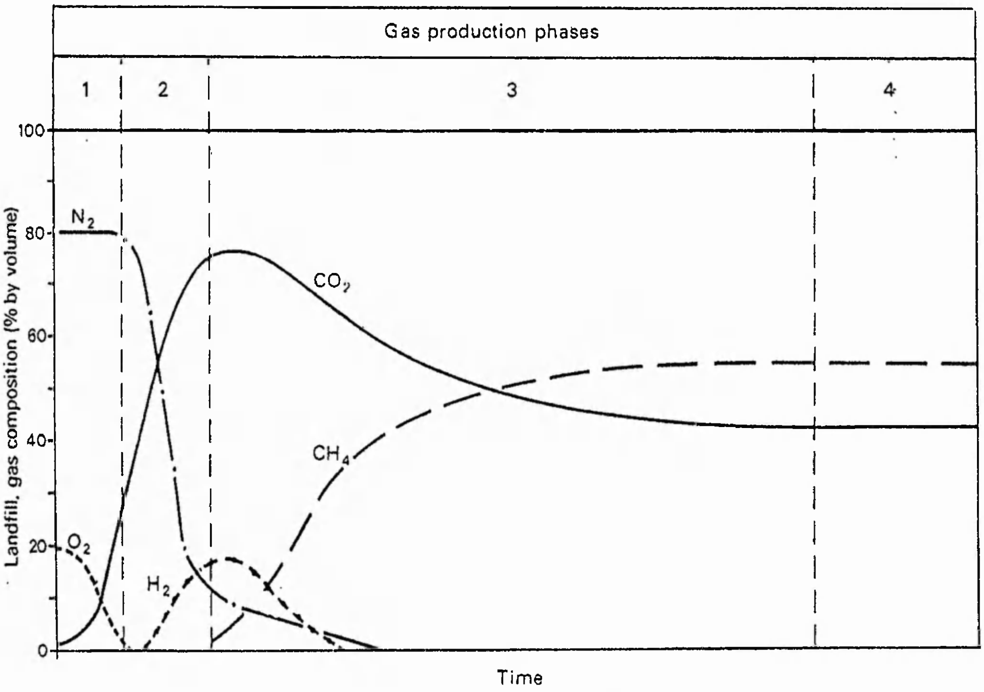


Figure 1.3 Typical Landfill Gas Production Profile

(As from Farquhar and Rovers, 1973[13])



The movement of gas is governed by a number of factors, all of which are site specific. These include the pressure developed within the site, the geology of the surrounding strata and the concentration gradients of the component gases.[15] Once outside the confines of the landfill, landfill gas can accumulate in confined spaces such as buildings or manholes and, given a source of ignition, cause explosions or fires. In addition, plant die back has frequently been observed where the root zone is exposed to elevated levels of landfill gas. Although methane is not toxic to plants, it can cause depletion of oxygen in the root zone, with less than 12% oxygen typically leading to tree death.[16]

1.5.3 Landfill Gas Management

Heightened awareness of the potential hazards posed by landfill gas migration has meant that gas control measures have become an integral part of waste management. Schemes currently employed for the extraction and control of landfill gas are essentially classified as either passive or active. Passive control systems are based on the principle that lateral migration of landfill gas can be minimised by reducing the gas pressure within the landfill. This is achieved by providing paths of lower permeability by installing a series of vents down into the solid waste mass and/or gravel packed trenches along the boundary of the landfill interior (Figure 1.4). The gas is then either burnt or allowed to disperse into the atmosphere. In active control schemes, energy in the form of an induced vacuum is used to control the flow of landfill gas via a network of horizontal or vertical gas extraction wells. The gas wells consist of 100-180mm polyethylene or polyvinylchloride pipes, with the lower half of the casing being perforated. The wells extend to about 80% of the depth of the waste in the landfill and are spaced so that their radii of influence overlap. In order to avoid pulling atmospheric gases into the landfill, which may affect methane-producing bacteria and can, by spontaneous combustion, lead to internal landfill fires, valves are placed on the top of each gas extraction well allowing the operators to reduce or increase the rate of gas extraction. The design of a typical gas extraction well is illustrated overleaf in Figure 1.5. Once the landfill gas is extracted, the usual method of treatment is thermal destruction. Methane and any other trace compounds are combusted in the presence of oxygen to carbon dioxide in a specially designed flaring facility. Concerns over air pollution have meant that modern flaring facilities have to meet rigorous operating standards to ensure that complete combustion of all the trace VOC's present in the landfill gas is achieved. Operating temperatures in excess of 850°C and a residence time of 0.3-0.5s are often quoted as the minimum requirements for the safety standards to be met.[17]

1.5.4 Energy Recovery from Landfill Gas

Although the majority of landfill operators use either passive venting or flaring as a means of managing landfill gas, an increasing number are using the gas to fuel modified engines for electricity generation. This has led to landfill gas becoming one of the UK's most successful renewable energy resources and it is estimated that by the year 2005, landfill gas utilisation schemes in the UK could produce 5.0 TWh. of electricity per. year.[18] One of the main reasons for this increase is the Non-Fossil Fuel Obligation (NFFO), which was introduced when the Electricity Supply Industry was privatised in 1990.

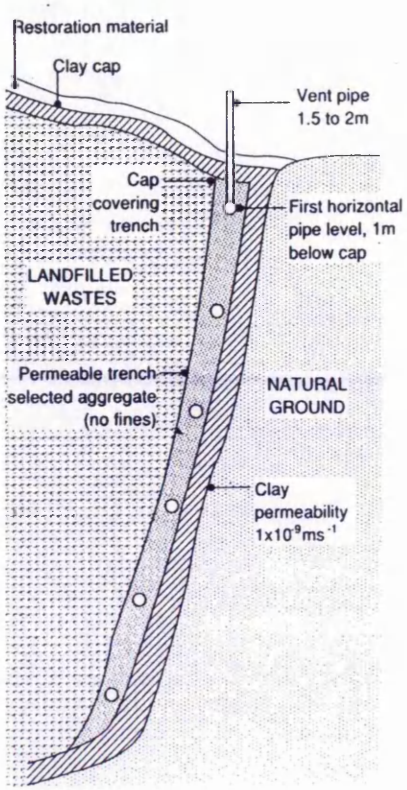


Figure 1.4 A Typical Permeable Trench Venting System

(As from Waste Management Paper 27)

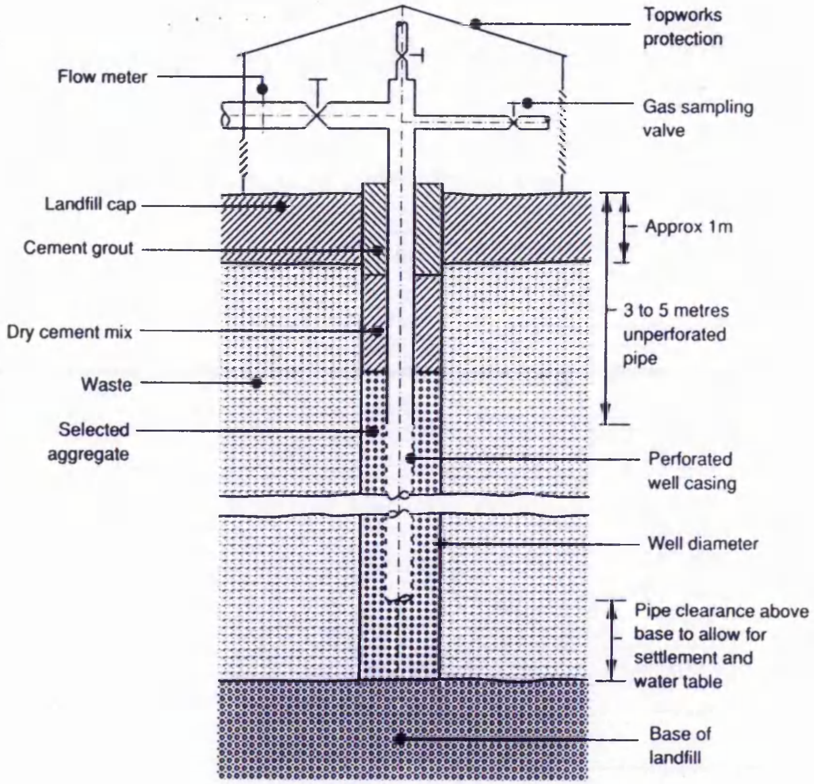


Figure 1.5 A Typical Landfill Gas Extraction Well

(As from Waste Management Paper 27)

The NFFO provides a guaranteed market at a premium price for electricity generated from non-fossil sources, which includes landfill gas. At the present time 42 landfill gas schemes with an installed capacity of 82MW have been awarded contracts.[18]

1.6 Trace Volatile Organic Compounds in Landfill Gas

The success of landfill gas utilisation schemes has renewed interest in a wide range of related topics such as the prediction of landfill gas yields, the duration of landfill gas production and the underlying mechanisms by which landfill gas is produced. The latter point has led to an examination of the composition and significance of the trace volatile organic compounds (VOC's) in landfill gas. The generic term "VOC" refers to the compound's inherent volatility and is derived from its vapour pressure. Substances are said to be volatile if, at standard temperature (298K) and pressure (1 atm), they exert a vapour pressure greater than 0.01kPa (10^{-4}atm).[19]

1.6.1 Composition of Trace Gases

The relative composition of both the principal and trace gas components are, to a large extent, dependent on the type of waste buried, the stage reached in the decomposition process and the method of site operation.[20] However, Keller[21] has postulated that all landfill gases contain the following six classes of trace compounds;

i. Saturated and unsaturated hydrocarbons which are insoluble in water and have a higher molecular weight than methane.

ii. Acidic hydrocarbons and organic alcohols, most of which are soluble in water.

iii. Aromatic hydrocarbons

iv. Halogenated compounds (generally chlorinated)

v. Sulphur compounds such as carbon disulphide and mercaptans

vi. Inorganic compounds

A limited number of authors have published data on the trace gas composition of landfill gases and a selection of their findings are summarised in Table 1.1. It is important to note that the significant variations in VOC's observed and their concentrations is in part due to the method of sampling and analysis employed. This point is further discussed in Chapter 2.

1.6.2 Origin of the Trace Volatile Organic Compounds

It is thought that the trace VOC's in landfill gas are derived from two sources;

i. The volatilization of compounds contained within the waste.

ii. The decomposition of the wastes within the landfill.

Although there are a small number of landfill sites in the UK which are licensed to accept controlled substances, such as pesticides, heavy metals, industrial solvents and asbestos, the vast majority are only used to dispose of household waste and inert materials such as building rubble. Household waste contains a range of compounds which have been subsequently identified in the landfill gas. These include chlorofluorocarbons, which are commonly found in plastic foam, aerosol propellants and refrigerants, and chlorinated solvents such as dichloroethane, which are commonly found in soaps, paints and varnishes.[22] It should be noted, however, that not all VOC's are derived from household waste. Vogt and Walsh suggest that the general concentrations of VOC's in household wastes are not very high and that it is the disposing of the aforementioned wastes with industrial and hazardous wastes which is responsible for the elevated levels observed at some landfill sites.[23] The lack of detailed records of the waste received at many of the older landfill sites and the potential for illicit dumping of wastes at sites which do possess accurate records, make it somewhat difficult to categorically state this observation as fact.

Table 1.1 Gaseous Trace Volatile Organic Compounds Identified in Landfill Gases.[1]

Compound	Rettenberger & Stegmann[24]	Dent, Scott & Baldwin[25]	Brookes & Young[26]
Total Alkanes	-	248-1311	619
Chlorofluoromethane	-	<0.1-110	1
Dichlorodifluoromethane	4-119	<0.1-276	4
Dichlorofluoromethane	5	0.1-602	5
Dichloromethane	0-6	0.1-397	140
Chloroethene	0-264	0.03-8.3	16
Ethanol	16-1450	-	>810
2-Butanol	18-626	-	110
Benzene	0.03-15	-	5
Toluene	0.2-615	-	15
Xylenes	0.2-383	-	34
Ethylbenzene	0.5-236	-	14
1-Limonene	3-269	-	240

1.6.3 The Effect of Trace Volatile Organic Compounds on Ambient Air Quality

The undesirable odour and perceived health risks associated with landfill gas has led to widespread complaints from residents living near landfill sites. Work undertaken by Young and

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[1] All values expressed in mgm^{-3}
- Compounds not analysed for or concentrations not quoted.

Parker[27] identified two groups of trace compounds which they considered to be responsible for the majority of odour complaints. The first group are the alkyl benzenes and limonene. The second group are dominated by esters and organosulphurs together with certain solvents and alcohols. It was suggested that at some landfill sites, a 10^6 dilution would be required to reduce the concentrations of some trace components below the human odour threshold, typically sub ppt levels.

In addition to the odorous trace compounds, landfill gas also contains a number of components which are known to be detrimental to health. These include benzene, tetrachloromethane and vinyl chloride. Long term exposure to one or more of these compounds may lead to acute or chronic effects on human health, or increase the risk of cancer.[14] The majority of atmospheric pollutants are transferred into the blood stream by the lungs. Exceptions include irritant gases with a relatively high solubility, which tend to be adsorbed by the moist secretions of the mucous membrane in the upper respiratory system. Upon reaching the lungs, non-irritant and insoluble gases may be absorbed into the blood through the pulmonary alveoli. Eventually, all adsorbed gases are transported in the blood stream to vital organs where they may accumulate. Vinyl chloride, for example, is known to accumulate in the liver and has been associated with a rare liver cancer.[28] Other adverse health effects caused by exposure to vinyl chloride include spleen damage, deterioration of certain bones and circulatory defects in the hands and feet.[29]

The increased occurrence of landfill gas burning in terms of both electricity generation and migration control, may also produce a range of unwanted combustion products. At the present time, little information exists on the precise characterisation or concentration of compounds emitted. Moss and Manley[30] have suggested that the utilisation of landfill gas as a fuel in internal combustion engines, could lead to the formation of polychlorinated dibenzodioxins and dibenzofurans. A study carried out by Greenburg[31] concluded that systems used to burn landfill gas emitted toxic compounds such as dioxins at levels far higher than those accepted at conventional incinerators used for the destruction of hazardous waste. However, because of the complexities of assessing the risk posed to landfill operatives and the general public, and the uncertainty surrounding the fate of compounds combusted in gas fuelled engines and flare stacks, there is little conclusive evidence to suggest that either landfill gas or the combustion products of landfill gas present a risk to health.

1.6.4 Corrosion of Landfill Gas Fuelled Engines

The combustion of halocarbons in landfill gas fuelled engines gives rise to the formation of corrosive products such as hydrochloric and hydrofluoric acid. These accumulate in the engine oil, reducing it's total base number (TBN). TBN is a measure of the oil's alkalinity and is expressed as milligrams of potassium hydroxide equivalents per gram of oil (Personal Communication, Fuchs Lubricants). As the TBN falls, the oil's buffering capacity is reduced and the potential for corrosion within the engine increases. This point was dramatically illustrated at the Braunschweigs landfill site in Germany where three internal combustion engines had been installed to power electricity generators.[32] The electricity produced was used at a sewage treatment works. After an operating period of only 889 hours, catastrophic failure of one of the three engines occurred. The investigation which followed revealed substantial corrosion of the connecting rod bearing shells at the crankshaft and the piston pins. Slight corrosion was also found to the piston rings, the piston heads, the piston boxes, the valve rockers, the camshaft, the crankshaft and the oil filter. Similar damage was observed in the remaining two gas engines. The cause of the corrosion was attributed to the relatively high concentrations (~ 600mgm^{-3}) of chlorinated hydrocarbons in the landfill gas. In order to keep the electricity generation plant operational, the operators found it necessary to modify the engine oil and replace certain parts within the engine with corrosion resistant materials.

1.7 Conclusions

The aim of this chapter was to provide a brief overview of the design and operation of landfill sites and in particular highlight the problems associated with the handling and control of landfill gas. It is clear that the landfilling of waste will continue to play an important role in the UK's future waste management strategy. Consequently, it is important to obtain a thorough understanding of the processes which occur within landfills and attempt to assess their impact on the environment. It is also clear from the preceding discussion that although VOC's account for less than 1% of the total emissions from landfill sites, they can potentially have a profound effect on both health and ambient air quality. The latter point was recently highlighted in a study published in the Lancet in which a link between birth defects, such as hole in the heart and spina bifida, and toxic waste disposal sites was tentatively identified.[33]

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Chapter 2

Theoretical Aspects of the Sampling and Analysis of Trace Levels of Volatile Organic Compounds

2.1 Introduction

In order to safeguard workers' health, the UK Health and Safety Executive (HSE) introduced the Health and Safety at Work Act of 1974[1] and, more recently, the Control of Substances Hazardous to Health Regulations[2]. The aim of the latter legislation was firstly to ensure that both employers and employees were aware of the potential hazards to health associated with a given process, and secondly, to reduce and, if applicable, prevent exposure to specific toxic and/or hazardous substances. Statutory compliance with the aforementioned legislation, necessitated the need for regular monitoring of workplace air over periods of up to 8 hours (average working day).

In order to verify that adequate controls on exposure were in place, the HSE published a list of Exposure Limits.[3] The limits, which are regularly updated as and when new evidence arises, are split into two categories; maximum exposure limits (MELs) and occupational exposure standards (OESs). OESs are defined as ".... the existence of a threshold above which there may be evidence of significant effects on health but below which, on existing knowledge, there are thought to be no adverse effects." For a substance to be assigned an MEL ".... there should be serious implications for the health of workers exposed to the substance." MELs are usually applicable to carcinogens and other substances where there is no obvious threshold value.[3]

The relatively low threshold values for highly toxic compounds such as benzene, have meant that a great deal of emphasis has been placed on both the collection and efficient transfer of the analytes from a sampling device to a gas chromatograph. Consequently, in the last decade a number of specialised techniques have been developed. The aim of this chapter is to review both practical and theoretical aspects of their operation and, in particular, assess their applicability to the analysis of VOC's in landfill gas. The first section provides a brief overview of chromatography theory and the range of detectors suitable for the analysis of VOC's. The second section summarises the methods available for the preconcentration of VOC's and the instruments used for their subsequent transfer to a gas chromatograph. The final section reviews the methods currently employed for the analysis of VOC's in landfill gas.

2.2 Gas Chromatography

Gas chromatography is a separation technique in which a sample mixture is subjected to a competitive distribution between two phases. There are essentially two separating mechanisms utilised in gas chromatography, adsorption and partitioning. In adsorption chromatography the sample constituents are separated by passing them through a bed (column) of adsorbent particles in a stream of carrier gas. In partition chromatography, separation is achieved by a partition between the moving phase, the carrier gas, and a liquid stationary phase. The latter chromatographic technique was used for the work presented in this thesis. Consequently, the remainder of this section will focus on the theory relevant to it.

2.2.1 Theoretical Aspects of Capillary Gas-Liquid Chromatography

The volume of mobile phase required to elute a band of component molecules is defined as the retention volume, V_R. Given that a constant flow of mobile phase through the column is F_C, then the retention volume, which is measured to the peak maxima, is given by;

$$V_R = t_R F_C \quad (cm^3) \qquad t_R = \text{Retention time (s)}$$

F_C can be calculated using;

$F_C = \mu (\pi d_C^2 / 4)$ μ = Average Linear Velocity of the mobile phase (cm/s)

d_C = Internal diameter of the column (cm)

The retention time and retention volume are usually corrected for the time taken for the mobile phase to pass through the chromatographic system. Corrected retention volumes (V'_R) and retention times (t'_R) are calculated by subtracting the "apparent retention time (t_m) or retention volume (V_m)" of an unretained component from that of a retained component;

$$t'_R = t_R - t_M$$

The relative affinity for the stationary phase of a given analyte, X, can be described using its distribution ratio, K_X;

$$K_X = [X_S] / [X_M]$$

Where: $[X_S]$ = Concentration of X in a unit volume of the stationary phase.

$[X_M]$ = Concentration of X in a unit volume of the mobile phase.

An increase in K_X results in an increase in retention time. Complete separation of a mixture of components is achieved when each individual component has a sufficiently different K_X value in a given chromatograhy column.

A more useful quantity than K, is the retention factor, k, which is the ratio of the concentration of the analyte in the stationary phase to the concentration per unit volume of the mobile phase. k is a measure of the actual retention properties of the stationary phase. The relationship between the distribution factor and the retention factor can be derived as follows;

$k_X = V_S [X_S] / V_M [X_M]$ but $K_X = [X_S] / [X_M]$ therefore $k_X = K_X (V_S / V_M)$

For wall coated open-tubular columns, V_M / V_S is referred to as the phase ratio, β, and can be calculated using;

$\beta = r / 2d_f$ r = Internal radius of the column (cm)

d_f = Film thickness (cm)

For a given stationary phase, temperature, carrier gas and carrier gas velocity, the distribution ratio, K_x will remain constant and is not affected by changes in column diameter or stationary phase film thickness. By contrast, the retention factor varies directly with the film thickness and inversely with the internal diameter of the column. Thus retention times for a given series of components can be increased by increasing the film thickness of a column or decreasing the internal diameter of the column. Film thickness was an important variable evaluated prior to selecting the column used for this study (Restek RTX®-1, 60m, 0.32mm ID, 1.5μm film thickness).

Column efficiency is usually described in terms of the number of theoretical plates (N) and the height equivalent to a theoretical plate (HETP or H).[4] The number of theoretical plates reflects the number of times the solute partitions between the stationary phase and mobile phase during its passage through the column. N can be calculated using;

$N = (t_R / \sigma)^2$ Where: t_R = Retention Time

σ = Solute Band Width Variance

Assuming the peak shape is Gaussian, then the solute band width variance, σ, can be calculated using;

$\sigma = w_b / 4$ Where: w_b = Base Width of the Peak at $\pm 2\sigma$

The height equivalent to a theoretical plate is calculated by dividing the length of the column by the number of theoretical plates. Capillary columns have very high column efficiencies, with N typically being of the order 10^3steps/m, 40-100,000 per column.

As the solute molecules move through the column, a number of random molecular processes occur which results in band broadening. These processes can essentially be described as either column effects or non-column effects. Non-column band broadening effects are caused by the dispersion of the solute molecules in the mobile phase within the injector and the connectors both before the column and between the end of the column and the detector. Non-column effects are minimised by designing injectors and connectors with minimal dead volumes. Column band broadening effects are the result of three molecular diffusion processes described by the van-Deemter terms A, B and C.[5] The A term describes the contribution from eddy diffusion, which arises from the non-uniformity of the flow velocities and path lengths around the packing material. In WCOT capillary columns, the A term is zero because the stationary phase is coated on the walls of the column and therefore does not directly obstruct the flow of carrier gas. The B term in the van-Deemter equation describes the axial or longitudinal diffusion of the solute within the mobile phase and is a function of the packing or bed structure and the solute diffusion coefficient in the mobile phase. The C term is a combination of two effects, C_S and C_M. The C_S term describes the diffusion in the stationary phase and is directly related to the film thickness, with thicker films potentially leading to increased band broadening. The C_M term describes the diffusion of the solute molecules in the mobile phase as they move to the stationary phase and is a function of the internal diameter of the column. A modified version of the van-Deemter equation, which was derived from the theory of open tubular columns, was postulated by Golay[6];

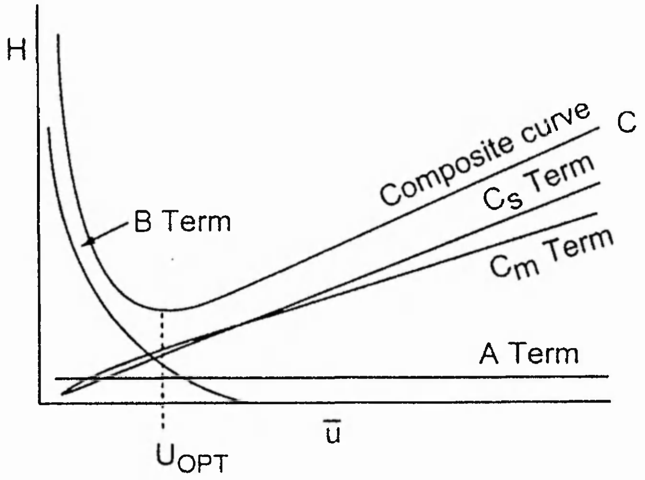
$$H^{WCOT} = B/\mu + C_M\mu + C_S\mu$$

Where; μ = Average Linear Velocity of the Carrier Gas (cms^{-1})

H^{WCOT} = HETP for Wall Coated Open Tubular Capillary Columns

It can be seen from the above equation, that all three terms are related to the linear velocity of the carrier gas. Columns operate most efficiently when the plate height, N, is at a minimum. This occurs when the carrier gas velocity is at an optimum (μ_{OPT}) and the band broadening processes are at a minimum. Figure 2.1 below, shows the variation of each of the terms in the van Deemter/Golay equation with linear gas velocity, together with a composite curve which illustrates the overall change in plate height with average linear velocity.

Figure 2.1 A Typical Van Deemter Plot of Plate Height Against Average Linear Velocity of the Carrier Gas (Braithwaite and Smith[4])



The carrier gas used for a given chromatographic separation will also affect the van Deemter plot and consequently the efficiency of the column. The three most frequently used in gas chromatography are nitrogen, helium and hydrogen. The relatively low diffusion coefficients of hydrogen and helium compared to nitrogen, result in increased separation efficiency and flatter van Deemter curves. The latter point is important because it minimises the effects of slight variations in the carrier gas flow rate. It also allows the use of linear gas velocities higher than the optimum value, thus decreasing analysis times, with only a small reduction in column performance. Landfill gas samples are complex, multi-component mixtures. As a consequence, careful evaluation of film thickness, column efficiency and, to a lesser extent, column length is necessary to achieve satisfactory resolution of all the VOC's.

2.3 Detectors for Gas Chomatography

The rapid evolution of capillary gas chromatography has led to the development of a range of highly sensitive methods of detection. These can essentially be classified as either selective or non-selective. Selective detectors include the nitrogen-phosphorus detector, the flame photometric detector and the electron capture detector (ECD). Examples of non-selective detectors include flame ionisation, thermal conductivity and mass selective detectors.

The use of the terms "selective" and "non-selective" is somewhat misleading as all detection systems exhibit a degree of selectivity. For "non-selective" detectors this problem can be partially overcome by using detector response factors. The output signal from a detector is directly proportional to the amount of a given analyte passing through it. The output signal for two different analytes, X and Y, at a concentration Z, however, will not necessarily be the same. Given that the method uses X as a calibration standard, the concentration of Y in an unknown sample can be calculated by multiplying the concentration determined from X by the response factor of Y relative to X. The response factor for Y can be determined by carrying out multiple analyses of a known concentration of X and Y and then substituting the values obtained into the following equation;

$$DRF_Y = A_Y / A_X \times C_X / C_Y$$

Where: DRF_Y = Detector Response Factor for Y

A_Y = Peak Area of Y C_Y = Concentration of Y in Standard

A_X = Peak Area of X C_X = Concentration of X in Standard

Given the range of concentrations and classes of compounds identified in landfill gas, of the detectors listed previously, only flame ionisation and mass selective detectors were considered to be suitable. The following sections briefly outline their operating principles.

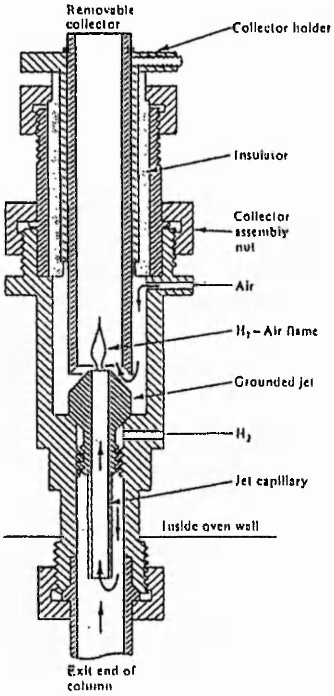
2.3.1 Flame Ionisation Detector

As the name suggests, the flame ionisation detector utilises a small hydrogen-air flame at the end of a jet to ionise the analyte molecules. The hydrogen is mixed with the column eluant prior to the jet. At the exit to the jet, the hydrogen-eluant mixture enters the air stream to form the flame, which then produces ions that are collected at an electrode. The magnitude of the ion current is directly proportional to the number of carbon atoms in the flame and consequently, the concentration of the analyte. The mechanisms responsible for the production of the ion current in an FID are still not fully understood. It is thought that direct ionisation only accounts for a small proportion of the ions formed and that other reactions such as thermal fragmentation, chemi-ionisation and ion molecule and free radical reactions are responsible for the production of the majority of the charged species.[7] These reactions are thought to include;

$CH_3^* + H^* \rightarrow CH_2^* + H_2$ $CH_2^* + H^* \rightarrow CH^* + H_2$ $CH^* + O \rightarrow CHO^+ + e^-$

A cross-section through an FID is illustrated below in Figure 2.2.

Figure 2.2 Flame Ionisation Detector

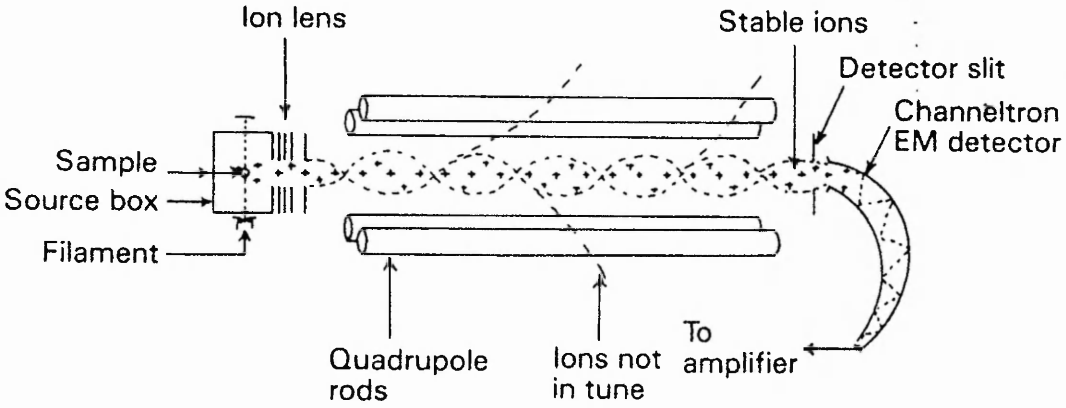


The main advantages of flame ionisation detectors are their low detection limits for hydrocarbons, typically about 10^{-12} g ml^{-1}, and their wide linear range. They also give little or no response to water and carbon dioxide. The main disadvantage of FIDs are their relatively low sensitivity to halogenated or oxygenated hydrocarbons and amines. In addition, external standards must be used to identify individual components as the output signal from an FID does not provide any structural information.

2.3.2 Mass Selective Detectors

Mass selective detectors (MSDs) essentially consist of three components, an ionisation chamber (the source), a mass analyser and an ion detector, all of which are under a vacuum of 10^{-4} to 10^{-6} Pascals. The relatively low flows of eluant required for capillary gas chromatography, have enabled GC columns to be inserted directly into the ion source, reducing sample loss and increasing detector sensitivity. The most common ionisation method utilised in MSDs is electron impact (EI). The source in an EI mass spectrometer consists of a hot filament, from which thermionic emission of electrons occurs, and an accelerator.

Figure 2.3 Quadrupole Mass Analyser



The accelerated electrons form an electron beam of 70eV energy which traverses the ion chamber to the collector anode. The eluting molecules interact with the electron beam and the resulting energy transfer is sufficient to ionise the majority of organic molecules. In most cases, the molecule is destabilised by this process and fragments to form a number of smaller ions. Upon formation, the resultant ions are expelled from the ion source by means of a small positive repelling potential and focussed into the mass analyser by a series of ion lens. Both magnetic sector and quadrupole analysers have been interfaced to capillary gas chromatographs, but modern instruments almost always employ the latter technique. The quadrupole mass analyser, which is illustrated in Figure 2.3, consists of four electrically conducting parallel rods, of hyperbolic cross section, positioned in a square array and mounted parallel to the z axis. A voltage, consisting of both a d.c. and r.f. component, is applied to opposite pairs of the rods, creating an oscillating field between them. This induced field causes the ions to oscillate in the x, y-directions between the rods. For a given set of d.c and r.f. values, only ions of one specific mass will retain a stable oscillation through the mass analyser and be detected by the electron multiplier. Linear mass spectrums are obtained by varying the magnitude of the r.f. and d.c. voltages whilst maintaining a constant r.f : d.c. ratio. In modern GC-MS analyses, the MSD is usually set to scan repetitively across a preset mass range for the entire length of the run, with the information obtained being stored by a computer. Software comparison of the mass spectra of the separated components with a library of "70eV" reference mass spectra allows the direct identification of unknown components without the use of external standards.

2.4 Preconcentration Techniques used in the Determination of Trace Volatile Organic Compounds

The development of a range of preconcentration techniques for the analysis of trace volatile organic compounds has greatly improved both the accuracy and sensitivity of ambient air and workplace monitoring. The choice of method used for a given application will depend upon a number of factors. These include the volatility and concentration of the analytes of interest, the timescale over which the sampling needs to be performed and the technique used for the subsequent transfer of the analytes from the sampling device to a gas chromatograph. The following section provides an overview of the methods currently employed together with a discussion of their relative advantages and disadvantages.

2.4.1 Cryotrapping

The technique of cryotrapping allows the on-line analysis of VOC's in ambient air and has been the method of choice in several studies.[8-9] The system consists of a U-shaped trap, usually either a borosilicate or stainless-steel tube, packed with glass beads or quartz wool. During the sampling process, the trap is submerged in liquid argon, liquid nitrogen or solid carbon dioxide. 1-10 litres of air are pumped through the trap at flow rates of 0.1-0.5 $lmin^{-1}$. The trap is subsequently heated and the retained VOC's swept onto a GC column with the carrier gas. The main advantage of this system is that on-line, real-time measurements can be taken, with the GC being the only instrument required. There are, however, several disadvantages. Firstly, the water vapour present in air tends to freeze within the trap and as a consequence, the trap can become blocked.[10] In addition, the retained water will also be introduced into the GC along with the VOC's, which may affect their subsequent separation. The second disadvantage is that the current range of commercially available instruments use large quantities of cryogenic fluid, which in turn leads to both additional logistical problems, such as access to remote sampling locations, and increased running costs.[11]

2.4.2 Membrane Extraction

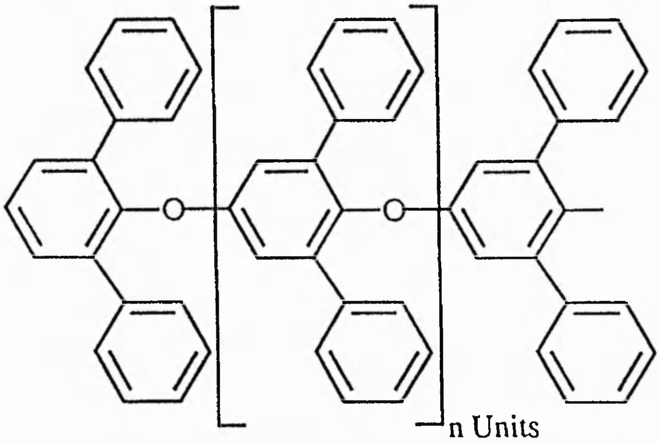
The technique of membrane extraction is essentially a refinement of the cryofocussing system. The main difference is that the VOC's in an air sample have to first diffuse across a membrane prior to the cryofocussing step. The method reported by Yang et. al.[12] utilised a hollow silicone fibre. The exterior of the fibre was exposed directly to the air sample whilst at the same time carrier gas was flushed through the centre core. As the VOC's diffused through the membrane, they were swept onto a cold trap which was cooled to -78°C with solid carbon dioxide. The trap was then heated and the VOC's desorbed directly onto a GC column. The main advantage of this system over conventional cryofocussing techniques, is that the membrane excludes water vapour. The main disadvantages of the system are the potential discrimination of polar compounds by the membrane and the elaborate calibration procedures.

2.4.3 Adsorbent Tubes

The use of adsorbent tubes for the preconcentration of VOC's in both ambient and workplace air is well documented.[13] The non-specific retention of VOC's by solid adsorbents arises from the weak van der Waals interactions between the analyte molecule and the adsorbent surface. Consequently, adsorptive strength is generally defined by the surface area of the adsorbent. The

International Union of Pure and Applied Chemistry (IUPAC) bases the characterisation of adsorbents on their pore sizes, which is essentially equivalent to the adsorbents surface area. By this definition, adsorbents with macropores (>50nm) are considered to be weak adsorbents, those with mesopores (2-50nm) are considered to be of medium strength and those with micropores (<2nm) are defined as strong adsorbents.[14] It should be noted that the latter definitions refer to non-specific interactions between the analyte molecule and the adsorbent surface and do not apply to all adsorbent-adsorbate systems. The adsorbents most often used for the analysis of VOC's, are porous organic polymers and carbonaceous materials. Styrene polymers and co-polymers account for the majority of porous polymers currently available, with the degree of cross-linking of divinylbenzene governing the pore size and hence the adsorbent's adsorptive strength. An example of the structure of a macroporous organic polymer, Tenax GC, is illustrated below in Figure 2.4.

Figure 2.4 Structural Configuration of Tenax GC (Phenyldiphenylene Oxide Polymer)



Carbonaceous adsorbents can be essentially divided into three categories, activated charcoals, which are formed by the charring of either coconut shell, wood, petroleum or coal, graphitised carbon blacks, which are formed by heating carbon blacks to approximately 3000°C in an inert atmosphere, and carbon molecular sieves, which are formed by the pyrolysis of proprietary polymeric materials.[15] Carbonaceous adsorbents tend to have higher thermal stabilities than the porous polymers and, with the exception of graphitised carbon blacks, higher surface areas. Thus they are commonly used to trap highly volatile components, such as the C2-C4 alkanes and chlorofluorocarbons, which are only partially adsorbed by the majority of porous polymers. The selection of the correct adsorbent(s) for a given application will depend upon a number of factors and will be discussed further in Chapter 3. Two sampling techniques have been employed for the preconcentration of trace VOC's using adsorbent tubes, active sampling, which involves drawing a known volume of air through the sample tube with a small pump, and diffusive sampling, which utilises the phenomenon of gaseous diffusion. For the latter technique, one end of the sampler is left exposed to the atmosphere being sampled and it is assumed that the adsorbent bed adsorbs all of the analyte in contact with it. This then creates a concentration gradient between the surface of the adsorbent and the atmosphere being sampled, which in turn results in a continuous diffusion of the analyte to the adsorbent surface. The rate of diffusion is related to the concentration of the analyte in the atmosphere. The latter can be calculated using a modified version of Fick's First Law[16] ;

$$Q = DA / L\,(C_1 - C_0)\,T$$

Where: Q = Weight of Analyte Adsorbed on the Tube (g)

D = Diffusion Coefficient of the Analyte (cm^2s^{-1})

A = Cross-Sectional Area Available for Diffusion (cm^2)

L = Diffusion Path Length (cm)

C_1 = Concentration of the Analyte in the Ambient Atmosphere (mgm^{-3})

C_0 = Concentration of the Analyte at the Adsorbent Surface (mgm^{-3})

T = Sample Time (s)

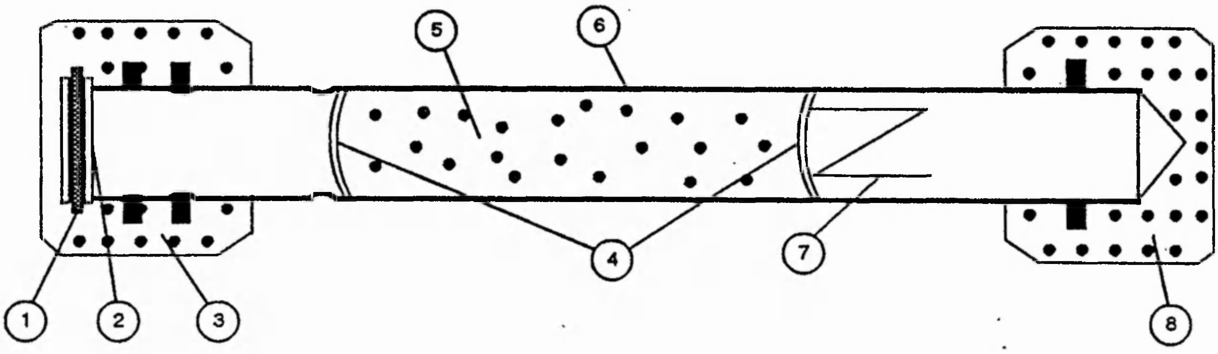
The term DA/L has units of cm^3s^{-1} and can therefore be considered to be analogous to the sampling rate of a pumped sampler. Given that the geometry of the sampling device and the diffusion coefficient of the analyte remain constant and can be measured, the concentration of the analyte in the atmosphere sampled can be calculated.

Although diffusive sampling is a relatively simple and cheap method of monitoring workplace and ambient air, it is not suitable for all monitoring applications. This is mainly due to three inefficiencies. Firstly, although there are a number of reported uptake rates,[17-20] there is still a wide range of compounds which have yet to be studied. Secondly, as only one adsorbent can be exposed to the atmosphere for a given sampler, they cannot be used for the analysis of samples containing analytes with a wide volatility range. Thirdly, due to their relatively low uptake rates, diffusive samplers are not suitable for the analysis of compounds with ambient concentrations of less than 1ppb.[11]

2.5 Thermal Desorption

Despite the fact that solvent desorption is still advocated for the extraction of chlorinated hydrocarbons retained on charcoal adsorbent tubes, thermal desorption is, in the majority of cases, regarded as the preferred method.[21] The main reason for this is that thermal desorption eliminates the use of solvents which dilute the sample, may cause interferences and can be detrimental to the analyst's health. At the present time, there are several commercially available thermal desorption units which fall into one of two categories, single-stage or two-stage. Single-stage thermal desorption units are somewhat limited in their application as the volume of gas required to desorb the retained VOC's directly from the sample tube is often too large for the direct introduction into a gas chromatograph.

Figure 2.5 Schematic Diagram of a Tube Type Diffusive Sampler (Reproduced by permission of Perkin-Elmer Ltd)



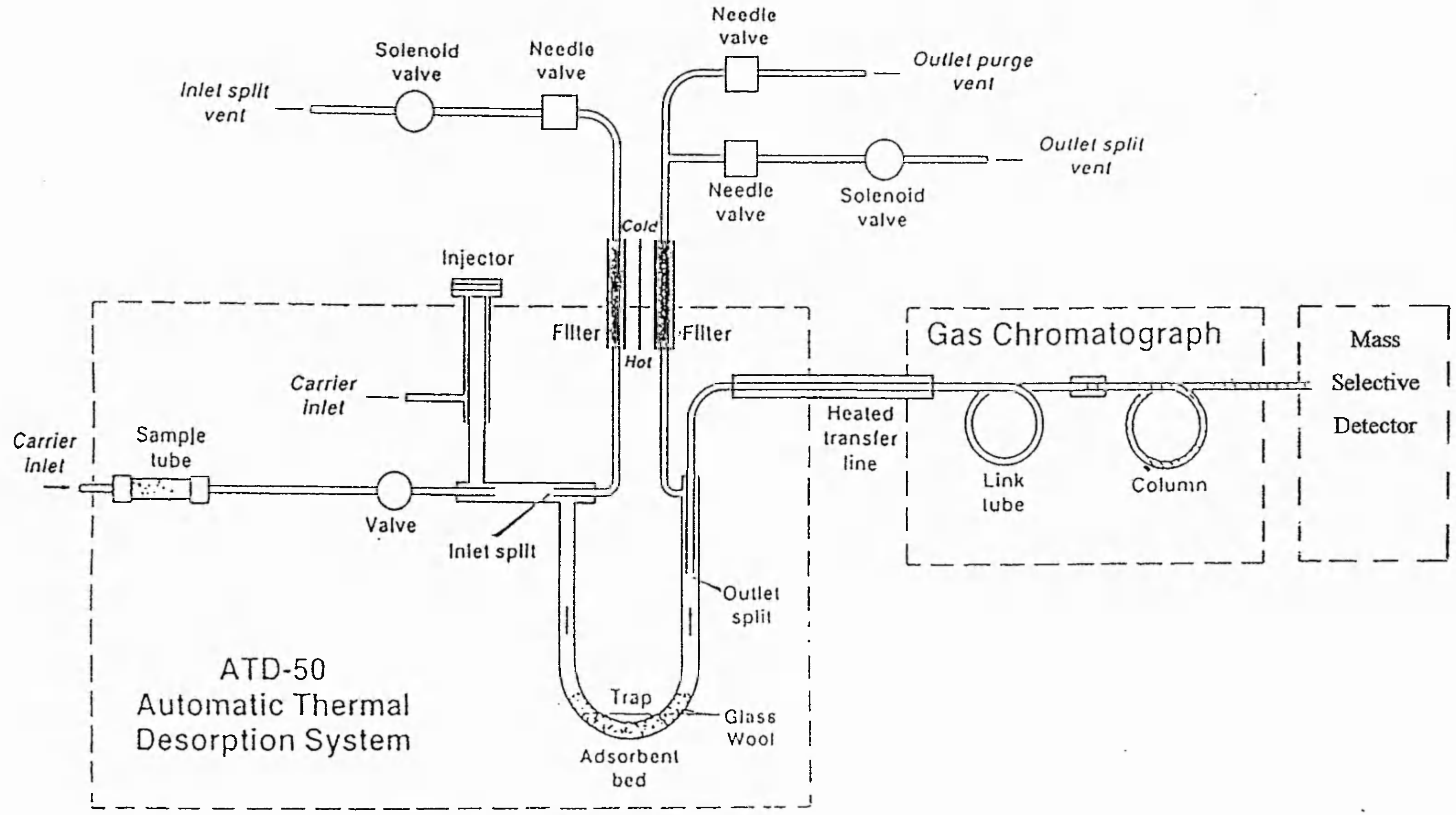
Legend

1. Stainless Steel Gauze	5. Adsorbent
2. Silicone Membrane (Optional)	6. Sample Tube
3. Diffusion Cap	7. Retaining Spring
4. Stainless Steel Gauze	8. Swagelok® End-cap

The use of two-stage desorption units eliminates this problem. The following section outlines the operation of two of the commercially available two-stage thermal desorbers, the Perkin-Elmer ATD50 and ATD400.

2.5.1 Perkin-Elmer ATD50

The ATD50, first introduced in 1980, 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 sample band width and chromatographic performance are not compromised. In the case of the ATD50, this is achieved by two stage desorption. In the primary desorption stage, the adsorbed VOC's are first extracted by purging the heated sample tube with either nitrogen or helium. The desorbed VOC's are then refocussed onto a second trap containing a weak adsorbent such as Tenax TA. The second trap is fitted with a peltier device which enables it to be cooled to a temperature of -30°C. Rapid heating (1200-2500°Cmin^{-1}) of the secondary trap ensures that the analytes are introduced into the gas chromatograph as a narrow band of vapour. Transfer of the analytes from the secondary trap to the column is accomplished by using a section of fused silica capillary, which is heated to 150°C. A schematic diagram of an ATD50 fitted with a multiple splitting accessory is illustrated overleaf in Figure 2.6. The multiple splitter 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). Inlet splitting allows the flow through the sample tube to be increased whilst maintaining a relatively low flow through the cold trap. This configuration is generally used for samples containing compounds with a wide range of boiling points as it ensures that the



Electrically cooled cold trap
Rapid inductive heating ~ 1300 °C/min

Figure 2.6 Schematic Diagram of a Perkin-Elmer ATD50

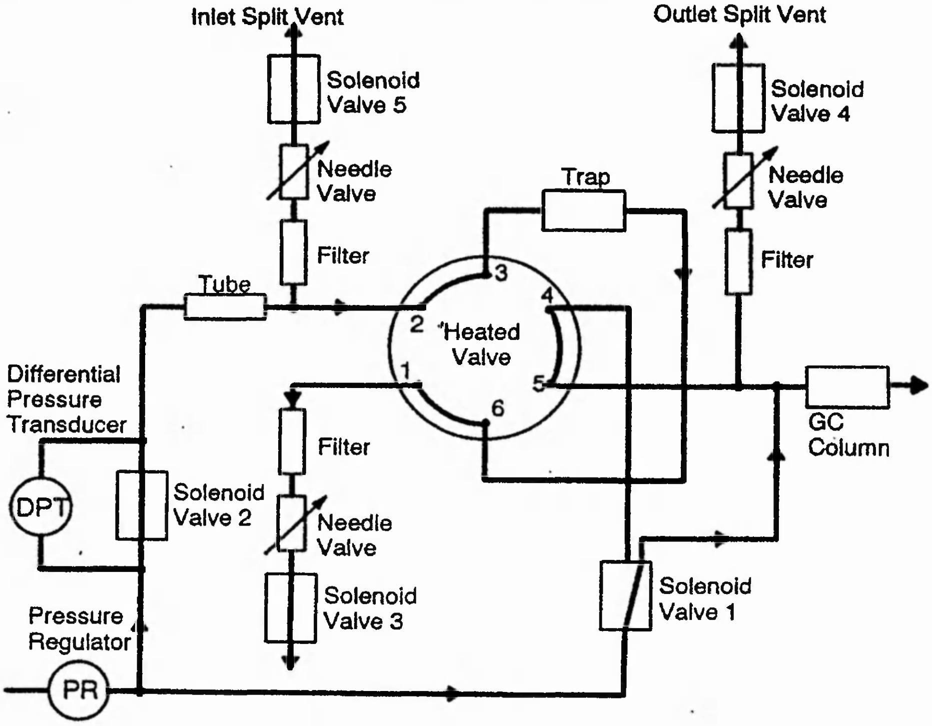
(Reproduced by permission of Perkin-Elmer Ltd)

desorption flow is sufficient to extract the high boiling point components from the sample tube without the low boiling point components eluting from the cold trap. The second configuration, outlet splitting, maximises the flow through the cold trap and is generally used in conjunction with capillary chromatography columns which only require relatively low carrier gas flow rates. In the majority of cases, the analyst will want to utilise the benefits of both inlet splitting and outlet splitting and as a consequence, the ATD50 is usually operated in the multiple splitting mode.

2.5.2 Perkin-Elmer ATD400

Although in principle the ATD400 is identical to the ATD50, there are a number of significant differences in its design.

Figure 2.7 Schematic Diagram of the Perkin-Elmer ATD400
(Reproduced by permission of Perkin-Elmer Ltd)



The most important of these is the heated six port valve which is used to direct the carrier gas flow during primary (tube) and secondary (trap) desorption. The main benefit of the heated valve is that it allows the direction of the carrier gas flow through the cold trap to be reversed during the secondary desorption stage. Consequently, higher boiling point components are more easily eluted from the cold trap and thus introduced into the GC column as a sharper band of vapour. In addition, the latter configuration also enables stronger adsorbents to be used in the cold trap, hence maximising trapping efficiency for highly volatile components. A schematic diagram of the ATD400 is given in Figure 2.7. The configuration shown illustrates the flow of carrier/sample gas during primary desorption.

2.6 A Summary of the Preconcentration Techniques used for the Analysis of Trace VOC's in Landfill Gas.

The majority of the methods developed for the analysis of trace VOC's in landfill gas have used adsorbent tubes. Of these, LaRegina and Bozzelli,[22] Wilkins,[23,24] Harkov et. al.[25] and Assmuth and Kelevi,[26] all used Tenax TA or GC (macroporous organic polymers) as the adsorbent. Brooks and Young,[27] Dent and Baldwin,[28] Young and Heasman[29] and Young and Parker[30] used a dual-tube system, one containing Tenax GC and the second containing Porapak Q (mesoporous organic polymer). In order to prevent breakthrough of the most volatile components, the second half of the Porapak Q tube was cooled to -80°C using solid carbon dioxide. All the above methods utilised thermal desorption for the transfer of the components from the sample tube to the gas chromatograph. The remaining reported methods used either direct injection of the landfill gas or cryofocussing. The former was used by Ikeguchi and Watanabe[31] for the analysis of C2-C6 and oxygenated hydrocarbons in landfill gas. The latter technique was used by Guy et. al.[32] to monitor air quality around landfill sites.

2.7 Conclusions

One aspect of the research described in this thesis was to review current analytical methodology for the sampling and analysis of VOC's. The results from this study were used to provide the basis for the development of a method for the analysis of landfill gas. The overiding factors governing the final choice of method were the need to access remote sites and sampling points and the unique composition of the sample matrix. Landfill gas contains a wide range of compounds of varying concentrations and differing volatilities. This precludes the use of diffusive monitoring and membrane extraction for the reasons outlined previously. In addition, landfill gas is saturated with water vapour, thus ruling out the use of cryotrapping techniques. Given the complexity of the sample matrix, active sampling using adsorbent tubes is the most attractive option. Although on-line measurements cannot be obtained using this technique, careful adsorbent selection can enable all of the trace VOC's to be determined from one analysis.

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Chapter 3

Adsorbent Selection

3.1 Research Aims

To determine the breakthrough volumes of a range of volatile organic compounds (VOC's) for five adsorbents, Tenax TA, Chromosorb 102, Chromosorb 106, HayeSep Q and Porapak Q. The information obtained will be used to assess their suitability for the preconcentration of the trace VOC's in landfill gas, a demanding problem due to their wide boiling point range (e.g. propane to undecane).

3.2 Introduction

The term "sorption" is used to describe both adsorption onto the adsorbent surface and weak polar interactions. For an adsorbent to be suitable for both the non-selective sorption and subsequent thermal desorption of volatile organic compounds (VOC's), it must satisfy the following criteria:[1]

i. It should have a relatively high affinity for a wide range of compounds.

ii. It should exhibit excellent thermal stability.

iii. The interaction between the analyte molecule and the adsorbent should be strong enough to retain the analyte over the sampling volume employed, but be sufficiently labile to allow its subsequent thermal desorption.

iv. It should have a relatively low affinity for water and be chemically inert.

Clearly, no single adsorbent can satisfy all the above criteria for all VOC's. Consequently, the choice of adsorbent will depend upon the range of target compounds to be analysed, their physical and chemical properties and the magnitude of the interaction required between the adsorbent and the compounds for sorption at ambient temperature and subsequent thermal desorption at elevated temperatures. The parameter most commonly used to evaluate the latter is the retention volume. Adsorbent tubes can be considered to be analogous to short chromatographic columns. As the sample is drawn through the adsorbent, the sorbed compounds will slowly migrate along its length. This effect ultimately results in the elution and consequent loss of the analyte. The volume of gas required to elute a given compound is known as its retention volume. Three methods have been used for the determination of retention volumes. The first utilises appropriate mathematical expressions to describe adsorption, desorption and dispersion of the compound and has generally been applied to active carbon.[2-7] The second method involves injecting a known volume of the compound under investigation directly onto the adsorbent tube. A stream of carrier gas is then used to simulate the flow of sample gas through the tube, with the eluting compound being measured directly in the eluent gas.[8-19] The third approach is essentially a refinement of the latter technique, the only difference being that the sample is introduced as a constant stream of gas containing a known concentration of the compound as opposed to a discrete injection.[20-33] The main advantage of this approach is that it allows the investigation of the effect of other factors such as sample humidity and analyte concentration, which have both been observed to affect retention volumes.[34-36] Although retention volume measurements can be obtained at ambient temperatures, the majority of workers carry out the measurements at temperatures above ambient. For a liquid-vapour boundary, the variation in vapour pressure with temperature is expressed mathematically by the Clausius-Clapeyron equation:[37]

$$d \ln P/dT = \Delta H_v / RT^2$$

Where: ΔH_v = Mean Heat of Vaporisation ($J\ mol^{-1}$) T = Temperature (K)

P = Vapour Pressure ($N\ m^{-2}$) R = 8.31441 $J\ K^{-1}\ mol^{-1}$

Assuming ΔH_v is constant over the temperature range used, integration of the above equation yields:

$$\log_{10}P = -\Delta H_v / 2.303RT + C$$

For the purpose of retention volume (R_v) measurements, it is assumed that the vapour pressure of a given compound is proportional to the retention volume. As $\Delta H_v / 2.303R$ is a constant, a plot of $\log_{10} R_v$ against 1/T yields a straight line. By solving the equation for the line, the retention volume of the component at ambient temperatures can be predicted. Figure 3.1 shows the variation in retention volume with temperature for benzene on Tenax TA. Figure 3.2 illustrates the concentration profile in a tube eluent as a function of eluent volume by both continuous and discrete injection.

Figure 3.1 Variation in Retention Volume with Temperature for Benzene on Tenax TA.

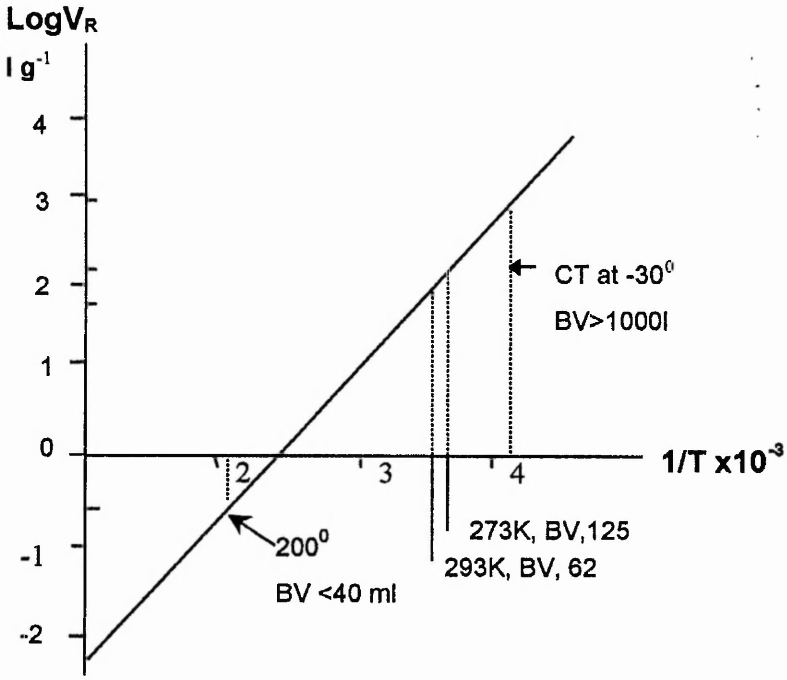
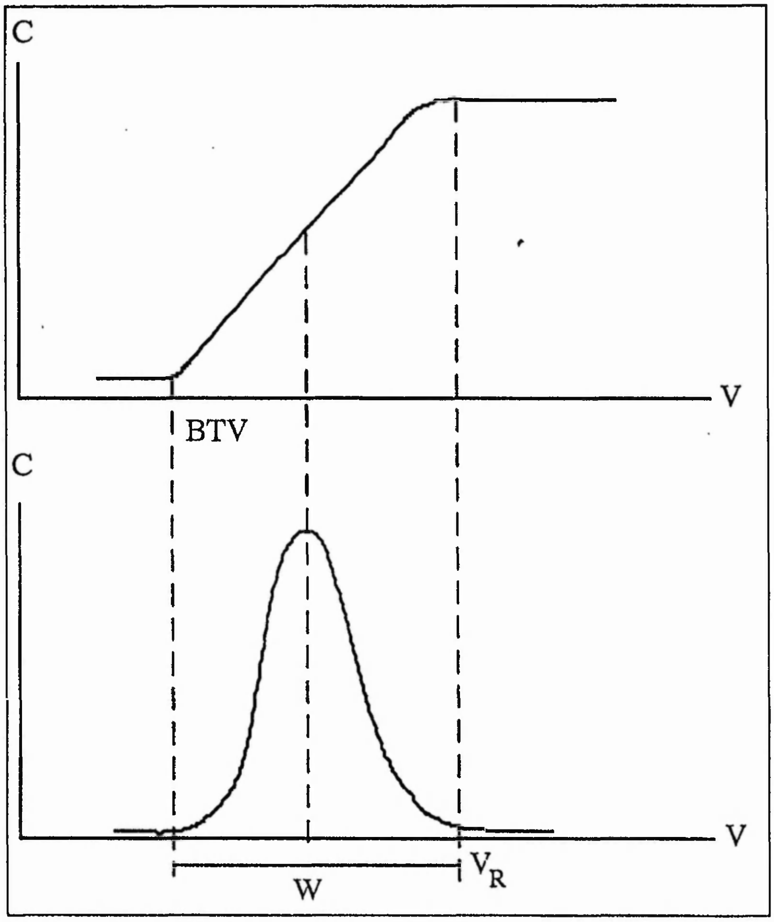


Figure 3.2 Typical Concentration Profile in an Adsorption Tube Eluent by both Continuous and Discrete Injection.



KEY

BTV = Breakthrough Volume

C = Analyte Concentration

V_R = Retention Volume

V = Eluent Volume

W = Peak Width

An alternative approach was postulated by Senum, who used the chromatographic concept of theoretical plates (N) as a measure of adsorbent collection efficiency.[38] In conventional chromatography theory, N is related to the peak width, with smaller N values typically leading to decreased column efficiency. Given that the sampling tube is essentially a short column, N would be expected to be small and can thus be used as a measure of adsorptive strength. N can be calculated from the following expression[38]:

$$N = (4R_v / w_b)^2$$

Where: N = Number of Theoretical Plates

R_v = Retention Volume (mm)

w_b = Base Width of the Peak (mm)

Senum concluded that for a sampling volume of half the retention volume, N must be at least 25 theoretical plates to achieve a collection efficiency of 99.9%. Senums calculations, however, were based on the assumption that the eluting front of the breakthrough curve is Gaussian in shape, which is not true for all adsorbent-adsorbate systems. Lovkist and Jonson, who evaluated a number of different mathematical expressions to describe a non-Gaussian eluting front, found that adsorbent-adsorbate systems with N values of 5 or more could be used for certain sampling applications.[39] They also reported that for a 99.9% sampling efficiency, N should be at least 10 for a sample volume of half the retention volume.

A review of published properties indicated that no single adsorbent could be used to analyse all of the VOC's identified in landfill gas because of their differing volatilities. As a consequence, a multiple-adsorbent sampling tube was developed. It was prepared by filling 6.4mm I.D. x 89mm stainless-steel tubes, supplied by Perkin-Elmer, Beaconsfield, with approximately 100mg of each of the following adsorbents packed in series; Tenax TA (80/100 mesh) / Chromosorb 102 (80/100 mesh) / Carbosieve SIII (60/80 mesh). In order to exploit their differing retention characteristics, the adsorbents were arranged in order of adsorptive strength. The first two adsorbents, Tenax TA and Chromosorb 102, essentially act as filters, removing the less volatile trace components which would otherwise be irreversibly adsorbed by the Carbosieve SIII. A summary of the physical characteristics of these and other selected adsorbents is given in Table 3.1.

Table 3.1 Physical Characteristics of Selected Adsorbents.

Adsorbent	Surface Area (m^2/g)	Polarity	Application Boiling Point Range (°C)
Tenax TA	35 - 40	Non-Polar	80 - 300
Chromosorb 102	300 - 350	Slightly Polar	50 - 200
Chromosorb 106	700 - 800	Non-Polar	30 - 200
Porapak Q	630 - 840	Non-Polar	30 - 200
Carbosieve SIII	820	Non-Polar	-40 - 50

The aim of the research described in this Chapter was to evaluate the retention characteristics of five adsorbents, Chromosorb 102 and 106, Tenax TA, Porapak Q and HayeSep Q. The results will then be used to assess their suitability as a "primary" adsorbent, to be used in conjuntion with Carbosieve SIII for the preconcentration of all the trace VOC's in landfill gas. Two different methods were used, discrete injection of individual components and continuous injection of a landfill gas which was known to contain a wide range of trace VOC's. Senum's method of calculating the number of theoretical plates was discounted as it was concluded that breakthrough volume data alone would allow the evaluation of the adsorbents retention characteristics.

3.3 Adsorbents Studied

The following section provides an overview of the six commercially available porous polymers evaluated. Although by no means exhaustive, the selection of adsorbents studied were considered to provide a fairly wide cross-section of surface areas and adsorptive strength.

3.3.1 Tenax TA

Since its introduction in the late 1960's, Tenax (2,6-diphenyl-p-phenylene oxide polymer) has become the most commonly used of all the porous polymer adsorbents. This has mainly been due to its high thermal stability (375°C), hydrophobic nature and its relative inertness to adsorbed species at both elevated temperatures and during long-term storage. The majority of the available literature concerns Tenax GC, which was originally developed as a gas chromatography stationary phase.[40-44] One of the more unique chromatographic applications reported, was the use of a modified Tenax GC for the analysis of Martian soil during the Viking Mars Lander mission in the 1970's.[40]

Sakodynskii *et al*[45] examined the retention of unsaturated and polar compounds on Tenax GC. They found that the retention of unsaturated compounds was dependant upon the number of double bonds in the molecule and for polar compounds, the dipole moment of the compound. Brown and Purnell investigated the effects of sampling flow rate, vapour concentration and humidity on the performance of a Tenax GC air sampling cartridge.[22] They found that increased sampling flow rate and analyte concentration reduced the retention volume of components absorbed on Tenax and that sample humidity had little effect. One of the major disadvantages of using Tenax GC for thermal desorption applications was found to be its contribution to the levels of impurities in blank chromatograms. Significant levels of toluene, xylenes and ethylbenzenes have all been observed in the blank following extended thermal desorption.[46] In addition, Neher and Jones noted the formation of 2,6-diphenyl-p-quinone whilst sampling stack gases.[47] The problem of artifact generation was largely overcome by changes in the process conditions of the Tenax. Mcleod and

Ames reported that the new adsorbent, Tenax TA, produced substantially less artifacts than Tenax GC without any change in the basic adsorptive properties of the material.[48] As with Tenax GC, however, the relatively large pore size (200nm) and low specific surface area ($35m^2g^{-1}$) of Tenax TA, limit its application to the analysis of C6-C14 hydrocarbons.[49]

3.3.2 Chromosorb 102 and 106

Chromosorb 102 is a styrene-divinylbenzene copolymer with a specific surface area of 300-$400m^2g^{-1}$ and a mean pore diameter of 9nm.[50] As with Tenax, the Chromosorb series of porous polymers were primarily produced as chromatographic stationary phases. They have, however, been successfully utilised for the preconcentration of VOC's in both air and water. Mieure and Dietrich demonstrated the hydrophobic properties of Chromosorb 102 whilst using it to extract a range of VOC's from aqueous solutions.[51] Butler and Burke assessed the effectiveness of Chromosorb 102 for the analysis of workplace air by determining the sampling capacity of acetonitrile, t-butanol, methylethylketone and benzene.[10] They found that for the compounds studied, the sampling capacity of Chromosorb 102 was significantly higher than that of Tenax GC, which was the adsorbent of choice for the majority of occupational hygiene applications at that time. Tanaka studied the adsorption of trichloromethane, tetrachloromethane and trichloroethane on Tenax GC, Chromosorb 102 and Porapak Q. Their results suggested that the adsorptive strength of Chromosorb 102 was similar to that of Porapak Q, but much greater than that of Tenax GC.[18]

Chromosorb 106 is a cross-linked polystyrene polymer with a surface area of 700-800m^2g^{-1} and a mean pore diameter of 5nm.[50] Due to its non-polar surface, it retains aliphatic hydrocarbons far longer than oxygenated compounds of the same chain length. Several authors have studied the adsorptive properties of Chromosorb 106 and in particular, the stability of compounds adsorbed onto it during thermal desorption. Peters and Bakkeren assessed the recovery and stability of dichloromethane, 1,1,1-trichloroethane, trichloroethene and tetrachloroethene.[27] They reported that Chromosorb 106 exhibited excellent adsorptive strength and stability for dichloromethane and 1,1,1-trichloroethane. By contrast trichloroethene and tetrachloroethene were found to be unstable on Chromosorb 106 and they suggested that Tenax GR was a more suitable adsorbent for these compounds. Cao and Hewitt examined the stability and recovery of isoprene, benzene, toluene, p-xylene, o-xylene, mesitylene, 1,2,4 and 1,2,3-trimethylbenzene, β-pinene and α-pinene.[11] The recovery of β-pinene from Chromosorb 106 was found to be low and it was initially thought that this was due to incomplete desorption or decomposition. Simultaneous desorption of β-pinene and α-pinene, however, led to a 79% recovery of β-pinene and a 124% recovery of α-pinene. As a result of this work they tentatively concluded that the low recovery of β-pinene was due to the rearrangement of the isomers at elevated temperatures. This effect was not observed on Tenax TA. 100% desorption of all the remaining compounds was achieved at 220°C, with no indication of decomposition.

The relatively low maximum operating temperature (250°C) of both Chromosorb 102 and Chromosorb 106 limit their suitability to the analysis of hydrocarbons in the range C_5 - C_{12}.

3.3.3 Porapak Q

Porapak Q is an ethylvinylbenzene-divinylbenzene copolymer with a specific surface area of 630-840m^{2}g^{-1} and a mean pore diameter of 7.5nm.[50] Although Porapak Q has largely been used as a chromatographic stationary phase,[52-53] several authors have advocated its use for the preconcentration of trace VOC's in ambient air. Noy *et al* assessed the suitability of Tenax, Carbopack A, charcoal, alumina and Porapak Q for the analysis of halocarbons in air.[54] They reported that of the adsorbents studied, Porapak Q was the most suitable because of its high sampling capacity and the relatively low temperatures required for the efficient desorption of the retained components. Melcher and Caldecourt described a method for the direct determination of a range of VOC's in ambient air.[55] Preconcentration was achieved by using a small pre-column packed with either Tenax or Porapak Q. The latter adsorbent was recommended for the analysis of highly volatile components such as chlorinated solvents. The retained components were desorbed directly onto the analytical column by applying a large current across the pre-column. They reported that a temperature of 125-150°C was sufficient for the desorption of all the retained components. As with Tenax GC, one of the main problems of using Porapak's can be the large amounts of degradation products in the blank chromatograms. Aubigne and Guichon assessed the thermal stability of Porapak Q and Porapak P, a styrene-divinylbenzene copolymer.[56] The main degradation products were found to be diethylbenzene, divinylbenzene, ethylvinylbenzene and styrene. The maximum operating temperature for Porapak Q was suggested to be 250°C. They also recommended that before its use, it should be conditioned at 100°C under an inert atmosphere. Prolonged conditioning at 300°C, was found to have little effect on the adsorbents thermal stability at lower temperatures.

3.3.4 HayeSep Q

As a result of insufficient quality control measures within the manufacturing processes, both the Porapak and Chromosorb series of porous polymers can exhibit irregular batch to batch performance, shrinkage and residual monomeric contamination.[57] As a consequence, the HayeSep series of polymers were marketed as direct replacements. The implementation of rigorous quality control steps during the HayeSep production processes, have minimised the aforementioned problems. The adsorbent utilised for this work, HayeSep Q, is a divinylbenzene polymer with a specific surface area of 500-600m^2g^{-1} and a maximum operating temperature of 275°C.[58] To date, no reference has been made to the applicability of HayeSep Q for the preconcentration of VOC's in the scientific literature.

3.3.5 Carbosieve SIII

Carbosieve SIII is a non-graphitic carbon molecular sieve[61] made from the controlled pyrolysis of pitch and porous polymer mixtures and has a specific surface area of approximately 800m^2g^{-1}. Its high surface area and high adsorption properties mean that it is suitable for trapping highly volatile components, but unsuitable for trapping compounds with high boiling points due to the relatively high temperatures required to efficiently thermally desorb them.[61]

3.4 Determination of Breakthrough Volumes by Direct Injection

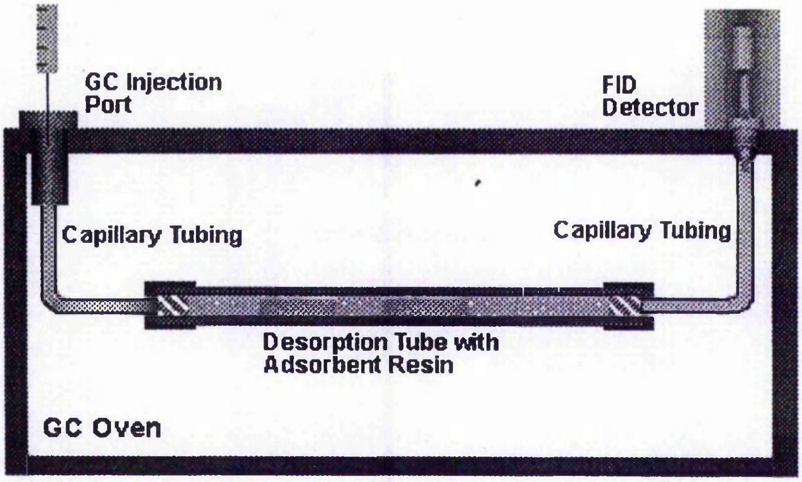
The following sections outline the instrumentation, experimental methods and results derived from the direct determination of breakthrough volumes for 12 selected VOC's on Tenax TA, Chromosorb 102 and 106, HayeSep Q and Porapak Q. A discussion of the results is presented in Section 3.6.

3.4.1 Instrumentation

A Pye-Unicam 304 series gas chromatograph fitted with a flame ionisation detector was adapted for the measurement of the breakthrough volumes. A schematic diagram of the system is shown in Figure 3.3. The GC column was substituted for two short lengths of 0.32mm I.D. stainless steel capillary tubing fitted with two 1/4" to 1/16" compression fittings. The length of capillary tubing between the injection port and the adsorbent tube and the adsorbent tube and the detector was kept to a minimum so as to reduce the dead volume of the system.

A 6mm silicone rubber o-ring (supplied by Pye-Unicam Ltd.) was used to form the seal between the compression fittings and both the injection port liner and the sample tube containing the adsorbent under investigation. For the breakthrough volume measurements, the FID operating conditions were as follows; detector temperature: 250°C; hydrogen and air pressure: 12 and 26psi respectively; carrier gas flow rate: 50ml min^{-1} nitrogen. The output signal from the FID was recorded using a Phillips PM8521 Chart Recorder.

Figure 3.3 Schematic Diagram of the System used for the Direct Determination of Breakthrough Volumes.



3.4.2 Experimental Methods

Each sample tube was prepared by first inserting a retaining gauze in the tube followed by approximately 300mg of the relevant adsorbent. The tube was then gently tapped on a bench-top to remove air gaps and produce a consistant packing density. The final retaining gauze was then inserted and the sample tube immediately sealed using swagelok® end-caps fitted with PTFE ferrules. The laser-etched reference number of each tube was noted. All of the adsorbents were preconditioned prior to their use in a modified GC injection port under a 100 ml min^{-1} flow of nitrogen. The GC was programmed to ramp from 20°C to 250°C at 1°C/min. The temperature was then held at 250°C for 12 hours.

The breakthrough volumes of the following twelve components were determined for each of the five adsorbents; ethanol, dichloromethane, hexane, benzene, cyclohexane, toluene, xylene, heptane, nonane, decane, 1-limonene and dodecane. These compounds were selected for two reasons. Firstly, they are all liquids at room temperature. Secondly, in terms of boiling points and physical properties, they are representative of the majority of trace VOC's identified in landfill gas. 0.05μl of each individual component was injected onto the sampling tube via the heated GC injector using a 0.5μl SGE syringe supplied by Alltech, Carnforth. The temperature of the injector was held at 200°C so as to ensure rapid volatilisation of the injected sample. The breakthrough volume was determined from the recorded chromatogram by measuring the distance to the front of the eluting peak and calculating the corresponding volume of carrier gas. Each set of measurements were carried out in triplicate at five different temperatures ranging from 70°C to 240°C. The temperatures used for any given dataset were governed by the magnitude of the adsorbent-adsorbate interaction.

3.4.3 Example Calculation

0.05μl of benzene was injected onto Chromosorb 102 at each of the following temperatures; 120, 130, 140, 150 and 160°C. The breakthrough volume (BTV) of benzene at each temperature was then calculated from the following expression;

$$\mathrm{BTV} = (L / CS) \times F_m$$

Where:

BTV = Breakthrough Volume (ml)

L = Distance to Front of Eluting Peak (mm)

CS = Chart Speed (mm min^{-1})

F_m = Carrier Gas Flow Rate (50ml min^{-1})

Table 3.2 Results Obtained from the Determination of the Breakthrough Volume of Benzene for 300mg of Chromosorb 102

Temperature (^oC)	**Average BTV (ml)**	**1/T (K^{-1})**	**log BTV (l)**
120	44.6	0.00254	-1.3509
130	30.0	0.00248	-1.5229
140	20.4	0.00242	-1.6899
150	14.0	0.00236	-1.8529
160	10.9	0.00231	-1.9821

Using the data contained in Table 3.2, a linear regression analysis of the line log BTV (l) against 1/T (K) generated the following equation;

$$Y = 2712.2x - 8.2544 \qquad R^2 = 0.9992$$

At 20°C (room temperature), x = 0.00341. Substituting this value into the above equation yields a BTV^{293K} of 10.05 l for the Benzene-Chromosorb 102 (300mg) system.

3.4.4 Results

The initial set of experiments were designed to ascertain the effect of analyte concentration on the predicted breakthrough volumes. The results from these experiments were then used to determine the optimum injection volume. In this context, the optimum injection volume is defined as the injection volume which produces the largest breakthrough volume whilst maintaining reproducible results. Two adsorbents were studied, Tenax TA, which has a relatively low surface area and is thus considered as a weak adsorbent, and Chromosorb 102, which is characteristic of medium strength porous polymer adsorbents. 0.3, 0.2, 0.1 and 0.05µl of ethanol, dichloromethane, heptane, xylene and dodecane were injected onto the adsorbent tubes and the breakthrough volumes calculated at 293K. The results are summarised below in Table 3.3. Example graphs are given in Figures 3.4 to 3.11.

Table 3.3 Variation in Breakthrough Volume with Volume of Analyte Injected[1]

Compound	0.05µl	0.10µl	0.20µl	0.30µl
Tenax TA				
Ethanol	0.15	0.10	0.10	0.10
Dichloromethane	0.65	0.50	0.35	0.25
Heptane	2.00	0.75	0.25	0.25
Xylene	26.7	10.9	4.20	2.40
Dodecane	267	133	23.0	8.50
Chromosorb 102				
Ethanol	0.40	0.35	0.30	0.30
Dichloromethane	1.70	0.90	0.85	0.85
Heptane	86.8	56.6	46.5	32.7
Xylene	324	240	140	74.9
Dodecane	132000	113000	67000	64000

The results contained in Table 3.3 clearly show that the volume of analyte injected significantly affects the observed breakthrough volumes, with increased injection volume resulting in lower breakthrough volumes. For example, the breakthrough volume of dodecane on Tenax TA, varies from 267 litres to 8.5 litres for injection volumes of 0.05 and 0.30µl respectively.

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[1] All values for breakthrough volume are quoted in litres and refer to a tube containing 300mg of adsorbent.

Figure 3.4 Chromosorb 102 : P-Xylene

Injection Volume: 0.05μl

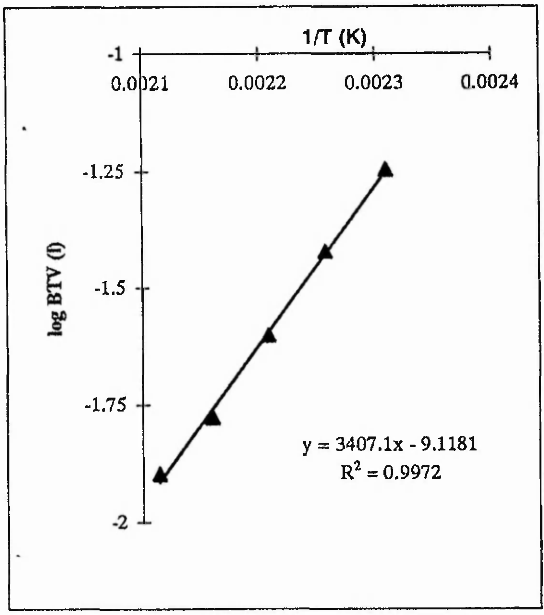


Figure 3.5 Chromosorb 102 : P-Xylene

Injection Volume: 0.30μl

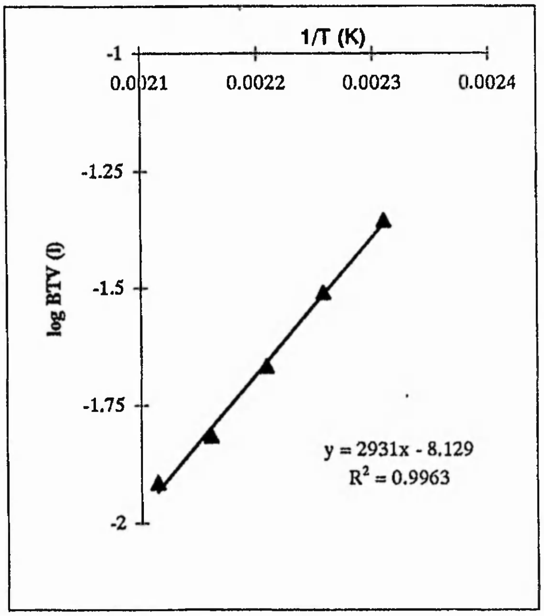


Figure 3.6 Chromosorb 102 : Ethanol

Injection Volume: 0.05μl

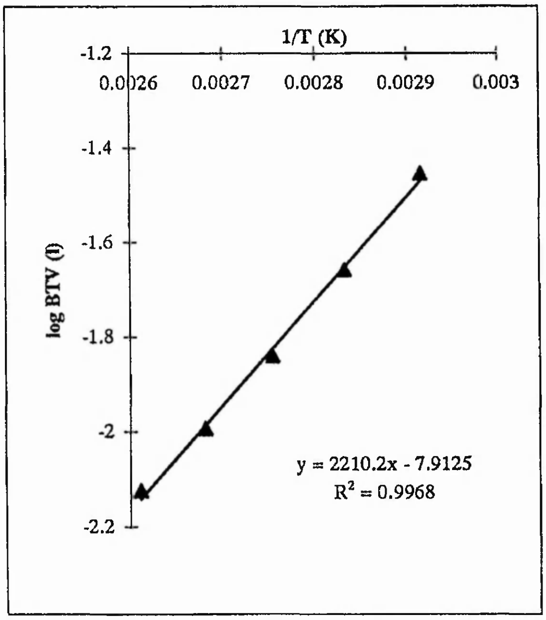


Figure 3.7 Chromosorb 102 : Ethanol

Injection Volume: 0.30μl

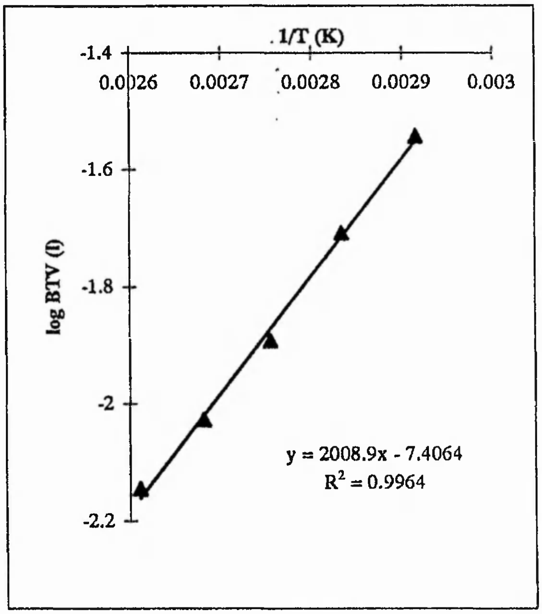


Figure 3.8 Tenax TA : p-Xylene

Injection Volume: 0.05μl

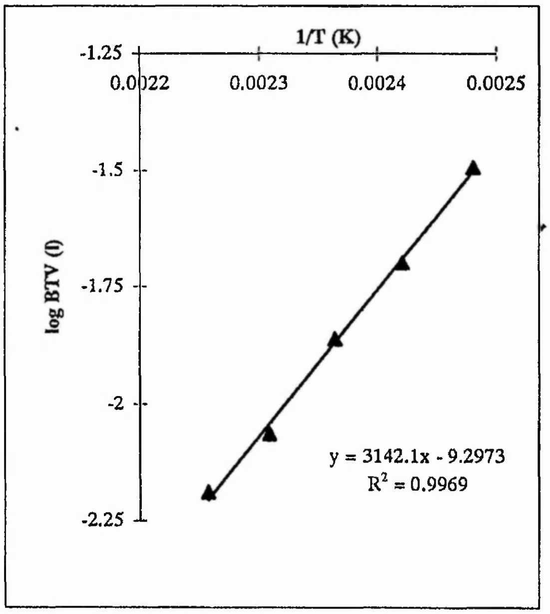


Figure 3.9 Tenax TA : p-Xylene

Injection Volume: 0.30μl

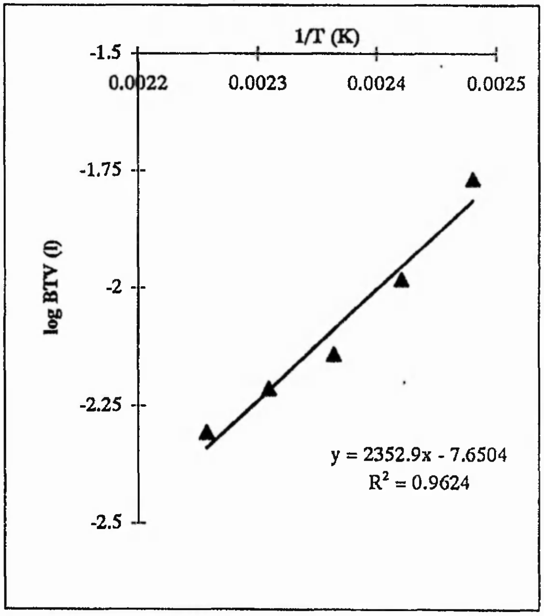


Figure 3.10 Tenax TA : Ethanol

Injection Volume: 0.05μl

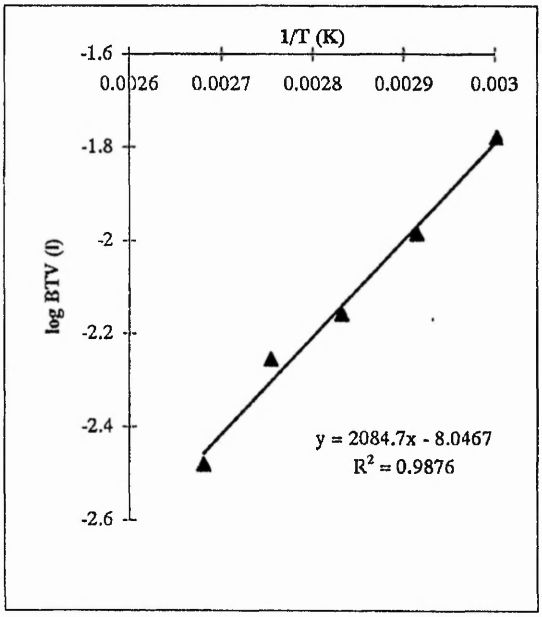
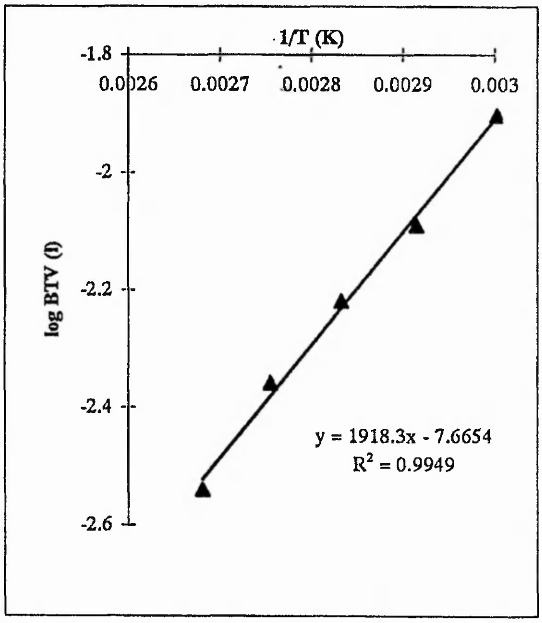


Figure 3.11 Tenax TA : Ethanol

Injection Volume: 0.30μl



Although the change is less pronounced for Chromosorb 102, the breakthrough volume is still reduced by a factor of 2 over the range 0.05-0.30µl. The magnitude of this effect decreases for the weakly retained components. This observation may be explained in terms of the surface area and heterogeneity of the adsorbents. Chromosorb 102 has a surface area of 300-350m^2g^{-1} and Tenax TA, approximately 35m^2g^{-1}. Given that the non-specific retention of VOC's by solid adsorbents arises from weak van der Waals interactions between the analyte molecule and the adsorbent surface,[49] Chromosorb 102 would be expected to have a much larger sample capacity than Tenax TA. Examination of the breakthrough volume data supports this theory as the relative change in breakthrough volume with injection volume is less pronounced for Chromosorb 102 than for Tenax TA. It is therefore probable that the relatively large amounts of analyte injected were completely saturating the available adsorption sites, with the effect being greatest for Tenax TA because of its low surface area. An additional factor may be the availability of active sites within the heterogeneous adsorbents. At low analyte concentrations, the surface coverage will be small. As the analyte concentration increases the surface coverage will also increase, with the active sites being the first to be occupied. Once all the active sites have been filled, additional analyte molecules will appear to be prematurely eluted from the adsorbent bed. Given the above discussion, it was concluded that the minimum injection volume, 0.05µl, provided the most accurate estimate of the components breakthrough volumes at the concentrations likely to be encountered in a landfill gas (0.1 - 500mg m^{-3}).

As a consequence, the breakthrough volume measurements for the remaining adsorbent-adsorbate systems were all carried out using an injection volume of 0.05µl. In order to directly compare each of the individual adsorbents, both the breakthrough volume per tube (c.a.300mg) of adsorbent and the specific breakthrough volume (BTV per gram of adsorbent) were calculated. The results are summarised in Table 3.4. All the predicted values are quoted in litres and refer to an air temperature of 293K. Examples of the graphs used to calculate the aforementioned breakthrough volumes are presented in Figures 3.12-3.31. A discussion of the results is given in Section 3.6.

Table 3.4 Breakthrough Volume Data Obtained for the five Adsorbents Studied [2,3]

Compound	Tenax TA	Chromosorb 102	Chromosorb 106	Porapak Q	HayeSep Q
Ethanol	0.15	0.40	0.85	0.95	0.95
	0.65	*1.00*	*2.30*	*2.50*	*2.50*
DCM	0.65	1.70	2.60	1.40	2.60
	2.90	*4.20*	*7.00*	*2.60*	*6.90*
Hexane	1.40	12.9	10.2	21.9	25.5
	6.20	*31.9*	*27.5*	*57.1*	*68.0*
Benzene	2.80	10.1	27.3	12.6	19.5
	12.4	*25.0*	*73.7*	*35.9*	*52.0*
Cyclohexane	1.25	9.05	29.4	13.6	34.0
	5.50	*22.4*	*79.3*	*207*	*90.6*
Heptane	2.00	86.8	150	137	134.1
	8.80	*215*	*405*	*358*	*357*
Toluene	11.5	58.6	256	95.2	120
	50.8	*145*	*691*	*248*	*320*
Xylene	26.7	324	1070	375	376
	118	*801*	*2880*	*978*	*1000*
Nonane	41.7	835	4030	3310	2850
	184	*2060*	*10900*	*8620*	*7590*
Decane	80.5	10800	32400	11400	9150
	356	*26700*	*87300*	*29600*	*24400*
1-Limonene	243	4320	9000	4720	6580
	1040	*10700*	*24200*	*12300*	*17500*
Dodecane	267	133000	1320000	277000	748000
	1180	*328000*	*3550000*	*722000*	*199000*

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[2] Reported breakthrough volumes are in litres per 300mg of adsorbent.

[3] Figures underlined refer to specific breakthrough volume (lg^{-1}).

Figure 3.12 Variation in BTV with Temperature for the Tenax TA: Benzene System.

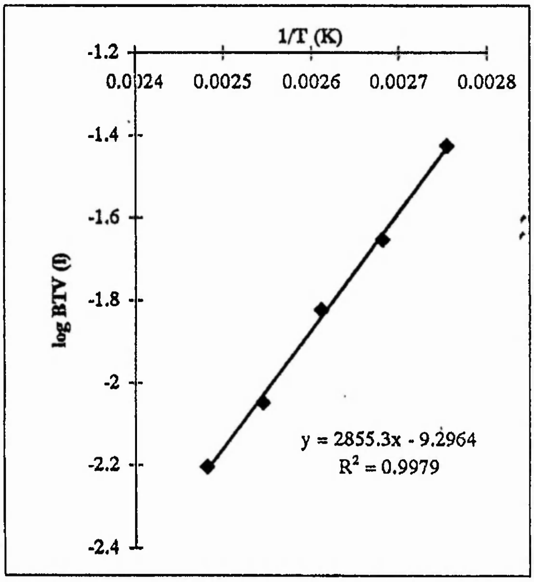


Figure 3.13 Variation in BTV with Temperature for the Tenax TA: Toluene System.

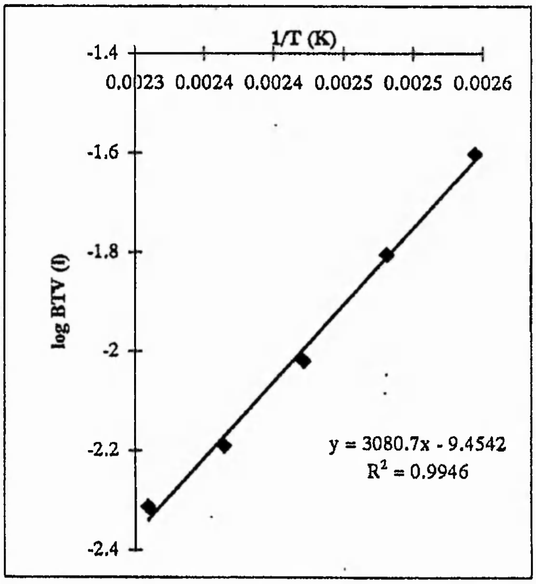


Figure 3.14 Variation in BTV with Temperature for the Tenax TA: 1-Limonene System.

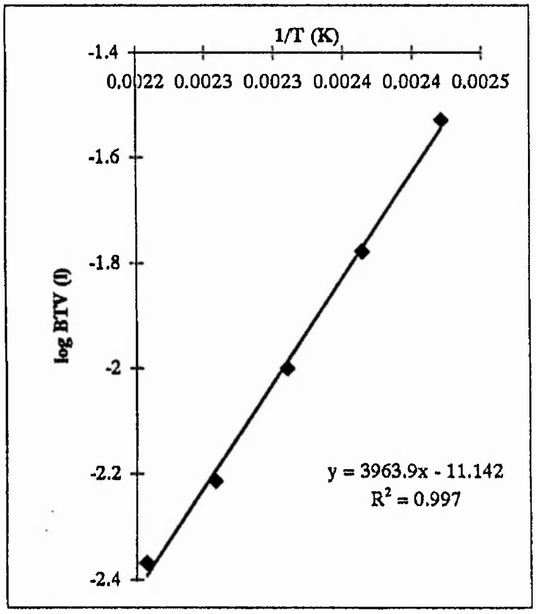


Figure 3.15 Variation in BTV with Temperature for the Tenax TA: Decane System.

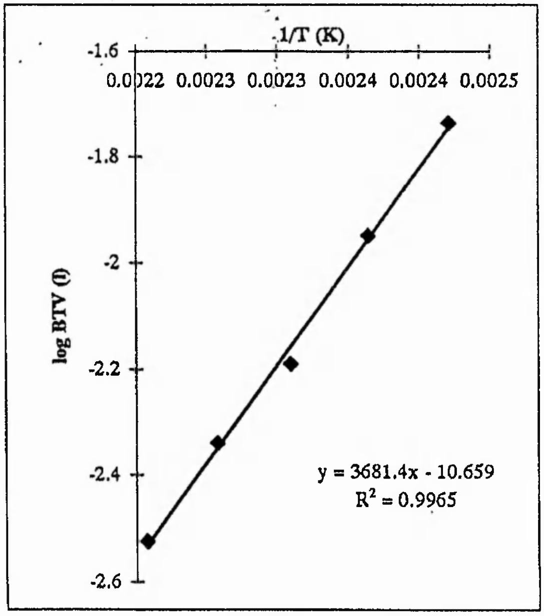


Figure 3.16 Variation in BTV with Temperature for the Chromosorb 102: Dichloromethane System.

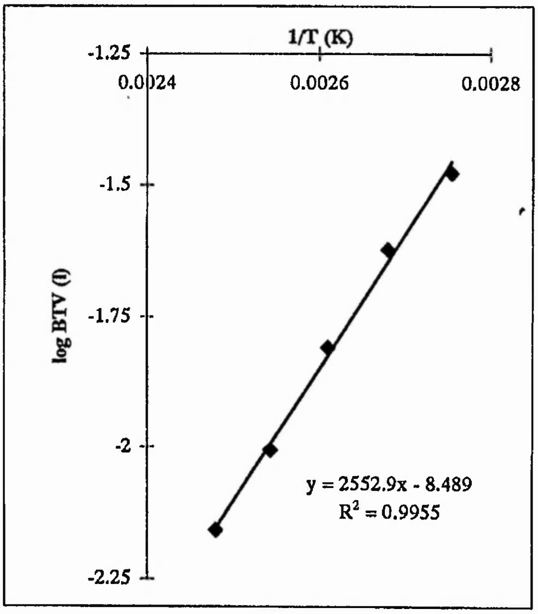


Figure 3.17 Variation in BTV with Temperature for the Chromosorb 102: Benzene System.

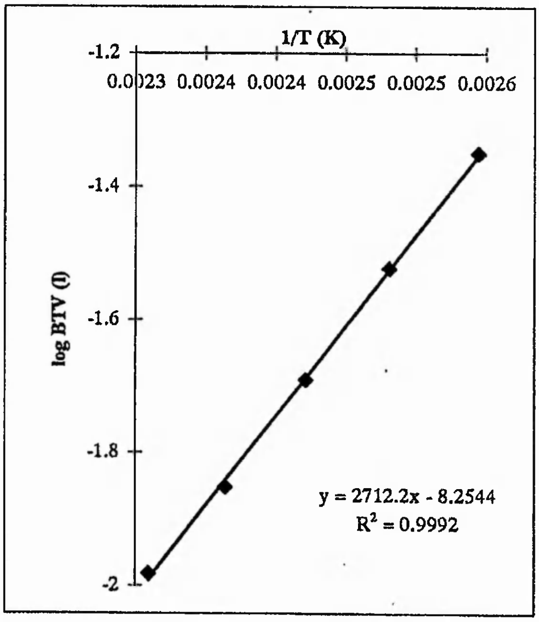


Figure 3.18 Variation in BTV with Temperature for the Chromosorb 102: Toluene System.

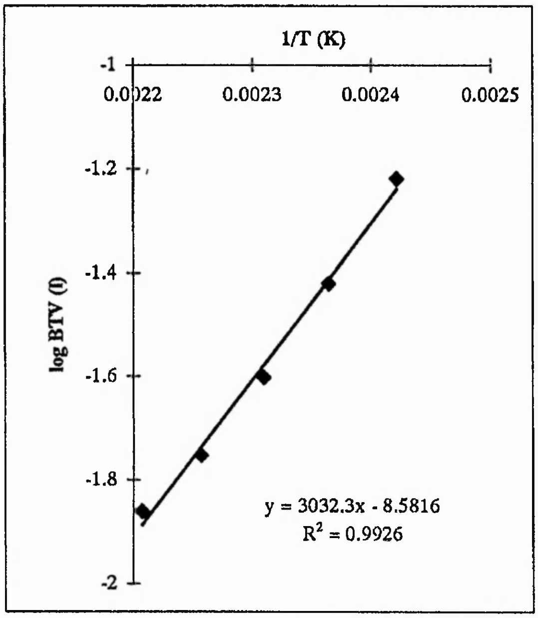


Figure 3.19 Variation in BTV with Temperature for the Chromosorb 102: 1-Limonene System.

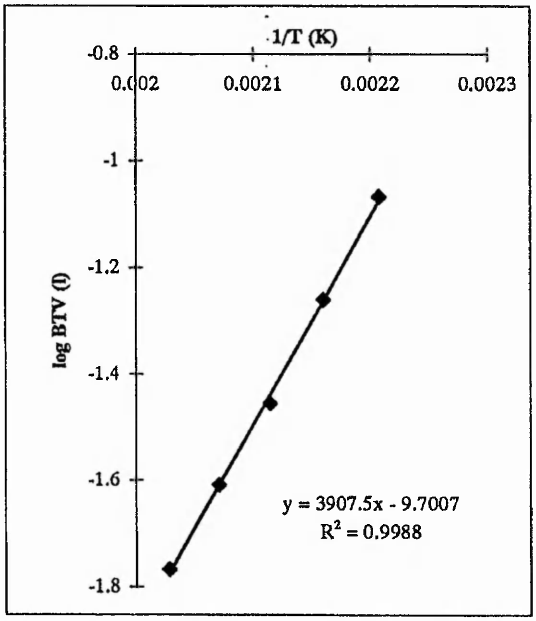


Figure 3.20 Variation in BTV with Temperature for the Chromosorb 106: Dichloromethane System.

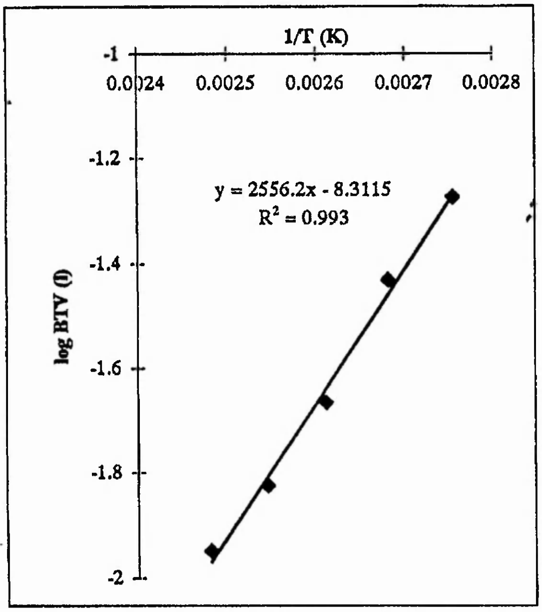


Figure 3.21 Variation in BTV with Temperature for the Chromosorb 106: Benzene System.

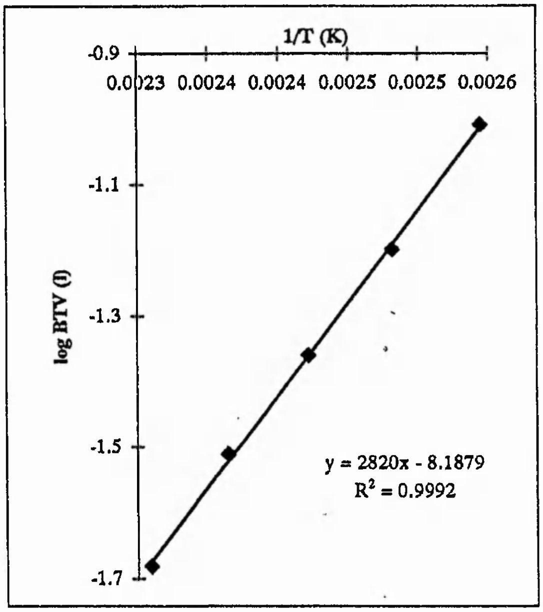


Figure 3.22 Variation in BTV with Temperature for the Chromosorb 106: Toluene System.

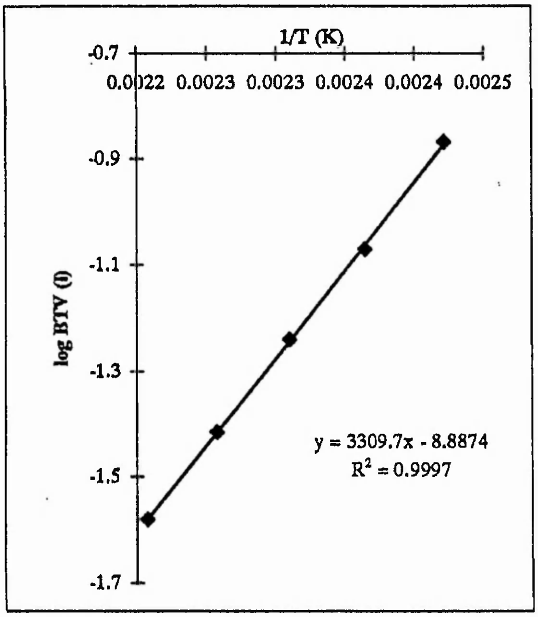


Figure 3.23 Variation in BTV with Temperature for the Chromosorb 106: 1-Limonene System.

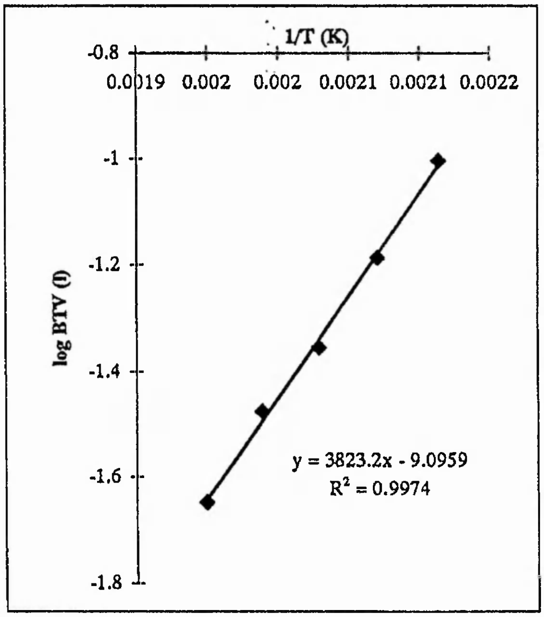


Figure 3.24 Variation in BTV with Temperature for the HayeSep Q: Dichloromethane System.

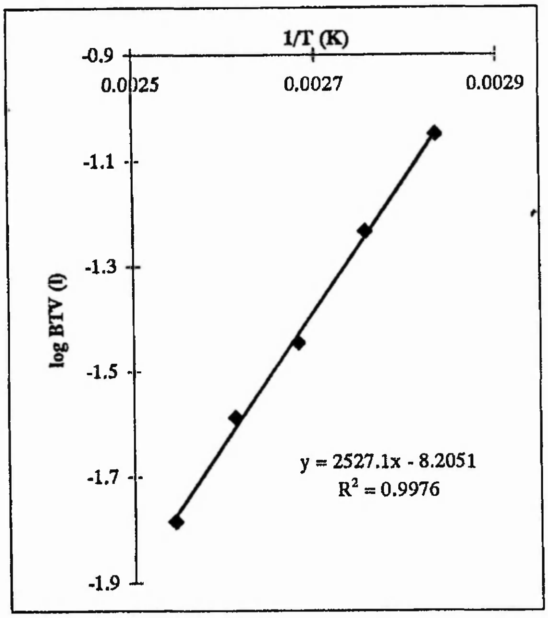


Figure 3.25 Variation in BTV with Temperature for the HayeSep Q: Benzene System.

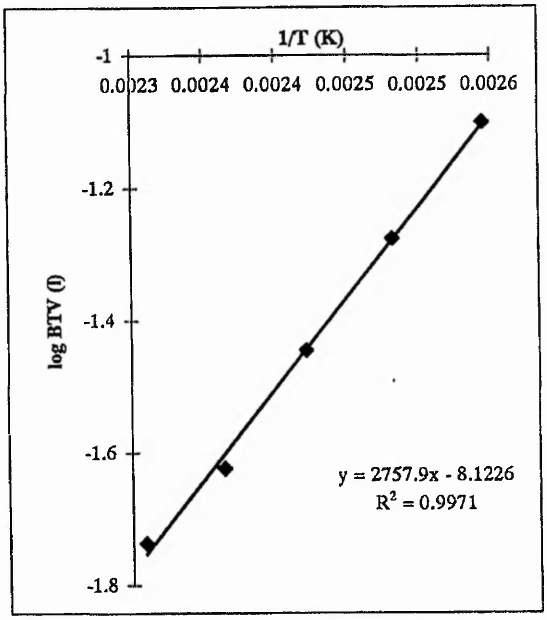


Figure 3.26 Variation in BTV with Temperature for the HayeSep Q: Toluene System.

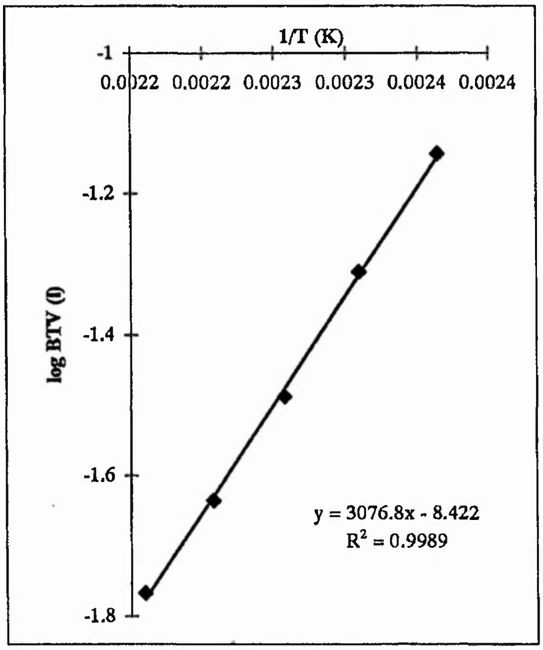


Figure 3.27 Variation in BTV with Temperature for the HayeSep Q: 1-Limonene System.

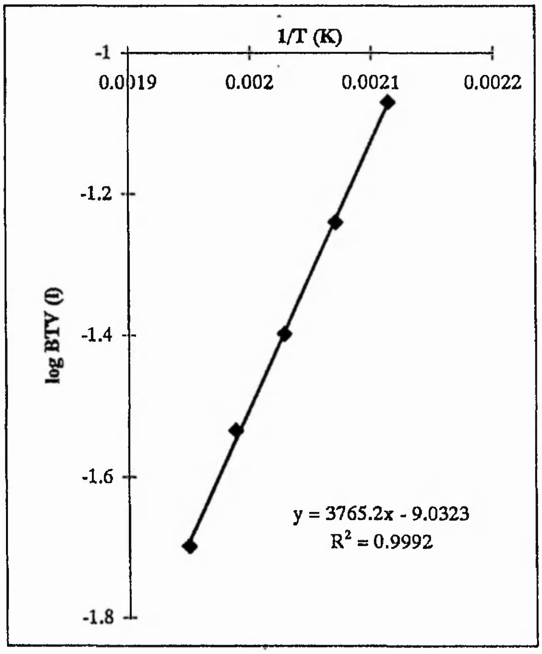


Figure 3.28 Variation in BTV with Temperature for the Porapak Q: Dichloromethane System.

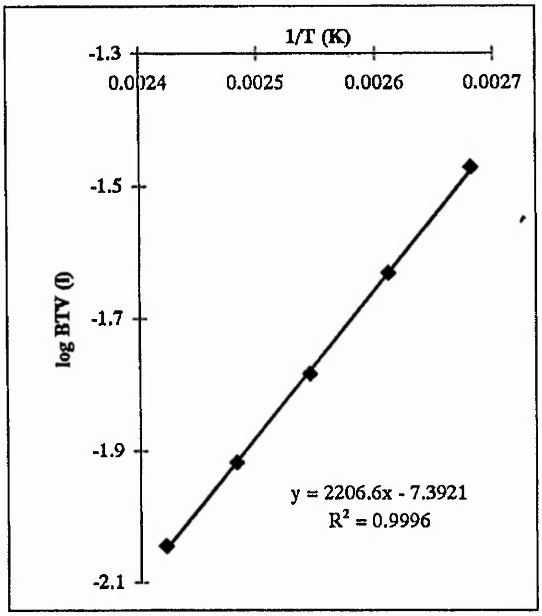


Figure 3.29 Variation in BTV with Temperature for the Porapak Q: Benzene System.

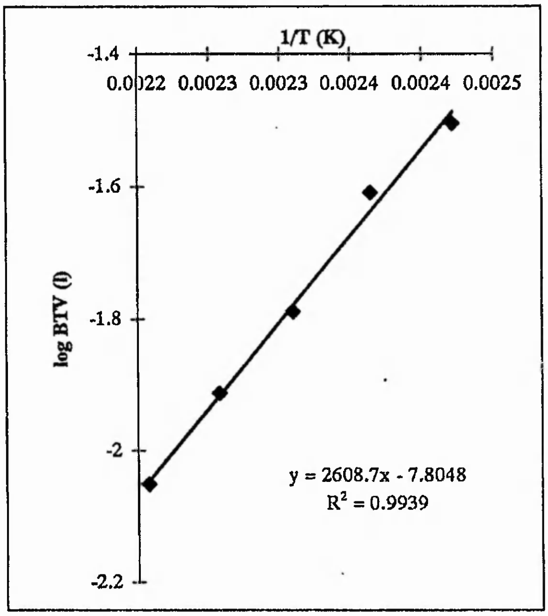


Figure 3.30 Variation in BTV with Temperature for the Porapak Q: Toluene System.

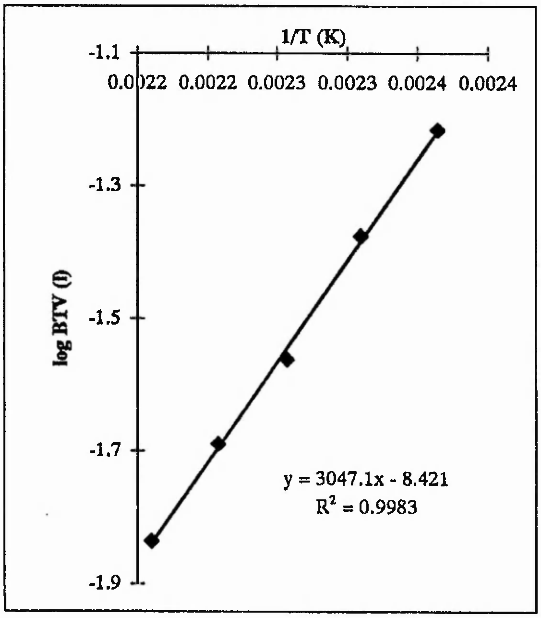
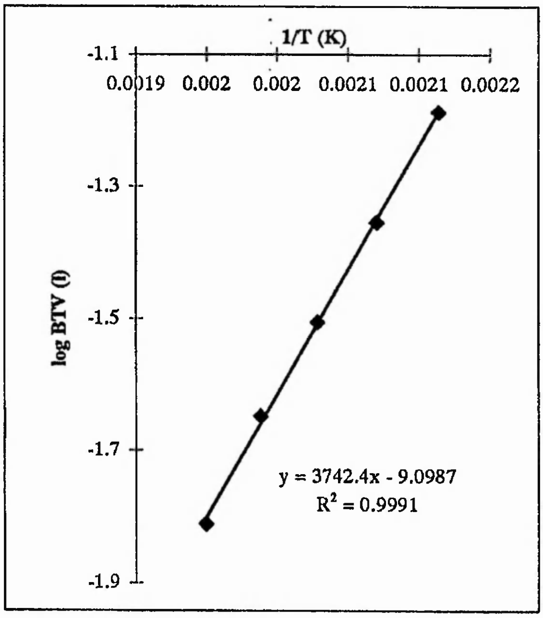


Figure 3.31 Variation in BTV with Temperature for the Porapak Q: 1-Limonene System.



3.5 Determination of Breakthrough Volumes by Continuous Injection of a Landfill Gas.

The following sections outline the instrumentation, experimental methods and results obtained from the investigation of the breakthrough volumes of the trace components present in a landfill gas. A discussion of the results is presented in Section 3.6.

3.5.1 Instrumentation

Analysis of the landfill gas samples was carried out using a Perkin-Elmer Automated Thermal Desorption System (ATD50) interfaced to a Hewlett-Packard 5890 Gas Chromatograph fitted with a HP5970 Quadrupole Mass Selective Detector (pages 40-42). The GC capillary column used for all the analyses was a 60m Restek RTX®-1 (100% dimethyl polysiloxane) column, 1.5μm film thickness, supplied by Thames Chromatography, Windsor. The above system was controlled with a Hewlett Packard 9000 workstation running HPMS-Chemstation software under UNIX. Compound identification was achieved by software comparison with the Wiley/NBS database of mass spectra and external reference compounds. The analytical conditions, which are discussed in detail in Chapter 4, are summarised in Table 3.5.

3.5.2 Experimental Methods

The landfill gas sample used for the breakthrough volume determinations, was taken directly from the gas extraction array at Site A, which had been installed to pipe the landfill gas from active areas of the landfill site to a flare stack and electricity generator (Chapter 5). The extracted gas was stored in a 65 litre Cali-5-bond™ gas sampling bag, obtained from Alltech, Carnforth. Known volumes of the landfill gas sample were drawn through the tube containing the adsorbent under investigation at 50 ml min^{-1} using a Gilian® Personal Air Sampler fitted with a constant low-flow module.

Table 3.5 Instrumental Setup.

Perkin-Elmer ATD50		**Hewlett-Packard 5890**	
Mode	Two-stage	**Injector Temperature**	250°C
Split-Ratio	200:1	**Detector Temperature**	250°C
Desorption Time	15 minutes	**GC Column**	RTX®-1; 60m; 1.5μm; 0.32mm ID.
Desorption Temperature	250°C	**Oven Temperature Programme**	35°C for 5mins, ramp at 5°C/min to 180°C.
Cold Trap Low	-30°C	**Carrier Gas**	Helium
Cold Trap High	300°C	**Linear Velocity**	21cmsec^{-1}
Trap Adsorbent	Tenax TA	**Detector Mass Range**	20-250amu

As the VOC's eluted from the first tube, they were trapped by a second multiple-adsorbent sample tube, containing a sandwich of three adsorbents, Tenax TA, Chromosorb 102 and Carbosieve SIII. Preparation of the multiple-adsorbent sample tubes is described in Section 3.2. Each sample tube was analysed twice to ensure that complete desorption of the retained components had been achieved. The percentage breakthrough of a given component was calculated by dividing the peak area of the component on the second tube, by the sum of the peak areas of the component on both of the tubes.

3.5.3 Example Calculation

Known volumes of landfill gas were drawn through a sample tube containing approximately 300mg of Chromosorb 102. A secondary multiple-adsorbent tube was placed in series with the sample tube and both tubes were analysed by ATD-GC-MS. Examples of the results are given in Table 3.6.

Table 3.6 Percentage Breakthrough of Selected Trace Components in Landfill Gas.[4]

Compound/Landfill Gas Volume (ml)	Peak Area Primary Tube	Peak Area Secondary Tube	Breakthrough of Analyte (%)
Chlorodifluoromethane			
200	24215662	82532102	77
300	21138289	128913321	86
500	10432877	211266140	95
700	16774558	293923994	95
Butane			
200	N/D	N/D	-
300	654469436	21744503	3
500	764938990	188292921	20
700	866708834	542950875	39
Dichlorofluoromethane			
200	N/D	N/D	-
300	43257563	N/D	-
500	66640981	5982032	8
700	90287863	28116919	24

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[4] N/D=Not detected

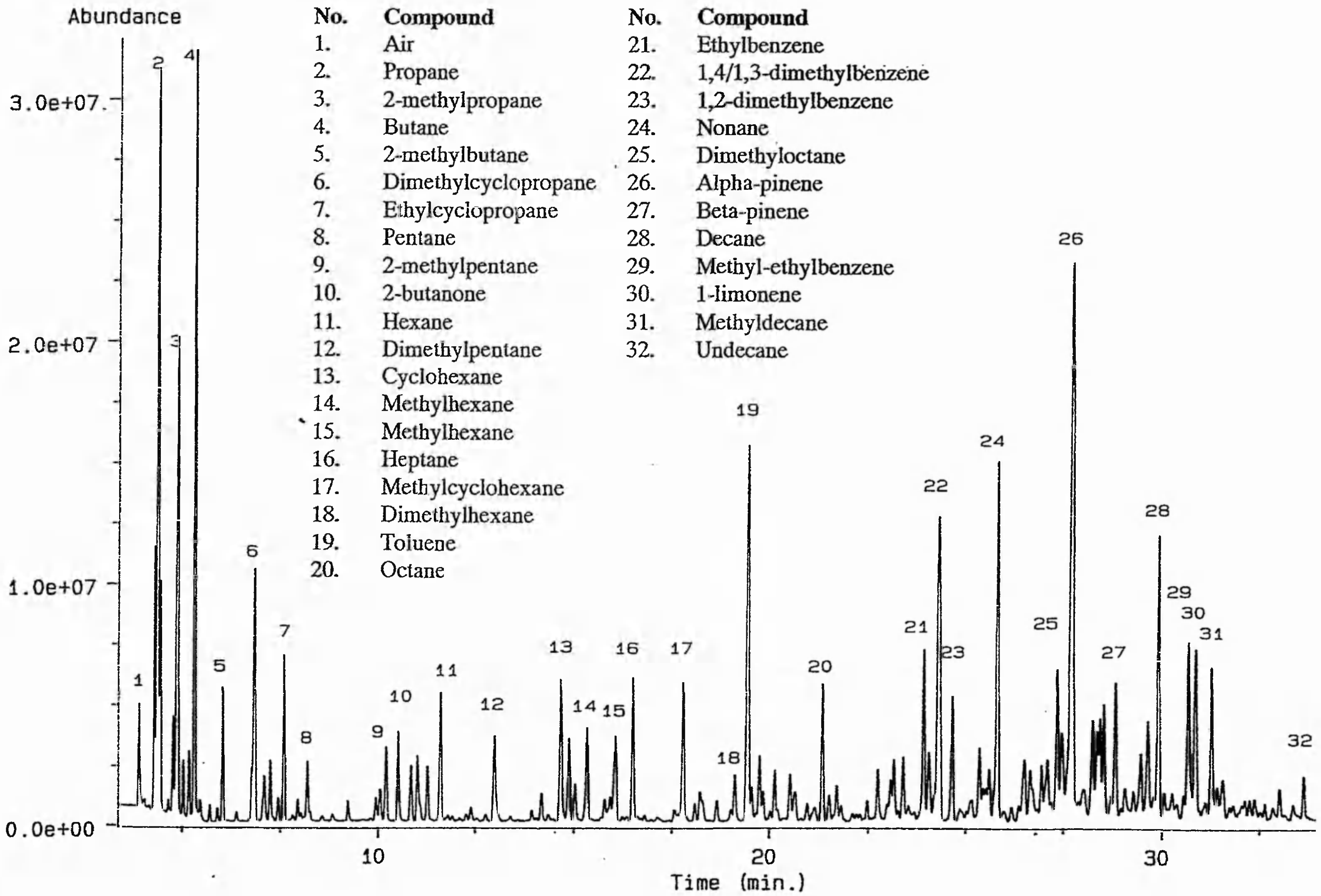
From the data contained in Table 3.6, the breakthrough volumes are predicted to be < 200ml for chlorodifluoromethane, 200-300ml for butane and 300-500ml for dichlorofluoromethane.

3.5.4 Results

A total of eight measurements (0.2, 0.3, 0.5, 0.7, 0.9, 1.2, 1.5 and 2.0 litres of landfill gas), were made for each of the adsorbents studied. Clearly, as the landfill gas volume increased there was a corresponding increase in the amount of VOC's "injected" onto the gas chromatograph. In order to prevent overloading of both the detector and the gas chromatography column, which occurred when the weight of individual VOC's adsorbed on the sample tube exceeded approximately 100μg, two litres of landfill gas was found to be the maximum that could be drawn through the adsorbent tube. A summary of the landfill gas composition is given in Table 3.7 and an annotated chromatogram of the landfill gas used is presented in Figure 3.32. The breakthrough volume data obtained for each of the adsorbents is summarised in Tables 3.8-3.10.

Table 3.7 Composition of the Landfill Gas used for the BTV Measurements.

Compounds	Concentration Detected (mg/m^3)
Total Alkanes	424
C2-C5 Alkanes	211
C6-C12 Alkanes	213
Total Alkanes	15
Total Alcohols and Ketones	24
Total Chlorinated Compounds	358
Total Cyclic Compounds	135
Total Aromatics	235
Total Pinenes	118
Bulk Gases (%)	
Methane	52
Carbon Dioxide	26
Oxygen	< 1



No.	Compound	No.	Compound
1.	Air	21.	Ethylbenzene
2.	Propane	22.	1,4/1,3-dimethylbenzene
3.	2-methylpropane	23.	1,2-dimethylbenzene
4.	Butane	24.	Nonane
5.	2-methylbutane	25.	Dimethyloctane
6.	Dimethylcyclopropane	26.	Alpha-pinene
7.	Ethylcyclopropane	27.	Beta-pinene
8.	Pentane	28.	Decane
9.	2-methylpentane	29.	Methyl-ethylbenzene
10.	2-butanone	30.	1-limonene
11.	Hexane	31.	Methyldecane
12.	Dimethylpentane	32.	Undecane
13.	Cyclohexane		
14.	Methylhexane		
15.	Methylhexane		
16.	Heptane		
17.	Methylcyclohexane		
18.	Dimethylhexane		
19.	Toluene		
20.	Octane		

Figure 3.32 Annotated Chromatogram of the Trace VOC's in the Landfill Gas Sample used for the BTV Studies Obtained using a Multiple-Adsorbent Tube.

Table 3.8 Predicted Breakthrough Volumes of Selected Trace components in Landfill Gas for 300mg of Tenax TA.

Compound	Breakthrough Volume (ml)
Chlorodifluoromethane	< 200
Propane	< 200
Dichlorodifluoromethane	< 200
Chlorofluoromethane	< 200
Chloroethane	< 200
Methylcyclopropane	< 200
Butane	< 200
1-Butene	< 200
Chloroethane	< 200
Dichlorofluoromethane	< 200
Pentane	< 200
Dichloromethane	200-300
Hexane	900-1200
Benzene	1500-1200
Cyclohexane	200-300
Heptane	1500-2000
Methylcyclohexane	900-1200
Toluene	> 2000
Octane	1500-2000
Xylene	> 2000
Alpha-Pinene	1200-1500
Decane	> 2000
1-Limonene	> 2000
Dodecane	> 2000

Table 3.9 Predicted Breakthrough Volumes of Selected Trace components in Landfill Gas for 300 mg of Chromosorb 102 and 106.

Compound	Chromosorb 102 BTV (ml)	Chromosorb 106 BTV (ml)
Chlorodifluoromethane	< 200	< 200
Propane	< 200	< 200
Dichlorodifluoromethane	< 200	< 200
Chlorofluoromethane	< 200	< 200
Chloroethene	< 200	200-300
Methylcyclopropane	200-300	300-500
Butane	200-300	300-500
1-Butene	300-500	500-700
Chloroethane	500-700	900-1200
Dichlorofluoromethane	300-500	< 200
Pentane	> 2000	> 2000
Dichloromethane	900-1200	1200-1500
Hexane	> 2000	> 2000
Benzene	> 2000	> 2000
Cyclohexane	> 2000	1500-2000
Heptane	> 2000	> 2000
Methylcyclohexane	> 2000	> 2000
Toluene	> 2000	> 2000
Octane	> 2000	> 2000
Xylene	> 2000	> 2000
Alpha-Pinene	> 2000	> 2000
Decane	> 2000	> 2000
1-Limonene	> 2000	> 2000
Dodecane	> 2000	> 2000

Table 3.10 Predicted Breakthrough Volumes of Selected Trace components in Landfill Gas for 300 mg of HayeSep Q and Porapak Q.

Compound	**Porapak Q BTV (ml)**	**HayeSep Q BTV (ml)**
Chlorodifluoromethane	< 200	< 200
Propane	< 200	< 200
Dichlorodifluoromethane	< 200	< 200
Chlorofluoromethane	< 200	< 200
Chloroethene	< 200	200-300
Methylcyclopropane	300-500	200-300
Butane	300-500	200-300
1-Butene	700-900	500-700
Chloroethane	700-900	500-700
Dichlorofluoromethane	700-900	500-700
Pentane	> 2000	> 2000
Dichloromethane	1200-1500	1500-1700
Hexane	> 2000	> 2000
Benzene	> 2000	> 2000
Cyclohexane	> 2000	> 2000
Heptane	> 2000	> 2000
Methylcyclohexane	> 2000	> 2000
Toluene	> 2000	> 2000
Octane	> 2000	> 2000
Xylene	> 2000	> 2000
Alpha-Pinene	> 2000	> 2000
Decane	> 2000	> 2000
1-Limonene	> 2000	> 2000
Dodecane	> 2000	> 2000

3.6 Discussion

The need to analyse trace levels of organic compounds in gaseous samples has led to the development of a wide range of porous polymer adsorbents. Many of these adsorbents differ in both adsorptive strength and selectivity. As a consequence, the correct choice of adsorbent for the sorption/thermal desorption of a given set of organic compounds is perhaps the most critical parameter in the analytical process. Breakthrough volume (BTV) is frequently used to describe the retention characteristics of a given adsorbent and is reported as being the volume of sample/carrier gas corresponding to the maximum concentration of eluted component. However, for this study the first appearance of the component in the eluent gas was measured as this was considered the true practical BTV for quantitative measurements.

The initial set of experiments reported in this chapter, were designed to ascertain the optimum analyte injection volume for the determination of breakthrough volumes for two of the adsorbents, Chromosorb 102 and Tenax TA. The results contained in Table 3.3 clearly illustrate that the volume of analyte injected has a significant effect on the values obtained, with increased injection volume resulting in lower breakthrough volumes. This observation may be explained in terms of the surface area and heterogeneity of the adsorbents. Chromosorb 102 has a surface area of 300-400m^2g^{-1} and Tenax TA, approximately 35m^2g^{-1}. Given that the non-specific retention of VOC's by solid adsorbents arises from weak van der Waals interactions between the analyte molecule and the adsorbent surface,[49] Chromosorb 102 would be expected to have a much larger sample capacity than Tenax TA. Examination of the breakthrough volume data supports this theory as the relative change in breakthrough volume with injection volume is less pronounced for Chromosorb

102 than for Tenax TA. It is therefore probable that the relatively large amounts of analyte injected were completely saturating the available adsorption sites, with the effect being greatest for Tenax TA because of its low surface area. An additional factor may be the availability of active sites within the heterogeneous adsorbents. At low analyte concentrations, the surface coverage will be small. As the analyte concentration increases the surface coverage will also increase, with the active sites being the first to be occupied. Once all the active sites have been filled, additional analyte molecules will appear to be prematurely eluted from the adsorbent bed. Given the above discussion, it was concluded that the minimum injection volume, 0.05µl, provided the most accurate estimate of the components breakthrough volumes at the concentrations likely to be encountered in a landfill gas (0.1-500mgm^{-3}).

A summary of the breakthrough volumes obtained by discrete injection of the individual compounds is presented in Table 3.4. In order to compare this data with that obtained using different adsorbents and by other authors, the specific breakthrough volume, which accounts for factors such as packing density and adsorbent weight, is also reported. For the n-alkanes, the breakthrough volumes were found to be directly related to the boiling point and molecular weight of the compounds. This was also the case for benzene, toluene and xylene, which exhibit a 2-20 fold increase in breakthrough volume with the addition of one and two methyl groups to the benzene ring respectively. This relationship, however, does not describe the retention behaviour of ethanol. Ethanol has a boiling point of 78°C and, given the assumption that vapour pressure is directly proportional to BTV (page 51), it would be expected to be more strongly retained than dichloromethane, which has a boiling point of 40°C. For all the adsorbents studied the opposite was observed, with the breakthrough volume of dichloromethane being on average twice that of ethanol. It is clear, therefore, that all five adsorbents exhibit a degree of selectivity, with non-polar compounds being more strongly retained than polar compounds. A comparison of the Tenax TA breakthrough volume data with those obtained by other workers is presented in Table 3.11.

Table 3.11 Comparison of the Reported Breakthrough Volumes (lg^{-1}) of the Twelve Components Studied for Tenax TA.

Compound / ***Bpt (°C)***	**This Work (Practical BTV)**	**Mastrogiacomo** ***et al*[26].**	**Phase Separations[59]**	**HSE (UK)**	**Manura[60]**
Ethanol *78*	0.65	1.3	0.9	-	1.8
DCM *40*	2.90	-	1.5	3.7	-
Hexane *69*	6.20	29	16	15-21	31.6
Benzene *80*	12.4	29	31	22-73	70
Cyclohexane *81*	5.50	-	-	-	-
Heptane *98*	8.80	-	85	-	100
Toluene *92*	50.8	-	190	-	400
Xylene *106*	118	-	1500	-	1550
Nonane *151*	184	-	-	-	2000
Decane *174*	356	8000	-	6000	3900
1-Limonene *176*	1040	-	-	-	12000
Dodecane *216*	1180	-	-	-	50000

All the values reported are specific breakthrough volumes at 20°C in units of litres per gram of Tenax TA. Although this study was primarily comparative and not a detailed investigation of the adsorbents retention characteristics, it is clear that there are significant differences between published BTV data. The obvious discrepancies can largely be accounted for by examining the methods used for their calculation. The method of sample introduction used by Manura[60] was identical to the system described in this chapter. Instead of measuring the distance to the leading edge of the eluting peak, however, Manura measured the distance to the peak maxima. This approach can lead to an over-estimation of the true BTV. If it is assumed that the eluting peak is approximately gaussian in shape, which was true for the majority of the adsorbent-adsorbate systems examined for this work, then the peak maxima corresponds to the volume at which half the analyte added has been lost from the end of the adsorbent tube. By contrast, the distance to the front of the eluting peak corresponds to a volume at which 1-5% of the analyte has been lost. Given the fact that breakthrough volumes are used as guidance for calculating the maximum volume of air that can be drawn through the tube without resulting in sample loss, the latter method is clearly more accurate.

The approach described by Mastrogiacomo[26] involved introducing a constant flow of a known concentration of each analyte. The observed breakthrough volume was then calculated by dividing the retention volume by two. Due to the fact that there are two definitions of retention volume in common usage and that Mastrogiacomo does not define which he used, it is impossible to comment on the accuracy of these results. However, continuous injection of the analyte does provide a more accurate representation of an actual sample than the discrete injection of an individual component, although both methods fail to reproduce the effects of differing sample compositions and humidity.

Thus, the breakthrough volume measurements were repeated using continuous injection of a sample of landfill gas. The information obtained from this study, which is summarised in Tables 3.8-3.10, identified a number of important points. Firstly, because of their low breakthrough volumes (< 500ml), none of the adsorbents examined were suitable for the preconcentration of the highly volatile components, such as the CFC's, propane and butane. Secondly, the breakthrough volume of cyclohexane was observed to be significantly lower than that predicted by indirect techniques. This may possibly be explained in terms of the competition for the available adsorption sites. The equilibrium between the amount of material in the adsorbed phase and the amount in the vapour phase is governed by the volatility of the compound and its relative affinity to the stationary phase. When more than one type of compound is present in the vapour phase, competition between the molecules for the available adsorption sites can take place. The non-planar structure of cyclohexane may result in it having a relatively low affinity for the adsorbent surface and as a result of the aforementioned processes, being prematurely eluted from the adsorbent bed. Thirdly, with the exception of Tenax TA, all alkanes containing six carbon atoms or more had breakthrough volumes in excess of 2 litres for 300mg of each of the adsorbents studied. By contrast, the BTV of hexane on Tenax TA (300mg) was predicted to be approximately 1000ml. A comparison of the data obtained from discrete injection of the individual components and continuous injection of a landfill gas for the 12 components contained in the calibration standard is given in Table 3.11.

Table 3.11 Variation in Breakthrough Volumes Observed for the Discrete Injection of Individual Components and the Continuous Injection of a Landfill Gas.[5]

Compound	Tenax TA	Chromosorb 102	Chromosorb 106	Porapak Q	HayeSep Q
DCM	0.65 (0.20-0.30)	1.70 (0.90-1.20)	2.60 (1.20-1.50)	1.40 (1.20-1.50)	2.60 (1.50-1.70)
Hexane	1.40 (0.90-1.20)	12.9 (>2.00)	10.2 (>2.00)	21.9 (>2.00)	25.5 (>2.00)
Benzene	2.80 (1.50-2.00)	10.1 (>2.00)	27.3 (>2.00)	12.6 (>2.00)	19.5 (>2.00)
Cyclohexane	1.25 (0.20-0.30)	9.05 (>2.00)	29.4 (1.20-1.50)	13.6 (>2.00)	34.0 (>2.00)
Heptane	2.00 (1.50-2.00)	86.8 (>2.00)	150 (>2.00)	137 (>2.00)	134 (>2.00)
Toluene	11.5 (>2.00)	58.6 (>2.00)	256 (>2.00)	95.2 (>2.00)	120 (>2.00)
Xylene	26.7 (>2.00)	324 (>2.00)	1068 (>2.00)	375 (>2.00)	376 (>2.00)
Nonane	41.7 (>2.00)	835 (>2.00)	4032 (>2.00)	3307 (>2.00)	2847 (>2.00)
Decane	80.5 (>2.00)	10783 (>2.00)	32371 (>2.00)	11350 (>2.00)	9152 (>2.00)
1-Limonene	243 (>2.00)	4320 (>2.00)	8965 (>2.00)	4721 (>2.00)	6580 (>2.00)
Dodecane	267 (>2.00)	132724 (>2.00)	1314935 (>2.00)	276905 (>2.00)	748340 (>2.00)

Several conclusions can be drawn from this data. Firstly, although a detailed comparison is impossible because of the maximum volume of landfill gas examined (2 litres), the correlation between the predicted BTV's obtained by the two methods is good. Secondly, both studies indicate that the adsorptive strength (BTV) increases in the order; Tenax TA << Chromosorb 102 < Porapak Q < HayeSep Q < Chromosorb 106. The retention characteristics of the latter four

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[5] Breakthrough volumes are all reported in litres per 300mg of adsorbent.
Figures in brackets refer to estimated BTV determined from the continuous injection of a landfill gas which was known to contain a wide range of trace volatile organic compounds.

adsorbents were all found to be similar. The final choice of adsorbents for use in the multiple-adsorbent tube is therefore somewhat subjective. The criteria for the selection of the primary adsorbent(s) were their desorption efficiencies for the less volatile trace compounds and their thermal stability. Desorption efficiency was assessed by carrying out multiple analyses of a landfill gas sample, and thermal stability, by analysing a batch of clean, freshly conditioned adsorbent. Of the adsorbents studied, Tenax TA and Chromosorb 102 were confirmed to be the most appropriate. Chromosorb 106 was discounted because the desorption efficiencies of undecane, dodecane and certain substituted aromatic compounds were found to be unacceptably low (less than 75%). HayeSep Q and Porapak Q were discounted for two reasons. Firstly, both exhibited relatively low thermal stability which led to artifacts in their blank chromatograms. The artifacts arise from partial degradation of the polymer matrix at elevated temperatures and thus cannot be completely eliminated. Secondly, given that only 500ml of sample is required for landfill gas analysis, Chromosorb 102 was chosen in preference to Porapak Q and HayeSep Q because of its lower breakthrough volumes and hence desorption volumes of the less volatile substituted aromatic compounds and alkanes. As an additional safeguard, Tenax TA was selected to trap the least volatile of the trace VOC's, such as the larger substituted aromatic compounds.

3.7 Conclusions

The aim of the research outlined in this chapter was to investigate the retention characteristics of five adsorbents, Chromosorb 102 and 106, Tenax TA, Porapak Q and HayeSep Q. This was achieved by examining the breakthrough volume data derived from discrete injection of individual components and the continuous injection of a sample of landfill gas. The information acquired was then used to assess the adsorbents suitability for use as a primary adsorbent in conjunction with Carbosieve SIII for the preconcentration of all the trace volatile organic compounds (VOC's) in landfill gas.

In terms of the compounds studied, the adsorptive strength was found to increase in the order; Tenax TA << Chromosorb 102 < Porapak Q < HayeSep Q < Chromosorb 106. Despite the observed dissimilarity, none of the adsorbents investigated were suitable for the analysis of all the trace VOC's present in landfill gas because of their diverse range of physical properties. As a consequence, a multi-adsorbent sample tube containing a sandwich of three adsorbents was developed. The sample tubes were prepared by filling 6.4mm I.D. x 89.0mm stainless-steel tubes with approximately 100mg of the following adsorbents packed in series; Tenax TA (80/100mesh), Chromosorb 102 (80/100mesh) and Carbosieve SIII (60/80mesh). The selectivity of each of the adsorbents was exploited by arranging them in order of increasing adsorptive strength. The main advantages of this approach are that it is a highly efficient, flexible and robust method of sampling a wide range of trace VOC's. The latter point is significant because the developed method will be used to sample a variety of landfill sites, each having different waste inputs and, as a result, differing landfill gas compositions.

3.8 References

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Chapter 4

Optimisation of the Sampling and Analytical Procedures

4.0 Research Aims

To develop, optimise and evaluate an analytical method for the determination of all the trace VOC's in landfill gas using a multiple-adsorbent sampling tube and analysis by thermal desorption - gas chromatography - mass spectrometry.

4.1 Introduction

The selection and development of a method for the analysis of all the trace VOC's in landfill gas requires careful consideration of the composition and physical properties of the sample matrix and it's influence on the performance of a given analytical system. For example, the relatively large amounts of water vapour present in the gas precludes the use of on-line cryotrapping techniques for the reasons outlined in Chapter 2.[1] The diversity of compounds present rules out the use of membrane extraction techniques and diffusive sampling.[2,3] As a consequence, active sampling using adsorbent tubes was chosen for further investigation.

The analytical process to be developed can essentially be divided into three stages; preconcentration onto an adsorbent tube, desorption and transfer from the adsorbent tube to the gas chromatograph and separation and detection. The first stage, which is discussed in detail in Chapter 3, utilises a sample tube containing a sandwich of three adsorbents, Tenax TA, Chromosorb 102 and Carbosieve SIII. The adsorbents were placed in order of increasing adsorptive strength which enabled a single sample tube to be used to trap all of the VOC's present in landfill gas.

The aim of the research described in this chapter was to optimise the processes involved in the transfer of the VOC's from the multi-layer sample tube to the gas chromatograph and their resultant separation and detection. For ease of reporting, each stage of the latter processes will be discussed separately. It is important to note, however, that the performance of each of the stages is partly governed by the effectiveness of the previous step and therefore cannot be completely considered in isolation.

4.2 Optimisation of the Perkin-Elmer ATD 50

The efficient transfer of the analyte compounds from the sampling tube to the gas chromatograph is dependent upon efficient thermal desorption of the VOC's and "injection" onto the gas chromatograph as a focussed sample band. As described briefly in Chapter 2 (Figure 2.6, pages 40-42), the Perkin-Elmer ATD50 was designed to facilitate the delivery of μg or ng quantities of VOC's from an adsorbent sampling tube to a gas chromatograph for their subsequent separation and detection. This is achieved by a two-stage desorption process. The first desorption stage involves heating the sample tube to a predetermined temperature whilst at the same time passing an inert gas through the tube at a constant, known flow rate. The eluting VOC's are then cryofocussed at -30°C onto a secondary trap containing a weak adsorbent, such as Tenax TA, using a peltier cooling element. Rapid heating of the secondary trap (100°C/s to 350°C) ensures that the retained components are transferred to the analytical GC column as a narrow band of vapour.[4] The following sections outline the experimental methods and results derived from the optimisation of the thermal desorption parameters.

4.2.1 Instrumentation

Analysis of all the samples was carried out using a Perkin-Elmer ATD50 interfaced to 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. Compound identification was achieved by software comparison with the Wiley/NBS database of mass spectra. A summary of the analytical conditions is given in Table 4.1. An empirical study of the inlet and outlet split flows on the ATD50 ascertained that the optimum settings were 27 and 19 ml min^{-1} respectively, giving anoverall split ratio of 200:1. The relatively high inlet split ratio was selected for two reasons. Firstly, the desorption flow through the sample tube is increased, leading to higher desorption efficiency and lower desorption time. Secondly, as a large proportion of the sample is vented to atmosphere, the amount of water vapour entering the cold trap is kept to a minimum. The latter point is important because water vapour freezes within the cold trap, which can affect trapping efficiency and lead to sample line blockages. The high outlet split ratio was selected to maximise desorption flow through the cold trap whilst at the same time maintaining the relatively low carrier gas flow rates required for capillary GC columns.

4.2.2 Experimental Methods

The standard mixture used for the investigations consisted of 12 components, all of which being liquids at room temperature. Each of the components was selected such that most of the compounds present in a typical landfill gas sample were either in the standard mixture or were isomers of one of the standards. A list of the components used is given in Table 4.2. Each sample tube was prepared by first inserting a retaining gauze in the tube followed by 120mg of Tenax TA. The tube was then gently tapped on a bench-top to remove air gaps and produce a consistant packing density.

Table 4.1 Instrumental Set-up.

Perkin-Elmer ATD50		**Hewlett-Packard 5890**	
Mode	Two-stage	**Injector Temperature**	250°C
Split-Ratio	200:1	**Detector Temperature**	250°C
Desorption Time	15 minutes	**GC Column**	RTX®-1; 60m; 1.5μm; 0.32mm ID.
Desorption Temperature	250°C	**Oven Temperature Programme**	35°C for 5mins, ramp at 5°C/min to 180°C.
Cold Trap Low	-30°C	**Carrier Gas**	Helium
Cold Trap High	300°C	**Linear Velocity**	21cm sec^{-1}
Trap Adsorbent	Tenax TA	**Detector Mass Range**	20-250amu

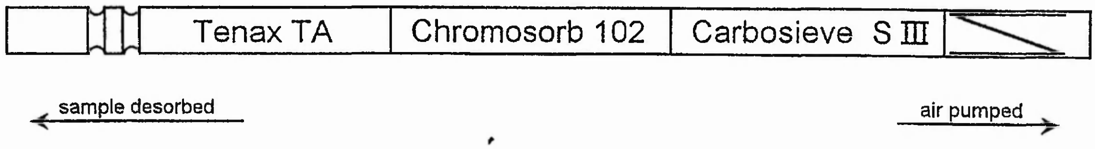
The process was then repeated with 120mg of Chromosorb 102 and 130 mg of Carbosieve SIII. The final retaining gauze was then inserted and the sample tube immediately sealed using swagelok® end-caps fitted with PTFE ferrules. The laser etched reference number of each tube was noted. All three adsorbents were preconditioned prior to their use in a modified GC injection port under a 100 ml min^{-1} flow of nitrogen. The GC was programmed to ramp from 20°C to 250°C at 1°C/min. The temperature was then held at 250°C for 12 hours. 0.5ml of each of the components were prepared on a daily basis using high purity HPLC-grade chemicals obtained from Fisher Scientific, Loughborough. In order to reduce evaporative losses during preparation, the components were added in order of increasing volatility. The standardised tubes were prepared as follows; the tubes were clamped in an upright position with a plug of silanised glass wool inserted into the top. A Gilian® Personal Air Sampler fitted with a constant-low-flow module was then used to draw a 50ml min^{-1} flow of clean air through the tube for a period of ten minutes. Immediately after switching the pump on, 0.5µl of the standard 12 component mixture was injected onto the silanised glass wool, taking care not to push the needle into the bed of the packing.

Table 4.2 Physical Properties of the Components in the Standard Mixture.[5]

Compound	Boiling Point (°C)	Density d_{20}(gcm^{-3})	Compound	Boiling Point (°C)	Density d_{20}(gcm^{-3})
Ethanol	78	0.7893	Toluene	111	0.8669
DCM	40	1.3266	p-Xylene	138	0.8611
n-Hexane	69	0.6548	n-Nonane	151	0.7176
Benzene	80	0.8765	n-Decane	174	0.7300
Cyclohexane	81	0.7785	1-Limonene	176	0.8411

The sample tubes were then immediately sealed with Swagelok® end-caps fitted with PTFE ferrules. Figure 4.1 illustrates the configuration of the tube and the direction of gas flow during sample preparation and thermal desorption. Whenever possible, each standardised tube was analysed immediately upon preparation under the conditions summarised in Table 4.1. Unless otherwise stated, each measurement was carried out in triplicate, with the reported values being an average of the three measurements.

Figure 4.1 Direction of Gas Flow During Sample Tube Preparation and Thermal Desorption.



4.2.3 Primary Desorption Temperature

The first parameter to be investigated was the primary desorption temperature. The primary desorption temperature controls the rate at which the components are desorbed from the sample tube. In order to reduce the effects of adsorbent degradation and eliminate reactions between the adsorbed species and the surfaces of the sample tube and the adsorbent at elevated temperatures, the primary desorption temperature should be kept to a minimum. A total of 8 measurements were made over a primary desorption temperature range of 75-250°C. A desorption time of 15 minutes was used for all the analyses.

Results and Discussion

Figures 4.2 and 4.3 illustrate the effect of the primary desorption temperature on the amounts of the twelve component mixture detected. As would be expected, the amount of each of the components detected increased with increasing desorption temperature, with the effect being more pronounced for the higher boiling point compounds, decane 1-limonene and dodecane.

Figure 4.2 The Effect of Primary Desorption Temperature on the Amount of Ethanol, Hexane, Cyclohexane, Toluene, Nonane and 1-Limonene Detected.

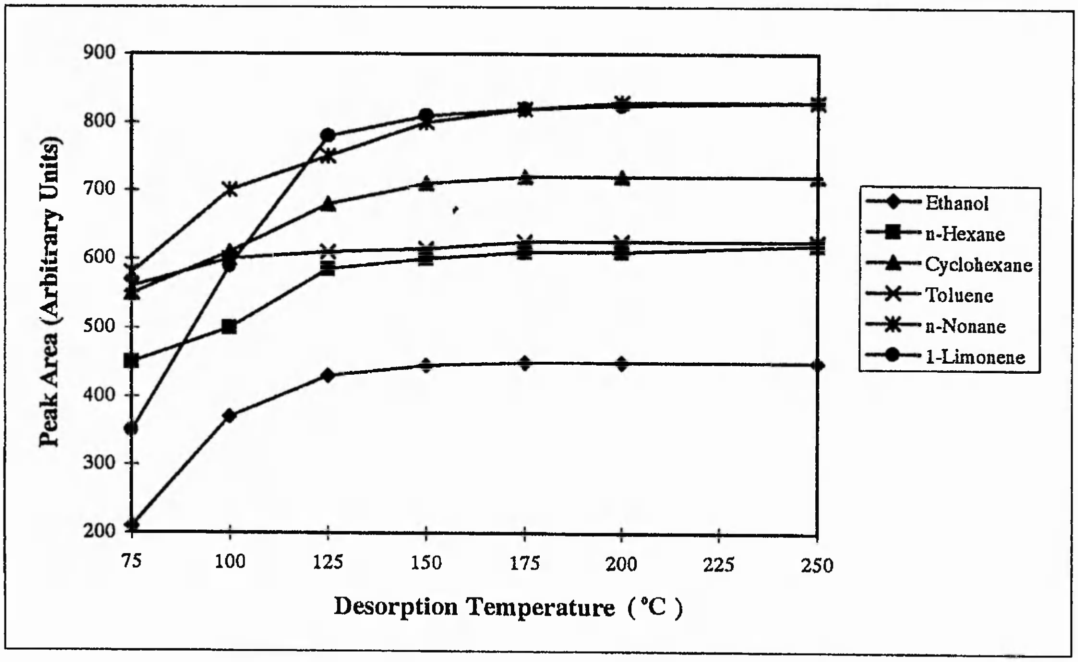
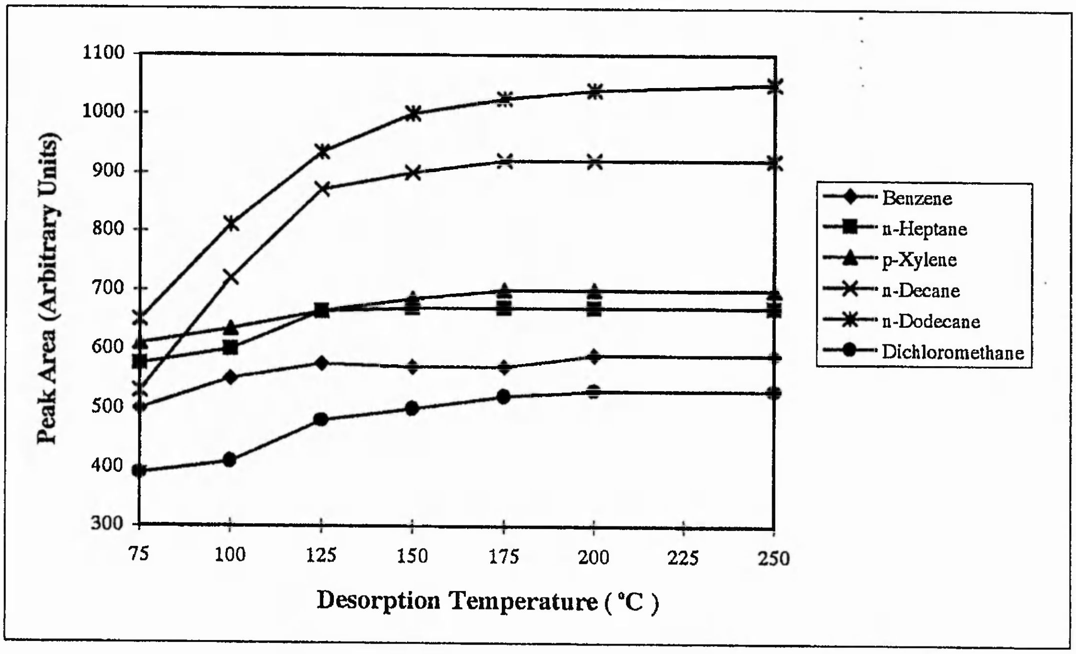


Figure 4.3 The Effect of Primary Desorption Temperature on the Amount of Dodecane, Decane, p-Xylene, n-Heptane, Benzene and Dichloromethane Detected.



Although complete desorption of all the remaining components appeared to be achieved at 175°C, the minimum desorption temperature for a desorption efficiency of >98% for the latter compounds was found to be within the range 200-250°C.

In order to ascertain if 200°C was sufficient to efficiently desorb all of the components contained in the standard mixture, a further six samples were analysed at both 200°C and 250°C and the precision of the resultant data calculated using the following equation;

% RSD = (Standard Deviation of the Peak Areas / Mean Peak Area) x 100

The results obtained are summarised in Table 4.3.

Table 4.3 The Effect of Primary Desorption Temperature on the Precision of the Standard Integration Data Obtained at 200°C and 250°C.

Compound	RSD (%) 200°C	RSD (%) 250°C	Compound	RSD (%) 200°C	RSD (%) 250°C
Ethanol	2.80	2.80	Toluene	2.45	1.60
Dichloromethane	2.50	1.80	p-Xylene	2.90	1.20
n-Hexane	3.40	1.90	n-Nonane	2.70	1.10
Benzene	1.95	1.85	n-Decane	2.60	2.30
Cyclohexane	1.90	1.65	1-Limonene	2.65	2.40
n-Heptane	2.10	1.50	Dodecane	4.50	2.60

With the exception of toluene, p-xylene, nonane and dodecane, there was found to be little change in both the peak areas of the compounds and the precision of the measurements. The observed increase in precision at 250°C for the aforementioned compounds may be explained by the strength of the adsorbent-adsorbate interactions. The Tenax TA breakthrough volume data, which is summarised in Chapter 3, indicates that toluene, p-xylene and nonane would all be expected to be efficiently adsorbed and thermally desorbed from Tenax TA at 200°C. However, as a consequence of using a multiple-bed sampling tube, the aforementioned compounds are able to partially elute from the end of the Tenax TA bed during sampling and, as a result, become adsorbed onto the Chromosorb 102. The increase in the strength of the van der Waals interaction between the adsorbate molecules and the Chromosorb 102 compared to that of Tenax TA, results in them being partially retained at 200°C. A primary desorption temperature of 250°C is high enough to outweigh this effect and thus efficiently desorb the analyte molecules. Although ethanol, dichloromethane, hexane, benzene and heptane would also pass through the Tenax TA bed and become adsorbed by the Chromosorb 102, the magnitude of the van der Waals forces for these compounds are substantially lower than that of toluene, p-xylene and nonane, and they are thus efficiently desorbed at lower temperatures. Decane, 1-limonene and dodecane are all adsorbed by the Tenax TA, with complete desorption of dodecane only occurring at a temperature of 250°C. The reproducibility of the recovery data showed no evidence of decomposition for any of the compounds studied at the latter value. It was concluded, therefore, that a primary desorption temperature of 250°C should be used for all the analyses.

4.2.4 Primary Desorption Time

As it's name suggests, the primary desorption time parameter is used to define the timescale over which the primary desorption step takes place, that is the time required to completely extract the analytes from the sample tube at a given temperature. In order to reduce analysis times, the primary desorption time should be kept to a minimum. A total of four measurements were taken at 4, 8, 12 and 16 minutes. A primary desorption temperature of 250°C was used for all the analyses.

Results and Discussion

The variation in the amounts of the 12 component mixture detected with primary desorption time is illustrated in Figures 4.4 and 4.5. For the more volatile components, such as ethanol, dichloromethane, hexane and cyclohexane, there was little change in the component peak areas over the range 4-16 minutes.

Figure 4.4 The Effect of Primary Desorption Time on the Amount of Ethanol, Hexane, Cyclohexane, Toluene, Nonane and 1-Limonene Detected.

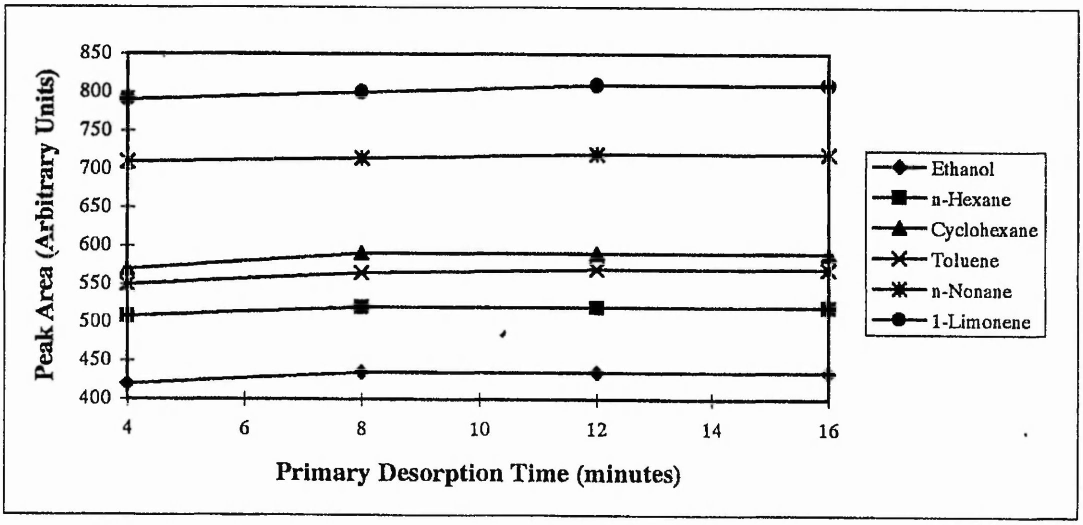
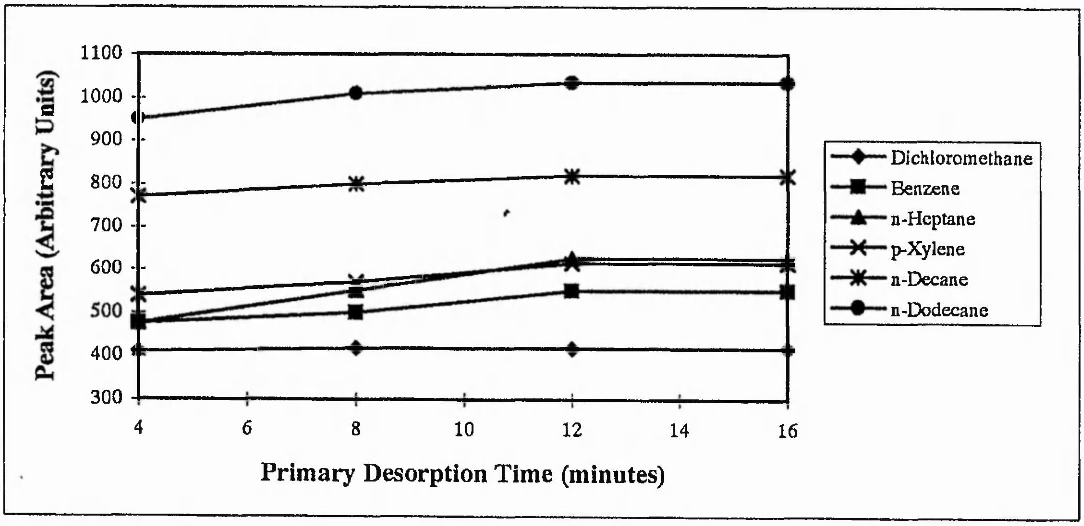


Figure 4.5 The Effect of Primary Desorption Time on the Amount of Dodecane, Decane, p-Xylene, n-Heptane, Benzene and Dichloromethane Detected.



By contrast, there was a pronounced increase in the recovery of the less volatile components, dodecane, 1-limonene, decane and nonane, up to a desorption time of 12 minutes.The amount of all the components detected was constant between 12 and 16 minutes, which suggests that complete desorption had been achieved at the former desorption time, and that routinely, desorption efficiencies (DE) of >99% should be expected. Although complete desorption of the standard mixture was achieved after 12 minutes, it was decided that the primary desorption time should be increased to 15 minutes in order to account for the increased complexity of the reported landfill gas compositions.

4.2.5 Sample Delay Time

Both the Perkin-Elmer ATD50 and ATD400 can be operated in single analysis mode, where only one tube is analysed under a given method, or in multiple analysis mode, where fully automated analyses of up to fifty sample tubes can be achieved.[4] The latter feature is of particular importance as it allows the operator to carry out the unsupervised analysis of routine samples overnight. Preliminary studies on the ATD-GC-MS had suggested that for certain compounds, it was not possible to obtain an RSD of less than 8% whilst operating it in the fully automated mode. Given that RSDs of 3% or less could be readily achieved whilst carrying out replicate analyses on a single sample tube under identical conditions, it was concluded that the automation process was resulting in sample loss and a corresponding loss in precision. For fully automated sample analyses the process of events is as follows; the ATD50 elevates the sample tube into the desorption position, purges the sample tube with helium and carries out a pressure test to ensure that the tube is correctly sealed. Given a satisfactory result to the pressure test, the ATD50 automatically proceeds to the second stage in the process, primary desorption and focussing of the VOC's onto the cold trap at -30 °C. Secondary desorption then occurs by flash heating the cold trap to 350 °C within 7 seconds. The VOC's are then transferred through a heated transfer line to the GC capillary column for separation followed by mass spectrometric detection. When the ATD50 is being operated in the fully automated mode, at a given time, which is defined by the sample delay function, the ATD50 lowers the analysed sample and loads the next sample for pressure testing. Desorption of the second sample tube does not commence until the gas chromatograph has completed it's temperature program and cooled down to it's initial temperature. The ATD50 then receives a trigger signal from the gas chromatograph operating system and continues the desorption cycle. The effect of changing the sample delay time from 20 minutes to 55 minutes, which corresponds to the full run-time for an analysis, that is the time from the injection of the sample to the point when the ATD receives the trigger signal from the gas chromatograph, is illustrated in Table 4.4.

Given that both sets of samples took the same length of time to be analysed, the reason for the obvious discrepancy in the precision of the data must be the automation process. The most likely explanation for the observed effect is partial heating of the sample tube. If the sample delay time does not allow sufficient time for the gas chromatograph to complete it's temperature cycle, the sample tube is held in the primary desorption position, adjacent to the desorption oven, until the ATD50 receives the trigger signal from the gas chromatograph.

Table 4.4 The Effect of Sample Delay Time (SDT) on the Precision of the Standard Integration Data.

Component	RSD (%) SDT=20min	RSD (%) SDT=55min	Component	RSD (%) SDT=20min	RSD (%) SDT=55min
Ethanol	9.85	0.75	Toluene	7.45	1.70
DCM	8.15	1.60	p-Xylene	6.90	1.10
n-Hexane	6.95	1.35	n-Nonane	5.70	1.40
Benzene	7.05	1.90	n-Decane	5.60	1.95
Cyclohexane	7.55	1.55	1-Limonene	4.65	1.80
n-Heptane	5.95	1.35	Dodecane	4.50	2.50

It would appear that this results in partial heating of the sample tube and the consequent loss of some of the more volatile analytes. By allowing sufficient time for the gas chromatograph to complete it's temperature program (55 minutes), this problem was eliminated.

4.3 Optimisation of the Detection and Quantification of the Trace VOC's

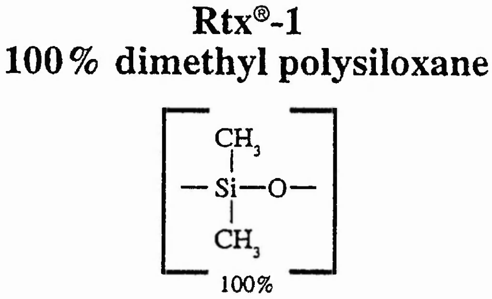
As stated previously, the aim of this work was to develop a method for the determination of all the trace volatile organic compounds in landfill gas by a single analysis. The first two stages in the process, adsorbent trapping followed by thermal desorption have already been discussed in detail and, to a large extent, have influenced the development and performance of the final stage in the analytical process, separation, detection and quantification of the individual components. The latter point is perhaps best illustrated in the choice of column. Initial work was carried out using a 25m BP5 Ultra 2 column, with 0.25μm film thickness. Although this was adequate for site screening purposes, the column produced poor resolution of the early eluting peaks; benzene and cyclohexane coeluted and the retention times were not reproducible. It was initially thought that the varying retention times were due to the percentage levels of methane affecting the partitioning of the VOC's between the mobile and stationary phase. It was thought that the methane was partially adsorbed by the carbosieve and consequently introduced into the GC along with the VOC's. Confirmational analysis by ATD-GC-FID showed that it was in fact due to water vapour and not, as originally suspected, methane.[6] These problems were largely overcome by using a 60m Restek RTX®-1 (100% dimethyl polysiloxane) column, 1.5μm film thickness, supplied by Thames Chromatography, Windsor. The lower phase ratio and increase in sample capacity of the column enabled reproducible retention times to be obtained. In addition, 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. In the case of the RTX®-1, column bleed only significant above 250°C and was minimal in the temperature range used for the VOC's analyses (35-180°C). Column performance was checked periodically throughout the duration of the project by calculating the resolution (R_s) of benzene and cyclohexane using the following expression;

$$R_s = (t_{RB} - t_{RA})/(w_{bB} + w_{bA})$$

t_R = retention time of components , w_b = width of the base of the peaks.

For a new column the resolution was typically about 2.2. If the R_s value fell below 1.5 (approximate baseline separation), the column was replaced.

Figure 4.6 Stationary Phase Structure of the Restek RTX®-1 Column.



The proceeding sections, which were all carried out on the RTX®-1 column, outline the experimental methods and results derived from the optimisation of the detection, identification and quantification of the trace volatile organic compounds in landfill gas.

4.3.1 Qualitative Analysis of the Trace VOC's in Landfill Gas using ATD-GC-MS

All the volatile organic compounds were identified using a benchtop quadrupole GC-MS. The mass spectrometer was tuned on a daily basis by using the automatic tuning procedures written into the ChemStation operating system software, with the mass peaks of perfluorotributyamine, at 69, 219 and 502, being used to ensure that the mass spectrometer met certain predefined performance criteria. These include:

- Mass 69.0 has a relative abundance of 100%.
- Isotope mass 70.0 has a isotope ratio of 0.5-1.6%.
- Mass 219.0 has a relative abundance of > 35%.
- Isotope mass 220.0 has an isotope ratio of 3.2-5.4%.
- Mass 502.0 has a relative abundance of > 1%.
- Isotope mass 503.0 has an isotope ratio of 7.9-12.3%.

Failure to meet the performance criteria was rectified by disassembling and cleaning the ion source.

The Hewlett-Packard HP5970B mass selective detector is capable of scanning between 10 to 800amu.[7] At the beginning of each scan, the quadrupole mass filter is set to the upper mass in the predefined scan range. The mass filter then moves in consecutive, discrete steps of 0.1m/z from the upper mass range to the lower mass range, with the ion abundance data being stored by a computer. The larger the mass range scanned, the slower the scan rate. Selection of a suitable working mass range and mass scan rate for a given analytical method is essentially a compromise between chromatographic and mass spectral quality. A high scan rate enables the accurate reconstruction of the chromatogram, but may result in the quality of the mass spectral data being poor. Conversely, if the scan rate is too slow, chromatographic quality is compromised, as only one or two scans may be taken as the component elutes. The latter is of particular significance to capillary GC, where the peak widths are typically 2 to 4 seconds wide. The mass range used for all analyses reported in this thesis was 20-250amu, with a corresponding scan rate of ~2.5 scans/minute. A lower limit of 20amu was selected to exclude interference from water vapour, and the upper limit, the largest mass fragment observed for the components contained in a typical landfill gas sample.

Compound identification was achieved by a combination of component retention time and fragmentation pattern identification by software comparison with the Wiley/NBS database of 70eV mass spectra, which contains approximately 130,000 spectra of 113,000 compounds.[7] The former process consisted of comparing the retention times with those of standards run under identical analytical conditions. The latter process utilises the probability-based matching (PBM) algorithm developed by Professor McLafferty and co-workers at Cornell University.[8-14] The search algorithm compares the unknown mass spectrum to the reference spectra using a reverse search routine. The reverse search verifies that the peaks in the reference spectra are present in the unknown spectrum. Since not all m/z values have the same intensities, the PBM algorithm uses both mass and abundance values to identify the most significant peaks. These peaks are then used to create a condensed reference spectrum, containing 15-26 ions, which are then used in the PBM search routine. In order to increase the efficiency of the search routine, a prefilter assigns a significance to each of the peaks in the unknown spectrum and uses these to find the most probable matches in the condensed reference library. These are then listed and given a probability value, expressed in percent. Probability values of <50% indicate significant differences between the unknown and reference spectra and the match should be assigned with caution. Probability values of >90% are defined as being Class IV reliability values, which essentially implies that the unknown compound may be an exact match, a member of the same homolologous series or an isomer of the reference compound.

In general, the matches obtained from the PBM searching facility were good, particularly for compounds with distinctive mass spectra such as the CFC's and chlorinated compounds. Poor fits were, however, obtained for compounds which have several isomers with similar mass spectra, such as the larger alkanes and substituted aromatics. The latter inaccuracy was generally overcome by using retention time data. The elution of non-polar compounds from the RTX®-1 column essentially occur in boiling point order. Thus in the case of a given alkane, the highly branched isomers elute before the less branched or linear isomers. Where an exact identification was not possible, a general structural confirmation was given. Although the operating software can be programmed to automatically identify each of the peaks, the complex composition of the landfill gas meant that each peak in the chromatogram had to be manually assigned an identification.

4.3.2 Quantitative Analysis of the Trace VOC's in Landfill Gas using ATD-GC-MS/FID

The accurate determination of analyte concentrations in a given sample matrix depends upon several factors. Firstly, the sample to be analysed should be representative of the bulk composition of the material to be investigated. Secondly, chromatographic resolution of the individual components should be sufficient to allow the integration of the resultant peak areas. Thirdly, the detector should respond in a reproducible manner to small variations in analyte concentration. The following sections provide a summary of the research conducted to address each of these requirements together with a discussion of the overall performance of the analytical method developed.

4.3.2.1 Analysis of the Twelve Component Standard by GC-MS

The GC-MS used for the research described in this thesis could be operated in two configurations; as a detector for gaseous phase samples, which are introduced via the ATD50, or as a detector for liquid phase samples, which are introduced via a fully integrated Hewlett-Packard 7673A autosampler. In order to assess the operating efficiency of the ATD-GC-MS, the latter configuration was used to determine the performance characteristics of the detector for the components contained in the calibration standard. A comparison of the results obtained from the autosampler and the ATD-GC-MS, is given in Section 4.3.2.3.

Experimental Methods

The calibration standards were prepared as follows; a known volume of the stock calibration mixture was pipetted into a clean 10ml graduated flask and made up to the mark with methanol. The latter solvent was used because it is only partially retained by the RTX®-1 column and therefore does not interfere with the elution of the components contained in the calibration mixture. Sequential dilution of each standard was used to produce the calibration curve. In order to prevent damage to the detector, a solvent delay of 4.5 minutes and a split ratio of 200:1 was used throughout. The remaining analytical conditions employed for the GC-MS are identical to those given in Table 4.1. Evaporative losses from the autosampler vials were minimised by preparing each standard in triplicate, with duplicate samples being taken from each of the three sample vials analysed. The volume of sample injected into the GC by the autosampler was 1µl.

Results and Discussion

In total, nine concentrations of standards were analysed, with the standard deviation, precision and mean peak areas calculated for each component. Examples of the results obtained from this study are given in Table 4.5 and Figure 4.7.

Table 4.5 Data from the Analysis of the Calibration Standards.

Compound	Retention Time (min)	Mass Injected (µg)	Precision (n=6) (%RSD)	Method Detection[1] Limit (µg)
Ethanol	5.08	65.80 - 0.51	14.4 - 0.6	0.0005
Dichloromethane	7.11	111 - 0.86	8.5 - 0.1	0.0005
Hexane	10.45	54.60 - 0.43	8.0 - 0.3	0.0002
Benzene	12.99	64.90 - 0.51	8.0 - 0.2	0.0003
Cyclohexane	13.48	57.00 - 0.45	5.1 - 0.3	0.0002
Heptane	15.35	72.20 - 0.56	4.6 - 0.3	0.0003
Toluene	18.25	58.80 - 0.47	3.4 - 0.2	0.0002
p-Xylene	23.14	60.80 - 0.48	3.3 - 0.4	0.0002
n-Nonane	24.66	70.10 - 0.55	2.5 - 0.2	0.0001
n-Decane	28.74	73.00 - 0.57	2.7 - 0.4	0.0001
1-Limonene	30.05	71.80 - 0.56	3.1 - 0.4	0.0002
n-Dodecane	36.06	62.50 - 0.49	4.9 - 0.4	0.0002

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[1] Method detection limit is defined as being three times the standard deviation from the baseline noise.[15]

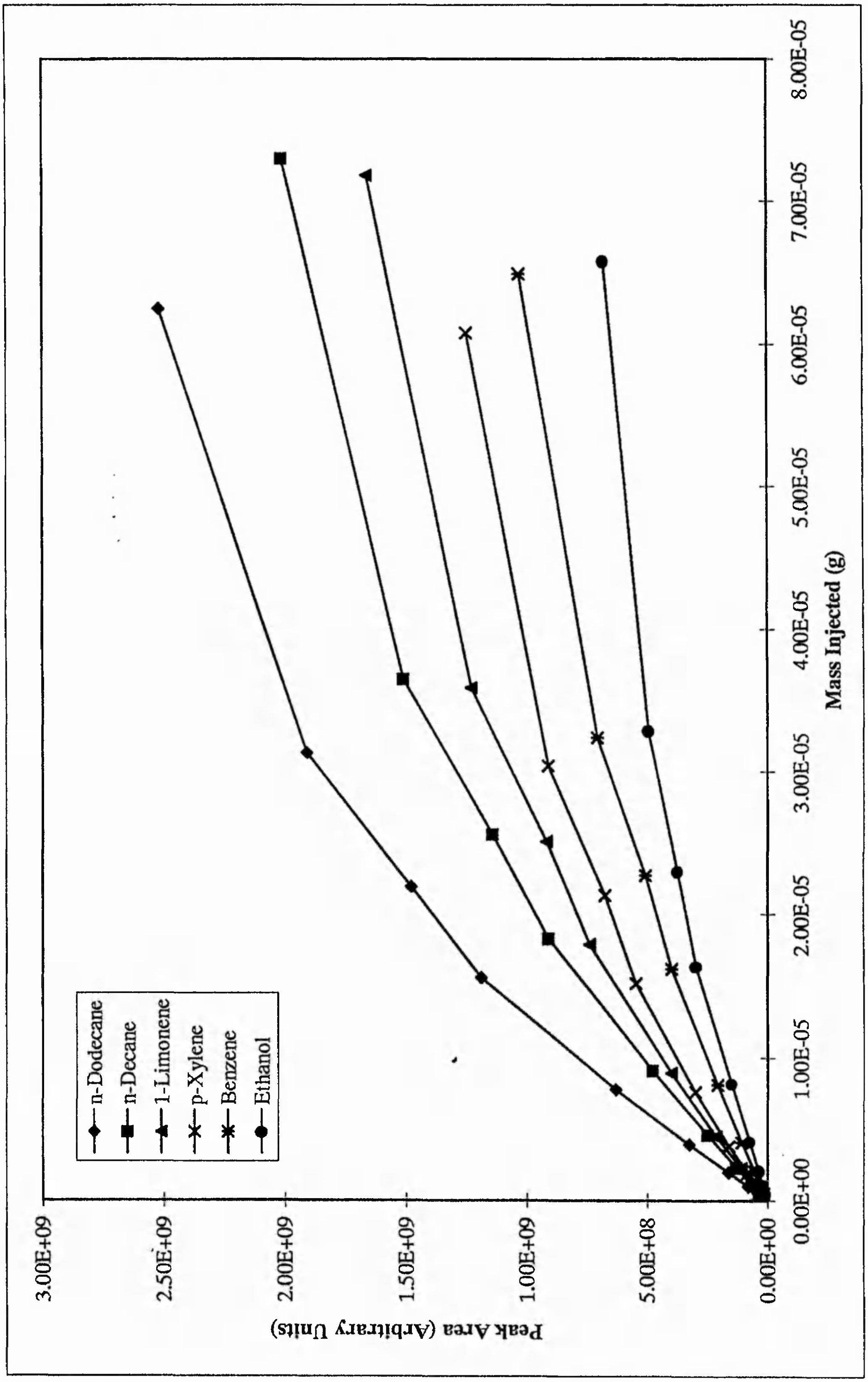

Figure 4.7 GC-MS Calibration Curves for n-Dodecane, n-Decane, 1-Limonene, p-Xylene, Benzene and Ethanol.

It is clear from Figure 4.7 that the detector response is not linear over the entire concentration range studied, with the resultant deviation from linearity being more pronounced for the higher molecular weight components. This was thought to be due to either reduced ion source efficiency and/or partial saturation of the detector at elevated analyte concentrations. The aforementioned effect is greater for the higher molecular weight components studied because they have a more complex fragmentation pattern than the lighter components, such as dichloromethane and ethanol, and thus larger detector response factors. The overall precision of the method was considered to be acceptable, with typical % RSDs being well below 5%. The particularly high % RSD for ethanol, which was observed for the lowest calibration standard, was thought to be due to interference from baseline noise in that portion of the chromatograph. Interestingly, the precision of the measurements made in the curved portion of the calibration graph (high analyte concentrations) for all components, were typically less than 1%. The would suggest that this region of the calibration graph may be accurately used for quantitative purposes.

4.3.2.2 Preparation of Standardised Adsorbent Tubes

There are two accredited methods for the preparation of standardised adsorbent tubes. The first, referred to as the dynamic loading method, involves preparing standard atmospheres of the analyte and pumping known volumes of the atmosphere through the adsorbent tube. The second method involves injecting known volumes of the analyte directly onto the adsorbent tube, usually in the form of a liquid. A study conducted by Krajewski *et al.* concluded that each of the methods were equally valid and produced similar coefficients of variation (Personal communication). As a consequence of this work and the relative difficulty of producing accurate standard atmospheres of a range of volatile organic compounds, the direct injection method was selected as the most appropriate for this application.

Experimental Methods

The sampling tubes and stock mixture of the 12 component standard were prepared using the procedures described in Section 4.2.2. Preparation of the standardised adsorbent tubes was carried out using the following methods:

i. Direct injection of 0.5µl of the 12 component standard onto the adsorbent tubes

ii. Direct injection of 0.5µl of the 12 component standard onto a plug of silanised glass

iii. Indirect injection of 0.5µl of the 12 component standard via a modified GC injection port injection port which was purged with a constant flow of helium (50ml/min) for 10 minutes.

Three sets of six standardised adsorbent tubes were prepared using each of the methods outlined above and the tubes analysed under the analytical conditions given in Table 4.1.

Results and Discussion

A comparison of the precision and recoveries calculated from the peak areas obtained by both direct and indirect injection of 0.5µl of the 12 component standard are given in Table 4.6 and Figure 4.8 respectively. Several conclusions can be drawn from this data. Firstly, the peak integration data for ethanol, dichloromethane, n-hexane, benzene, cyclohexane, n-heptane, toluene and xylene are similar for both direct and indirect injection, although the precision of the data obtained by the latter technique is substantially lower. This would suggest that evaporative losses are minimal for the direct injection methods.

Table 4.6 The Effect of Indirect and Direct Calibration Techniques on the Precision of the Calibrant Peak Areas.[2]

Component	RSD (%) Indirect	RSD (%) Direct	Component	RSD (%) Indirect	RSD (%) Direct
Ethanol	3.65	2.60	Toluene	5.40	2.50
Dichloromethane	5.60	3.30	p-Xylene	4.75	2.00
n-Hexane	4.90	3.90	n-Nonane	5.95	1.95
Benzene	5.30	3.55	n-Decane	6.15	2.60
Cyclohexane	3.10	3.90	1-Limonene	6.55	2.35
n-Heptane	4.25	2.70	Dodecane	5.95	3.60

Secondly, direct injection onto an adsorbent tube as opposed to onto silanised glass wool inserted into the top of an adsorbent tube, had little effect on either the magnitude or precision of the peak integration data. Thirdly, the peak areas obtained for n-nonane, n-decane, 1-limonene and n-dodecane by the indirect injection, are significantly lower than those obtained by direct injection. This is thought to be due to surface adsorption of the higher boiling point components onto the walls of the GC injector. Although this problem could be largely overcome by heating the GC injection port, direct injection was preferred because of its simplicity.

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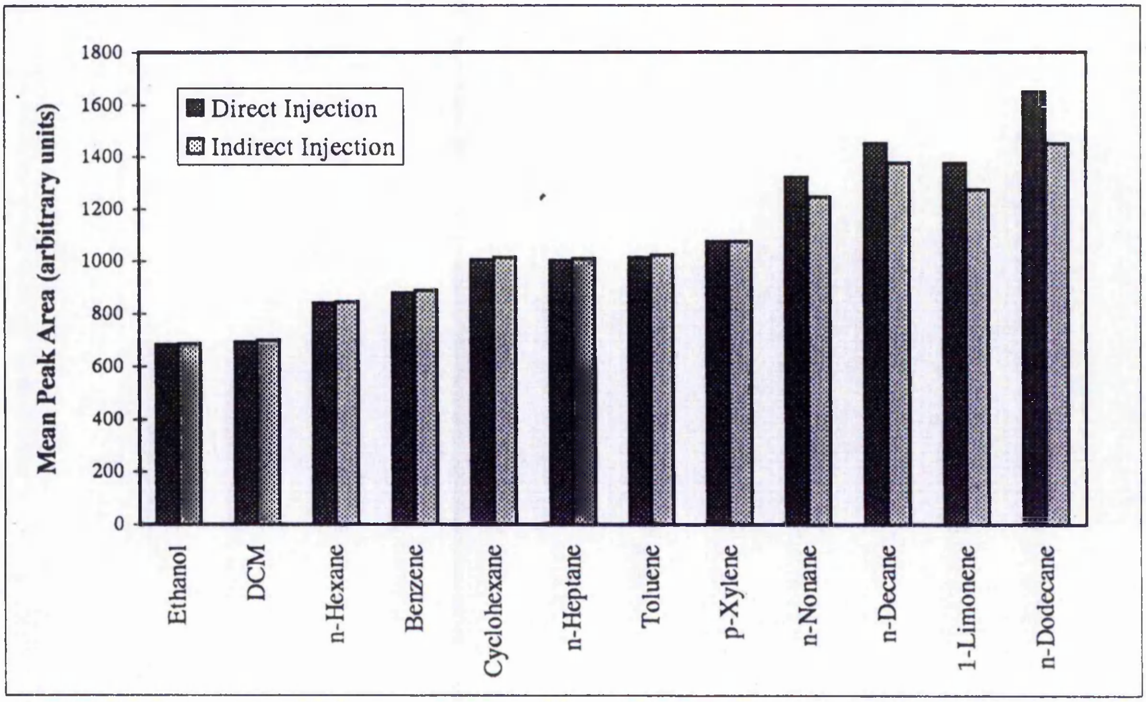
[2] RSD=Relative Standard Deviation (n=6).
Indirect: Injection via a modified GC injection port.
Direct: Injection onto the adsorbent tube.

Figure 4.8 The Effect of Indirect and Direct Calibration Techniques on the Peak Areas Obtained for the Twelve Component Standard.



4.3.2.3 Analysis of the Twelve Component Standard by ATD-GC-MS and ATD-GC-FID

The following section summarises the results obtained from the analysis of the 12 component standard by ATD-GC-MS and ATD-GC-FID, using the optimised analytical conditions described in Sections 4.2 and 4.3. A discussion of the performance of the two analytical systems is given, together with a comparison of the results obtained by GC-MS (Section 4.3.2.1).

Experimental Methods

The sampling tubes and stock mixture of the 12 component standard were prepared using the procedures described in Section 4.2.2. 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. Gilian® personal air samplers were then used to draw a 50 ml min^{-1} flow of clean air through the tubes for a period of 10 minutes. Immediately after switching the pump on, a known volume (0.05-0.5µl) of the neat 12 component mixture was injected onto the silanised glass wool, taking care not to push the needle into the bed of the packing. The analytical conditions employed for the ATD-GC-FID are given in Table 4.7, and those for the ATD-GC-MS, Table 4.1. Although a Perkin-Elmer ATD400 rather than an ATD50 was interfaced to the GC-FID, the operational configurations were identical.

Table 4.7 Instrumental Set-up for the ATD400-GC-FID.

Perkin-Elmer ATD400	Perkin-Elmer 8500 Gas Chromatograph
Mode Two-stage desorption	**Injector Temperature** 250°C
Inlet Split 27 ml min^{-1}	**Detector** FID
Outlet Split 19 ml min^{-1}	**Hydrogen/Oxygen Pressure** 22/12 psi
Overall Split Ratio 200:1	**Sensitivity** High
Primary Desorption Time 15 minutes	**Detector Temperature** 250°C
Cold Trap Low -30°C	**GC Column** RTX®-1; 60m; 0.32mm ID; 1.5µm d_f
Cold Trap High 300°C	**Oven Temperature Programme** 35°C for 5 min, then ramp at 5°C min^{-1} to 180°C.
Trap Adsorbent Tenax TA	**Carrier Gas** Helium (21 cm sec^{-1})

Results and Discussion

An example chromatogram of a calibration standard obtained by ATD-GC-MS is given in Figure 4.9. 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. Typical calibration curves for both the ATD-GC-MS and ATD-GC-FID are given in Figures 4.10 and 4.11 respectively. The results from statistical analysis of the calibration procedure are tabulated in Table 4.8.

Table 4.8 Data from the Analysis of Calibration Standards by ATD-GC-MS/FID.[3]

Compound	Weight on Tube (μg)	GC-MS %RSD	GC-FID %RSD	GC-MS MDL(mgm^{-3})	GC-FID MDL(mgm^{-3})
Ethanol	3.29 - 32.88	5.1 - 1.6	7.9 - 3.2	0.06	0.002
DCM	5.53 - 55.29	4.6 - 1.1	9.9 - 4.2	0.08	0.010
n-Hexane	2.75 - 27.54	6.0 - 1.2	9.9 - 4.1	0.03	0.001
Benzene	3.65 - 36.52	4.4 - 2.2	9.8 - 3.9	0.04	0.001
Cyclohexane	3.25 - 32.49	4.7 - 0.6	8.7 - 3.5	0.03	0.001
n-Heptane	2.85 - 28.49	3.8 - 1.0	10.0 - 4.1	0.03	0.001
Toluene	3.61 - 36.12	4.8 - 2.8	10.9 - 4.2	0.04	0.001
p-Xylene	3.58 - 35.83	6.8 - 2.4	10.8 - 3.5	0.04	0.001
n-Nonane	2.99 - 29.90	6.9 - 2.4	10.9 - 3.7	0.03	0.001
n-Decane	3.04 - 30.42	7.8 - 1.7	12.1 - 3.5	0.02	0.001
1-Limonene	3.51 - 35.08	6.2 - 1.0	10.2 - 4.2	0.03	0.001
n-Dodecane	3.12 - 31.19	5.5 - 1.6	11.4 - 4.2	0.02	0.001

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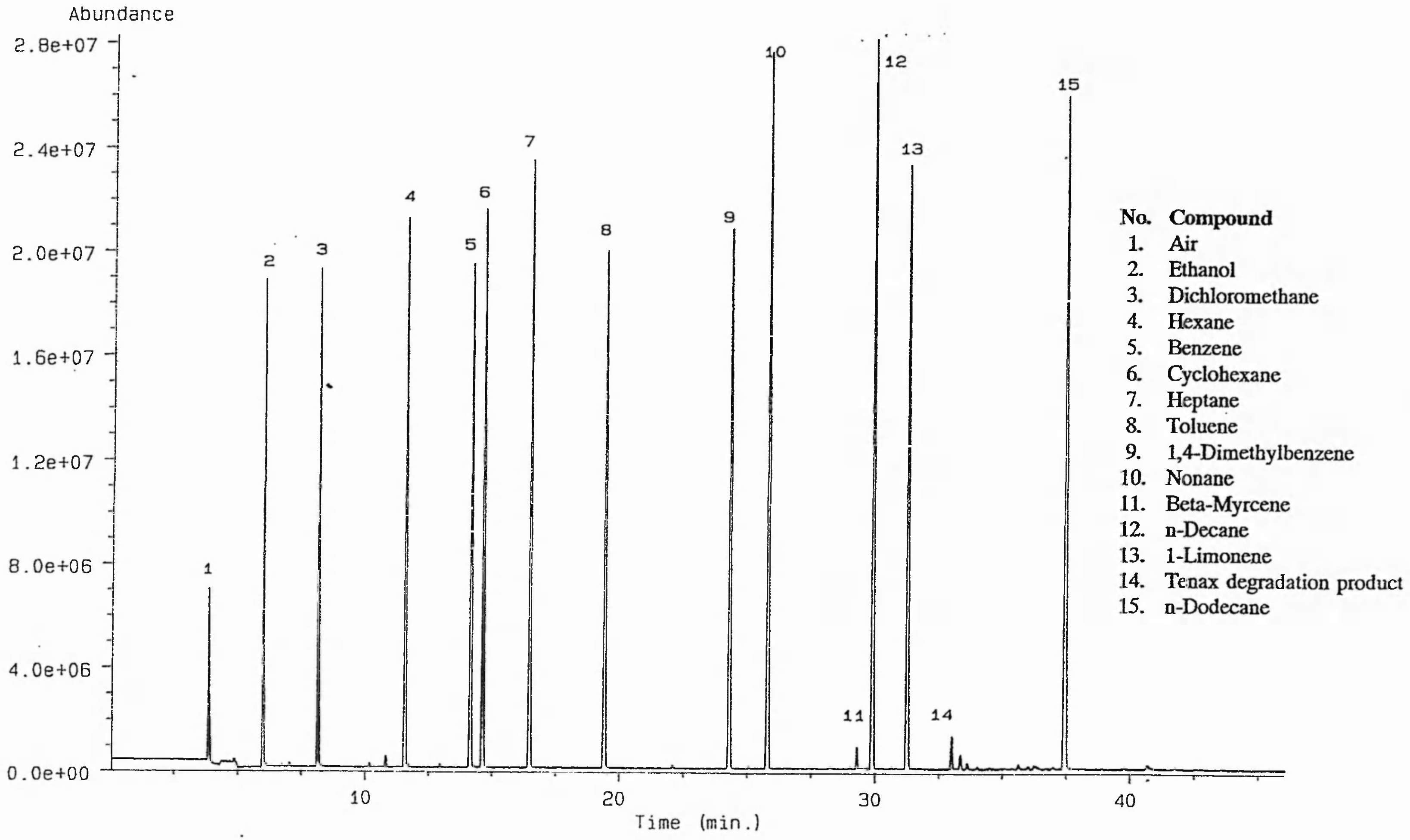
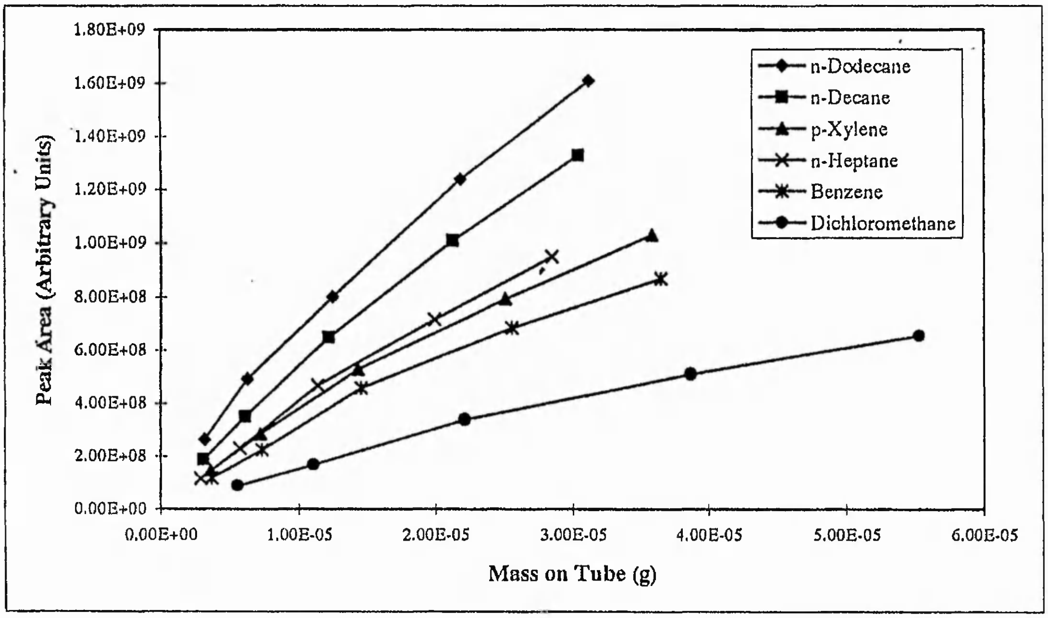
[3] MDL=Method detection limit calculated from three times the standard deviation from the baseline noise. RSD=Relative standard deviation (n=6).



No.	Compound
1.	Air
2.	Ethanol
3.	Dichloromethane
4.	Hexane
5.	Benzene
6.	Cyclohexane
7.	Heptane
8.	Toluene
9.	1,4-Dimethylbenzene
10.	Nonane
11.	Beta-Myrcene
12.	n-Decane
13.	1-Limonene
14.	Tenax degradation product
15.	n-Dodecane

Figure 4.9 Annotated ATD-GC-MS Chromatogram of a Calibration Standard.

Figure 4.10a ATD-GC-MS Calibration Curves for n-Dodecane, n-Decane, p-Xylene



4.10b ATD-GC-MS Calibration Curves for 1-Limonene, n-Nonane, Toluene Cyclohexane, n-Hexane and Ethanol.

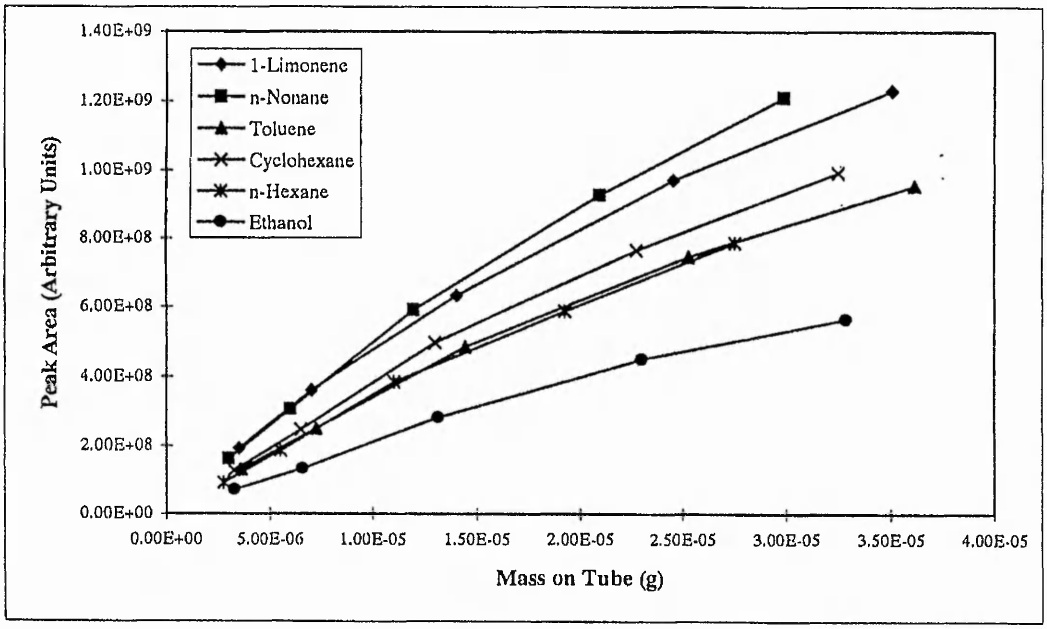


Figure 4.11a ATD-GC-FID Calibration Curves for n-Dodecane, n-Decane, n-Nonane, Ethanol and Dichloromethane.

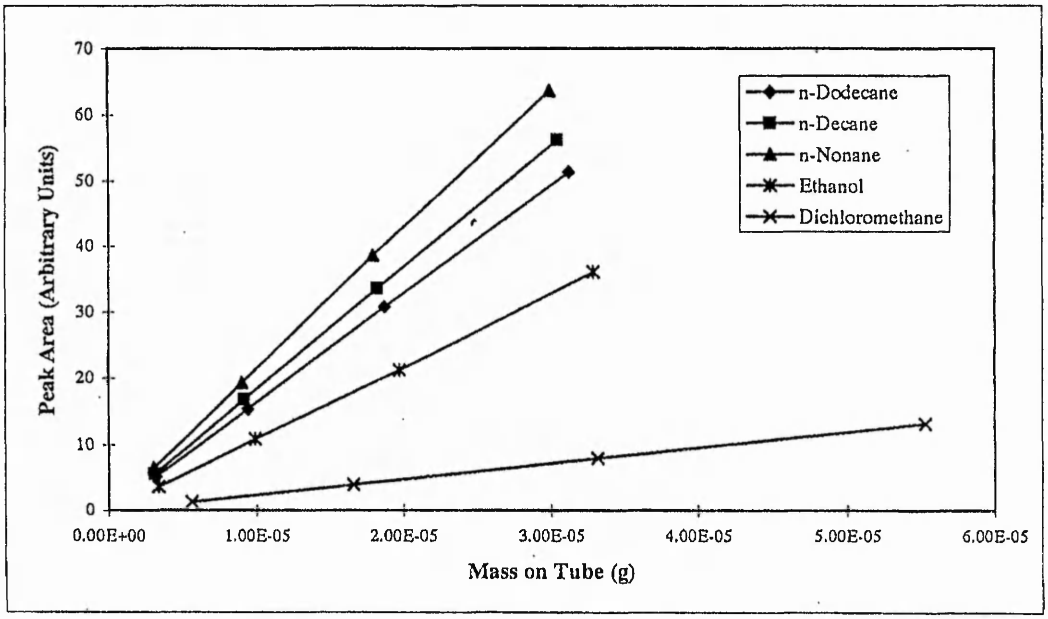
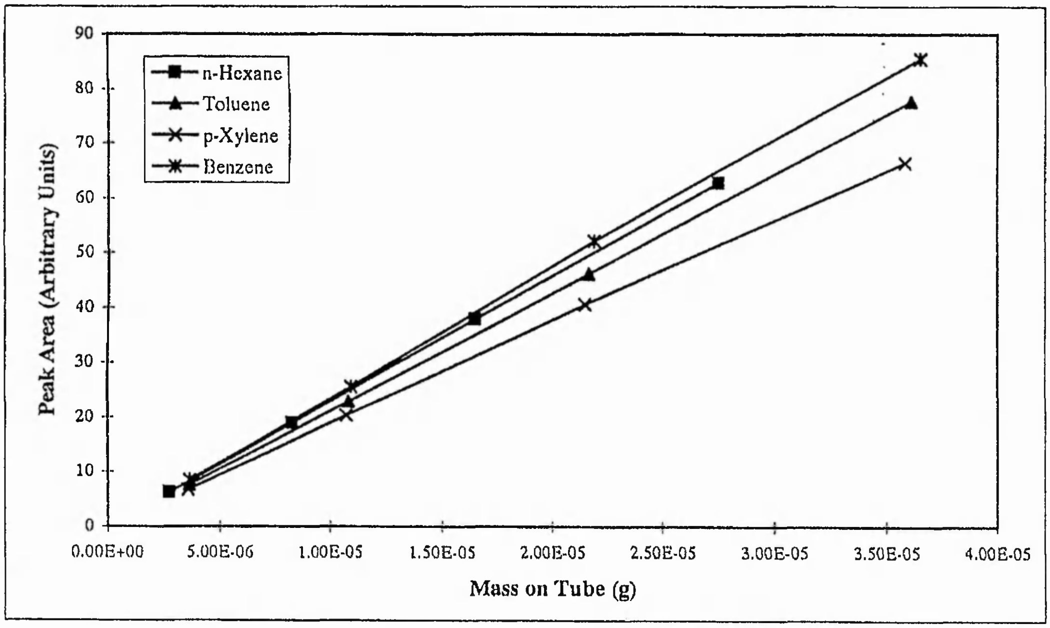


Figure 4.11b ATD-GC-FID Calibration Curves for n-Hexane, Toluene, p-Xylene and Benzene.



The performance characteristics of the two detectors were found to be significantly different. With the exception of dichloromethane, the detection limits for the FID were at least an order of magnitude lower than those calculated for the MS. The FID was also found to have a much wider linear range than the MS. The latter point is of particular importance because a conventional y=mx+c relationship between detector response and analyte concentration greatly simplifies the quantification procedure, thus reducing overall analysis time. The results obtained by ATD-GC-MS are consistent with those obtained by GC-MS (Section 4.3.2.1). For a given component, the detector response is linear for adsorbent tube loadings of ~ $1.8\text{x}10^{-5}$g or less. For adsorbent tube loadings above this value, the detector response is non-linear. The magnitude of the deviation from linearity was found to be compound specific. Given the complex nature of landfill gas, and in particular the large variations in component concentration, it is impossible to restrict the mass loadings of all the analytes on the adsorbent tube to within the linear portion of the calibration curves. Thus in order to accurately assess the analyte concentrations, a number of calibration standards would need to be run for each set of landfill gas samples analysed, with the concentration of the individual trace VOC's being manually calculated from the resultant calibration curves.

On the basis of the aforementioned discussion, analysis by ATD-GC-FID would appear to be the most appropriate method. There are, however, several disadvantages in using flame ionisation detection for this application. Firstly, the output signal from an FID does not provide any structural information. Although this is not a problem for routine environmental analyses, the large number of peaks contained in a typical landfill gas chromatogram means that it is often difficult to unequivocally assign a structural confirmation to a given peak on the basis of its retention time alone. This problem is of particular significance for landfill gas samples that contain components which have not previously been encountered. The second disadvantage of using an FID is that they have a relatively low sensitivity to certain halogenated and oxygenated hydrocarbons.[16] For example the CFC's, which are ubiquitous in landfill gases, were found to produce little or no response at the concentrations encountered in landfill gas. Given the importance of this group of compounds in terms of both environmental impact and landfill gas management (Chapter 5), this essentially precludes its use, although ATD-GC-FID could be used to provide complimentary information to alternative techniques such as ATD-GC-MS. Clearly if a laboratory had either the finance or facilities, a dual detection system, which utilises the benefits of both mass spectrometry and flame ionisation detection, would be the system of choice.

The results from statistical analysis of the calibration procedure, which are summarised in Table 4.8, indicate that the precision of both the ATD-GC-FID and ATD-GC-MS are less than 12% and 8% respectively. It is thought that the lower precision of the measurements obtained by ATD-GC-FID was due to the fact that the ATD400 desorption parameters had not been optimised. The precision of the measurements obtained by ATD-GC-MS were comparable to those obtained by GC-MS (Table 4.5). As a consequence of this result and the number of stages involved in the preparation and analysis of the standards, the overall precision of the calibration procedure was considered to be excellent.

4.3.2.4 Detector Response Factors

The output signal from a detector is proportional to the amount of a given analyte passing through it. The output signal for two different analytes, X and Y at a concentration Z, however, will not necessarily be the same.[15] Given the complex composition of landfill gas, it is clear that not all of the components present can be directly quantified. As a consequence, relative response factors, that is the detector reponse of a given analyte relative to an analyte contained in the standard calibration mixture, were determined for a number of the most abundant VOC's identified in landfill gas.

Experimental Methods

Stock mixtures containing 1ml of each component were prepared using high purity HPLC-grade chemicals obtained from Fisher Scientific, Loughborough, with 0.25μl of each mixture being injected onto a sampling tube. In order to reduce experimental error, each component was weighed, and each analyses carried out six times. Relative response factors of the components contained in the first mixture, which contained dichloromethane, 1,2-dichloroethane, 1,1,1-trichloroethane, tetrachloromethane and trichloroethene, were calculated from the detector response of dichloromethane. Relative response factors of the components contained in the second mixture, which contained hexane, acetone, diethylether, tetrahydrofuran, 2,2,4-trimethylpentane and 4-methylpentan-2-one, were calculated from the detector response of hexane, and in the third mixture, which contained ethanol, methanol, 2-propanol, 1-propanol, 1-butanol, 1-pentanol and 1-hexanol, the relative response factors were calculated from the response of ethanol. In addition, relative response factors for the two most abundant CFC's, chlorodifluoromethane and dichlorodifluoromethane and also for chloroethene, were determined. As all three compounds are gases at room temperature, a known volume of 100ppm certified standards, purchased from Cryoservice, Worcester, were pumped through a sampling tube, with the resultant peak areas being compared to the peak area of dichloromethane.

Results

The relative response factors (RRF) were calculated from the following expression;

$$\text{RRF} = \text{Area}_Z \text{ x } \text{Mass}_{\text{STD}} / \text{Area}_{\text{STD}} \text{ x } \text{Mass}_Z$$

Area_Z = Peak area of analyte.

Mass_Z = Mass of analyte on the sampling tube (μg).

Area_{STD} = Peak area of standard.

Mass_{STD} = Mass of standard on the sampling tube (μg).

Assuming dichloromethane has a detector response of one, the relative response factor for chlorodifluoromethane can be calculated as;

$$\text{RRF}_{\text{Chlorodifluoromethane}} = (3.06 \text{ x } 10^8) \text{ x } (27.638) / (1.48 \text{ x } 10^8) \text{ x } (26.842)$$

$$\text{RRF}_{\text{Chlorodifluoromethane}} = 0.213.$$

A summary of all of the relative response factors are presented in Table 4.9.

In general, for an FID, the magnitude of the ion current and therefore the detector response, is directly proportional to the number of carbon atoms in the flame. Exceptions to this rule include oxygenated and halogenated compounds. Given that the mechanisms responsible for the production of the ions in the flame are still not fully understood[16] and that the majority of the components studied consisted of the latter classes of compounds, a detailed discussion of the results was considered to be beyond the scope of this thesis. There is, however, a general increase in observed detector response with increasing carbon chain length within each class of compounds, which is consistent with the aforementioned processes.

Table 4.9 Mean (n=6) Relative Response Factors (RRF) for some of the Components Identified in Landfill Gas.

Compound	ATD-GC-FID RRF	ATD-GC-MS RRF	Reference Standard
Acetone	0.60	0.43	n-Hexane
Diethylether	0.62	0.83	n-Hexane
Tetrahydrofuran	0.69	0.76	n-Hexane
iso-Octane	1.17	1.10	n-Hexane
4-Methylpentan-2-one	0.77	0.84	n-Hexane
Methanol	0.87	0.53	Ethanol
1-Propanol	0.95	0.92	Ethanol
2-Propanol	0.96	1.09	Ethanol
1-Butanol	0.87	1.28	Ethanol
1-Pentanol	0.88	1.36	Ethanol
1-Hexanol	0.87	1.53	Ethanol
Cyclohexanol	1.03	1.64	Ethanol
Chlorodifluoromethane	-	0.21	Dichloromethane
Dichlorodifluoromethane	-	0.21	Dichloromethane
Chloroethene	-	1.28	Dichloromethane
1,2-Dichloroethane	1.75	1.19	Dichloromethane
1,1,1-trichloroethane	1.36	1.20	Dichloromethane
Tetrachloromethane	0.47	0.98	Dichloromethane
Trichloroethene	1.28	1.00	Dichloromethane

For the mass selective detector, the variation in detector response can largely be attributed to either the ionisation efficiency or the stability of the ions formed in the source. The mass selective detector used for this work utilised 70eV electron ionisation. The electrons are emitted from a heated filament in the ion source and attracted towards an anode. As the sample molecules drift through the beam they may be struck by an electron, which may in turn impart sufficient energy to remove an electron, resulting in the production of the molecular ion. Given that the energy of the electrons emitted from the filament is approximately 70eV, far in excess of that required to ionise most organic molecules, some of the extra energy will be transferred to the ion in the form of excess rotational, vibrational or translational energy.[17] If the excess vibrational energy is sufficiently large, then the elastic limit of some of the bonds will be exceeded and the parent ion will fragment, forming a new ion and a neutral particle. As covalent bonds are generally of the order of 10-20eV, the molecule may fragment several times in succession until the positive ion no longer has sufficient energy to break further bonds.[18] The relative abundance of a given fragment ion formed by this process is governed by its stability. Although the aforementioned process affects the abundance of the individal ions contained in their spectra, the particularly low detector response factors obtained for both chlorodifluoromethane and dichlorodifluoromethane, approximately a fifth of the detector response of dichloromethane, was thought to be due to their low ionisation efficiency.

4.3.2.5 Analysis of a Certified Standard Gas Mixture of Dichloromethane

In order to assess the accuracy of the calibration mixture, a gas mixture containing 108ppmv/v (±2%) of dichloromethane in nitrogen was obtained from Cryoservice, Worcester.

Dichloromethane was selected for this study because it is the most volatile of the components contained in the standard mixture and is thus the most susceptible to evaporative losses during preparation of the standardised adsorbent tubes.

Experimental

The certified sample tubes were prepared as follows; a sample tube was connected directly to the outlet valve on the gas cylinder using a 1/4 inch swagelok fitting. The flow of gas through the tube was set and monitored at 50 ml min^{-1} using an Alltech flow meter supplied by Alltech, Carnforth. 150ml of the certified gas mixture was passed through the tubes which were then immediately sealed using swagelok end-caps. The tubes were analysed by ATD-GC-MS and the predicted concentration of dichloromethane calculated using the calibration procedure described in Section 4.3.2.3.

Results and Discussion

The mean, standard deviation and precision of the dichloromethane peak area obtained from preconcentration of the certified gas mixture was 4.42×10^8, 12852920 and 2.91% respectively. The actual mass of dichloromethane on the tube was calculated as follows;

Concentration of dichloromethane in gas mixture = 108ppm v/v.

Volume of dichloromethane per litre of nitrogen = 1.08×10^{-4} litres.

Therefore, number of moles DCM per litre of nitrogen = $(1.08 \times 10^{-4}/24.4) = 4.43 \times 10^{-6}$.

Weight of dichloromethane per litreof nitrogen = $4.43 \times 10^{-6} \times 84.9324 = 3.7625 \times 10^{-6}$g.

Weight of dichloromethane on tube = $(3.763 \times 10^{-6} \times 150/1000) = 56.438$μg

The mass of dichloromethane on the sample tube, predicted from the calibration curve, was 56.95μg. Given that the actual mass on the tube was calculated to be 56.438μg, the overall error in the measurement was less than 1%. On the basis of this result, it can be concluded that evaporative losses of dichloromethane during preparation of the calibrated adsorbent tubes are minimal and that the accuracy and precision of the calibration procedure is excellent.

4.4 An Assessment of the Reproducibility of Gilian Personal Air Samplers

The overall aim of all environmental analyses is to obtain a sample which is representative of the bulk material from which it was taken. For water and soil samples, this is often straightforward, the only requirement being the use of a suitable container and conforming to predefined sampling strategies. In cases such as these, the main sources of error arise from the extraction and analytical processes. By contrast, if there are insufficient safeguards in place, the main source of error associated with the measurement of gaseous phase analytes using adsorbent tubes, arises from the sampling process. The latter includes the use of too higher sample flow rates or the wrong adsorbents, both of which can lead to breakthrough and the consequent loss of analytes, and inefficient pumps, which can lead to errors in calculating the total volume of air that has been drawn through the tube. As the former processes have been addressed in Chapter 3, the aim of this work was to assess the performance of the Gilian Personal Air Samplers. The model used for this work, PN800518, supplied by Quantitech, Milton Keynes, was microprocessor controlled and was fitted with a constant low-flow module. According to the manufacturers, this allows the pump to automatically adjust to small changes in backpressure and also accurately maintain flows down to 5ml/minute.

4.4.1 Experimental

All procedures were carried out using the Gilian® Personal Sampler fitted with a constant low-flow module. Although a standard operating procedure was used for the packing of adsorbent sample tubes, it was found that it was virtually impossible to maintain a consistent packing density and thus a constant backpressure to the pump. As a consequence the flow through ten different tubes was measured at thirty second intervals over a ten minute period using an Alltech Gas Flow Meter obtained from Alltech, Carnforth.

4.4.2 Results and Discussion

Given the large amount of data generated, only the standard deviation, mean and precision are reported in Table 4.10 for each data set.

Table 4.10 Statistical Analysis of the Gilian® Air Sampler Performance Data.

	Tube 1	Tube 2	Tube 3	Tube 4	Tube 5	Tube 6	Tube 7	Tube 8	Tube 9	Tube 10
Mean (ml/min)	50.1	50.0	49.9	49.8	49.9	49.9	49.7	49.9	49.8	49.7
Standard Deviation	0.07	0.09	0.06	0.07	0.10	0.07	0.05	0.07	0.07	0.06
% RSD (n=20)	0.15	0.18	0.11	0.14	0.20	0.15	0.10	0.14	0.13	0.12

It is clear from the data contained in Table 4.10, that the small differences in packing density between sample tubes had little effect on the pump performance and that the overall accuracy and precision of the Gilian® Personal Air Samplers is excellent. Given that 500ml of landfill gas was pumped through the sampling tubes at a flow rate of 50 ml min^{-1}, the overall error associated with the sampling process was predicted to be less than 1%. It should be noted, however, that calibration of the pump should be performed with a sample tube that is representative of the batch of tubes to be used for a given application. Calibration of the pump without a tube in-line for example, resulted in a 30% error in the set flow rate when the pump was placed under load.

4.5 Sample Storage

Both the method of storage and timescale over which samples are stored can have a significant effect on both the accuracy and·precision of an analytical result. In this context, accuracy is defined as being the nearness of the analyte concentration to that at the time of sampling as opposed to at the time of analysis. Although the latter two values should be the same, sample degradation due to reactions between or evaporation of the absorbed species can occur if the samples are stored incorrectly. A study published by the UK HSE indicated that a wide range of compounds absorbed onto Tenax TA and stored at room temperature were stable for in excess of 11 months.[19] Recoveries were found to be >99% and the mean coefficient of variation less than 2%. At the present time, however, an equivalent study has not been conducted for multi-adsorbent or sandwich tubes. The main difference between single and multi-adsorbent systems is thought to be the effect of molecular diffusion (Personal Communication). For multi-adsorbent tubes, the adsorbed species, which are in constant equilibrium with the species in the vapour phase within the adsorbent pore spaces, are able to diffuse and migrate between the different adsorbent layers. If a highly volatile component diffuses from a strong adsorbent to a weak adsorbent to which it is only partially sorbed, it may be lost when the sampling tubes are uncapped. Conversely, if a relatively involatile component diffuses from a weak adsorbent to a strong adsorbent, it may become irreversibly sorbed. Both effects result in a loss of analyte and thus can contribute to the overall error in a given measurement. In order to address this problem, two storage methods were assessed. The first consisted of storing landfill gas in a gas sample bag until the time of analysis. The landfill gas was then pumped through a sampling tube and immediately analysed. The second method involved storing both sample and calibration tubes in an air conditioned laboratory (20°C) and in a fridge (5°C). The tubes were then periodically analysed over a two week period and the resultant data compared with freshly prepared calibrated tubes.

4.5.1 Experimental

For the first storage method, two different types of gas sample bag were assessed, Cali-5-bond and Tedlar. The former was obtained from Alltech, Carnforth, and, as it name suggests, consists of five polymer layers. The inner layer is polyethylene, followed by a layer of polyamide, an aluminium foil barrier, a layer of PVC and an outer layer of polyester. The manufacturer claims that it's unique design means that it is suitable for the storage and transportation of all gas samples. The second type of gas sample bag, which was also obtained from Alltech, consists of a single layer of PVF. Marketed as a cost effective alternative to Teflon, Tedlar is claimed to have the lowest permeability of all the films from which gas sampling bags are made and is recommended for the analysis of volatile analytes.[20] Gas samples were taken directly from the gas extraction array which had been installed to pipe landfill gas from active areas of the site to an electricity generator at a municipal waste disposal site in North Nottinghamshire. The sampling procedure was as follows; firstly an adsorbent tube sample was taken using the procedures outlined in Chapter 5. The 47l Cali-5-bond gas sample bag was then filled. A second adsorbent tube sample was then taken, followed by the filling of the 2.5l Tedlar gas sample bag. Finally, a third adsorbent tube sample was taken and all the samples transported to the laboratory and stored at 20°C overnight. Duplicate sub-samples of the gas contained in the two gas sample bags were then obtained and analysed. The recovery of the trace VOC's was assessed by comparing the resultant data with that obtained from the analysis of the three adsorbent tubes taken at the landfill site. For the second method, a total of twenty gas samples were taken directly from the gas extraction array. A further twenty calibrated gas sample tubes were prepared using the procedure outlined in Section 4.3.2.3. Both sets of samples were split, with half being stored in an air conditioned laboratory at 20°C and half being stored in a fridge at 5°C. Duplicate samples were then analysed at the following intervals; Day 1, Day 3, Day 7, Day 10 and Day 14. Analyte recoveries were calculated from the data obtained from the analysis of freshly prepared calibrated gas sample tubes.

4.5.2 Results and Discussion

An assessment of the suitability of gas sample bags for the storage of landfill gas was initially going to be undertaken over a 14 day period. This, however, was revised after the analysis of the first subsample, after 24 hours. A summary of the resultant data and a comparison of the chromatograms obtained is given in Table 4.10 and Figure 4.12 respectively.

Figure 4.12a Chromatogram obtained from the Analysis of Landfill Gas Stored In a Tedlar Gas Sample Bag.

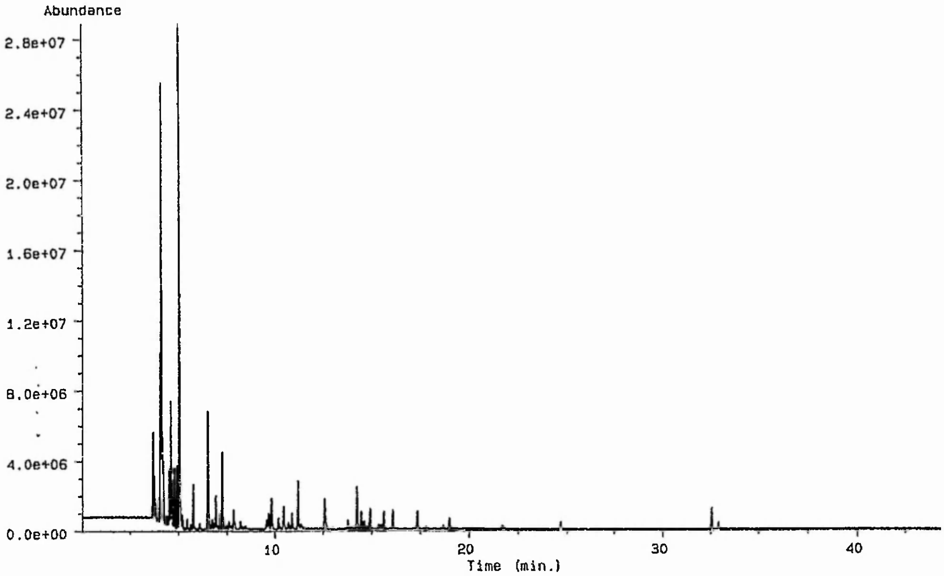


Figure 4.12b Chromatogram obtained from the Analysis of Landfill Gas Stored In a Cali-5-bond Gas Sample Bag.

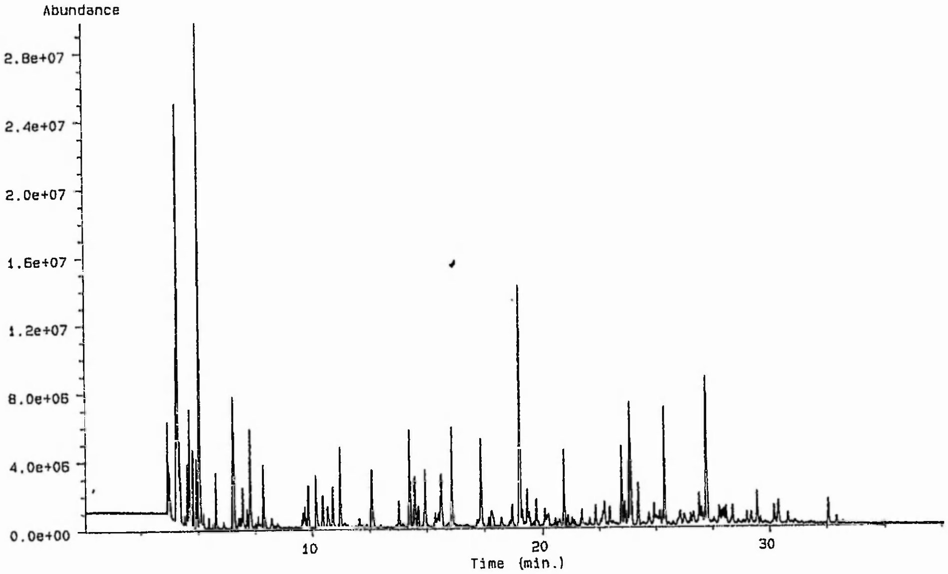


Figure 4.12c Chromatogram Obtained from the Direct Analysis of Landfill Gas.

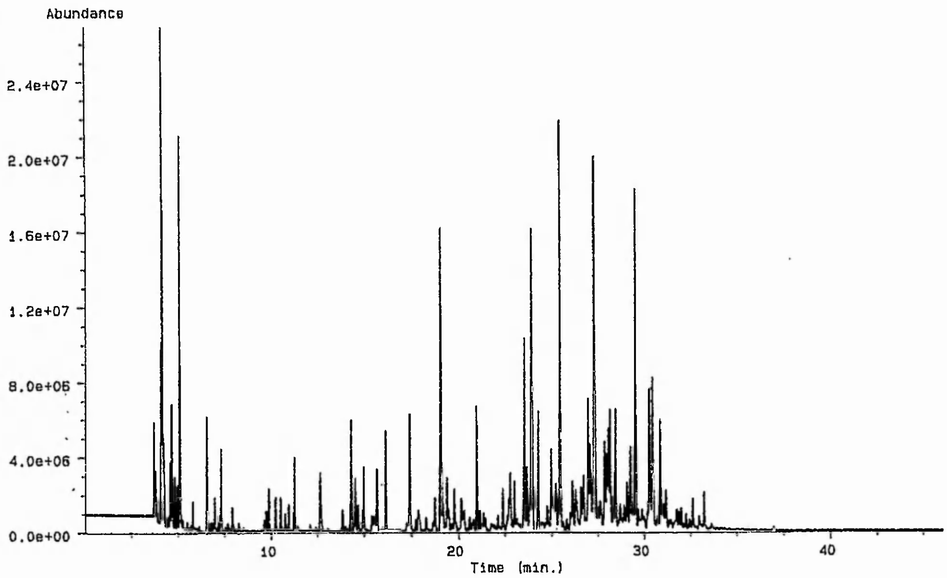


Table 4.10 A Comparison of the Predicted Landfill Gas Composition following Storage for 24 hours at 20°C in a Tedlar and Cali-5-bond Gas Sample Bag and an Adsorbent Tube.

Compounds	Tedlar (mg/m^3)	Cali-5-bond (mg/m^3)	Direct (mg/m^3)
Total Alkanes	209	330	455
C2-C5 Alkanes	182	195	159
C6-C12 Alkanes	28	135	297
Total Cyclic Compounds	25	84	166
Total Aromatic Compounds	5	131	337
Total Chlorinated Compounds	141	177	135
Total Alkenes	13	15	19
Total Pinenes	< 0.5	39	130
Total Alcohols and Ketones	3	10	14

It is clear that the storage of landfill gas in both Tedlar and Cali-5-bond gas sample bags can lead to a gross underestimation of the composition of some of the trace VOC's in landfill gas. It is thought that this is due to adsorption onto the walls of the sample bags. This appears to be supported by the distribution of the results. Although the landfill gas sampled from the Cali-5-bond bag has similar concentrations of the more volatile C2-C5 alkanes, chlorinated compounds, alkenes, alcohols and ketones to the initial landfill gas, it has 50% less C6-C12 alkanes, 50% less cyclic compounds, 60% less aromatic compounds and 70% less pinenes. Although more pronounced, a similar effect was also observed for gas stored in the Tedlar gas sample bag which had 90% less C6-12 alkanes, 85% less cyclic compounds, 98% less aromatic compounds and 100% less pinenes. Given that diffusive losses would be expected to be greatest for the lighter more volatile compounds and that the Tedlar gas sample bag is less permeable than the Cali-5-bond, this again would suggest that surface adsorption is the main reason for the observed differences. Although this effect may be partially overcome by heating the gas sample bags, it was concluded that for this particular application, both the Tedlar and Cali-5-bond gas sample bags were unsuitable for sample storage.

The results from the second study, which assessed the stability of both calibration standards and landfill gas samples on adsorbent tubes over a 14 day period, are summarised in Table 4.11 and 4.12 respectively. Both studies indicate that the loss of analytes is neglible over a fourteen day period and that the samples are stable at both ambient and sub-ambient temperatures. As a consequence of these findings, any landfill gas samples that were not analysed on the day they were taken were placed in an air-tight container and stored at 5°C.

Table 4.11 Mean Recovery (%) of the Calibrated Adsorbent Tubes over a 14 day Period.

Compound	Day 1 5°C	Day 1 20°C	Day 3 5°C	Day 3 20°C	Day 7 5°C	Day 7 20°C	Day 10 5°C	Day 10 20°C	Day 14 5°C	Day 14 20°C
Ethanol	97	99	98	98	99	99	99	96	99	99
DCM	100	101	97	99	98	95	98	101	98	99
Hexane	99	99	97	98	103	97	99	99	98	101
Benzene	106	99	98	99	97	99	101	98	99	98
Cyclohexane	95	98	99	102	95	99	99	98	99	97
Heptane	99	99	100	101	98	97	99	98	100	101
Toluene	99	100	98	94	99	101	100	98	99	97
p-Xylene	100	99	97	98	102	98	99	100	96	99
Nonane	96	98	99	99	97	98	102	99	100	101
Decane	99	98	100	97	98	99	100	98	99	96
1-Limonene	98	100	99	98	103	101	102	99	100	104
Dodecane	100	99	97	101	102	99	101	98	100	99

Table 4.12 Recovery of Trace VOC's from Adsorbent Tubes over a 14 Day Period.

Compounds	Day 1 5°C	Day 1 20°C	Day 3 5°C	Day 3 20°C	Day 7 5°C	Day 7 20°C	Day 10 5°C	Day 10 20°C	Day 14 5°C	Day 14 20°C
Alkanes	325	331	314	324	337	329	334	307	321	311
Cyclic	106	101	111	109	120	104	119	127	108	113
Halogenated	433	401	447	438	421	419	423	445	437	429
Aromatics	244	263	215	248	234	222	237	256	256	241
Alkenes	17	15	19	18	16	14	18	17	15	15
Alcohols	29	31	27	26	27	29	33	28	31	34
Pinenes	119	131	128	117	129	112	123	128	112	134

4.6 Conclusions

The aim of the research outlined in this chapter was to develop, optimise and evaluate an analytical method using active sampling and adsorbent tubes, followed by desorption and analysis using thermal desorption - gas chromatography - mass spectrometry. The optimum analytical conditions for the multi-layer adsorbent tubes and 500ml of landfill gas were found to be as follows; for the Perkin-Elmer ATD50, an overall split ratio of 200:1 was selected together with a cold trap low and high of -30°C and 300°C respectively. The desorption temperature and time selected were 250°C and 15minutes. Following desorption, the GC conditions were as follows; the column temperature was maintained at 35°C for 5minutes and then programmed to ramp at 5°C/minute to 180°C, which was then maintained for 15minutes. The column selected was a 60m Restek RTX-1®. Two methods of detection were assessed, flame ionisation and mass selective. The latter was chosen in preference to flame ionisation detection because of its lack of specificity. The accuracy and precision of the calibration procedure, which involved the direct injection of known amounts of a range of components onto the adsorbent tube, was found to be comparable to the Hewlett-Packard auto-sampler. The error associated with the measurement of a certified gas standard of dichloromethane was less than 1%.

The performance of the Gilian® Personal Air Sampler was found to be excellent, with the contribution of the pump to the overall error in the sampling process being predicted to be less than 1%. Once adsorbed, the analytes on both calibration and sample tubes were found to be stable for in excess of 14 days. By contrast, the storage of landfill gas samples in two commercially available gas sample bags was found to significantly affect the observed landfill gas compositions, with the concentration of some of the analytes being reduced by 100%. It was thought that this was due to adsorption of these compounds onto the gas sample bag surfaces. It was concluded, therefore, that all landfill gas samples should be stored on tightly capped adsorbent tubes in an air-tight container. A standard operating procedure for the analysis of the trace VOC's in landfill gas is given in Appendix 1.

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Chapter 5

A Study of the Trace Volatile Organic Compounds in Landfill Gas at Seven UK Landfill Sites

5.0 Research Aims

To evaluate the performance of the analytical method by analysing a range of landfill gas samples obtained from seven municipal waste disposal sites. The information derived from this study will then be used to assess the potential environmental impact of the trace volatile organic compounds.

5.1 Variation in Landfill Gas Composition at Site A over a Fifteen Month Period

The objective of analytical quality control (AQC) is to maintain a measurement process in a desired state of stability and reproducibility. This is usually achieved by the strict adherence to standard operating procedures together with the use of matrix matched quality control samples of a known value which, like the unknown samples, are taken through the entire analytical procedure.[1] The variability in the measured concentration is plotted on a Shewart chart, which is set-up using the mean and standard deviation (s) of the quality control standard from initial performance testing data or from the results obtained whilst the method is in general use. The mean is used to define normal system performance, with warning (±2s) and action (±3s) limits being set either side of the mean. Exceedance of the 3s limit indicates that the method is out of statistical control and as a consequence the data should be regarded as indicative of the analyte concentration and not a true measurement.

Implementation of the procedures described above can, for the most part, eliminate the majority of uncertainty associated with the analytical measurement and thus allow the correct interpretation of the data to be made. By contrast, the assessment of the significance of the environmental measurement is somewhat more problematic. For example, in the case of ambient air samples, climatic conditions such as wind speed and temperature can both have a significant influence on the observed analyte concentration and thus the overall interpretation.[2,3] In the case of landfill gas analysis, the transient nature of both gas formation and concentration can be a potential problem when attempting to both interpret and compare measurements from different sites. In order to assess the magnitude of the variation in landfill gas composition at a given site and thus the significance of a single analysis dataset, a long-term monitoring programme was undertaken at a landfill site in North Nottinghamshire, Site A. Site A, which was used for the majority of the field testing during the development of the analytical method, has been in operation since 1984 and receives a combination of trade (33%) and domestic waste (67%). The waste has been deposited to a height of 15 metres and completed areas progressively restored. Both landfill gas and leachate migration has been minimised by the construction of a compacted colliery shale barrier and a gas extraction system. The latter consisted of a series of vertical wells and gas transmission lines that convey the landfill gas to a blower. The landfill gas is then either burnt or used to fuel an electricity generation system.

5.1.1 Experimental Methods

The landfill gas samples were extracted from a sampling point on the gas extraction array. 500ml of landfill gas was drawn through the triple-adsorbent sampling tubes at 50mlmin^{-1} using a Gilian personal air sampler fitted with a constant low flow module. Each sampling tube was then immediately sealed with swagelok end-caps fitted with PTFE ferrules and stored at 4°C until analysed, usually within 24 hours. A field blank, which remained sealed at all times, was analysed with each batch of samples taken. Initially three samples were taken in succession at each visit to establish the precision of the method and thereafter at regular intervals as a quality assurance check. In addition to the measurement of the trace VOC's, methane measurements were taken using a portable landfill gas monitor supplied by Scottish Anglo.

5.1.2 Results and Discussion

A total of 15 samples were taken at monthly intervals between August 1994 and November 1995. The results from this study are summarised in Figure 5.1. The observed fluctuations are thought to be due to a number of factors such as changes in gas production rates, atmospheric pressure and both ambient temperature and the temperature of the landfill itself. Given that this work was primarily concerned with the qualitative and quantitative analysis of the trace VOC's, a thorough examination of the aforementioned parameters was not undertaken. The extreme changes in both bulk and trace gas components at approximately 150, 225 and 300 days are thought to be due to changes in gas extraction rates due to servicing of the gas extraction equipment. When the gas extraction system is shut off, there is no means of removing the landfill gas and as a consequence the pressure within the landfill increases together with a corresponding increase in both the levels of methane and VOC's. Following the recomissioning of the 'blowers', the control valves on the extraction system are balanced so that the gas entering the engine is of sufficient quality to be used as a fuel. The correct balance is often achieved by trial and error (personal communication). This is illustrated by the large drop in methane levels observed at approximately 225 days, which was due to the extraction rate being set higher than the gas production rate on the gas-line being sampled for this study. Air is drawn into the landfill, essentially diluting the landfill gas being extracted.

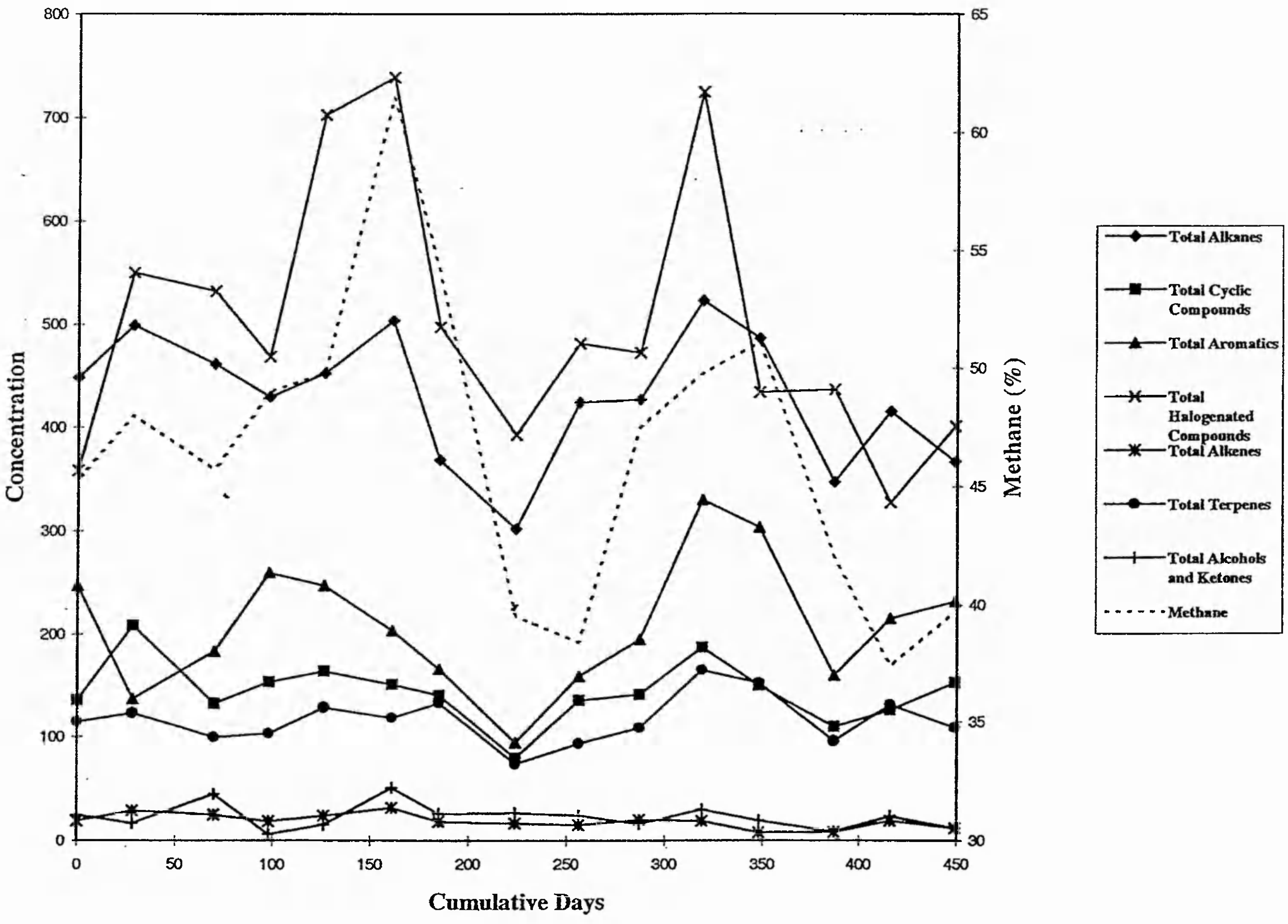


Figure 5.1 Variation in Landfill Gas Composition at Site A over a 15 Month Period

Allowing for the latter point, concentrations of the VOC's in landfill gas appear to be reasonably consistent over the timescale studied and directly related to the levels of methane. It is therefore possible to draw the following conclusions. Firstly, in order to directly compare data between sites, samples should only be extracted when the site is operating under normal conditions, that is when both gas production and extraction rates are in a state of equilibrium. Secondly, the study suggests that ambient conditions, such as pressure and temperature, have a minimal effect on the observed levels of VOC's. Thirdly, despite the overall fluctuation in total VOC's concentration, the relative proportions of each of the classes of compounds remains approximately the same. On the basis of these findings, it can be concluded that a single analysis dataset can provide a fairly accurate estimate of the typical levels of trace VOC's in a given landfill gas.

5.2 Trace VOC's Identified at Seven UK Landfill Sites

Landfill gas is a product of the natural biological decomposition of organic material contained in wastes deposited in landfills. The latter includes paper, animal and vegetable matter and garden wastes.[4] The production of the principal landfill gas components occurs in four more or less sequential phases, with the final phase being characterised by the constant production of methane (60%) and carbon dioxide (40%).[5] The latter gases, which are assigned the generic description of "landfill gas", continue to be produced until the majority of the organic material contained within the waste has been degraded. The trace VOC's are formed as either part of the degradation process or from the direct volatilisation of compounds contained within the waste. As a consequence, both the levels and classes of VOC's present in a given landfill gas are dependant upon the waste input. Keller postulated that all landfill gases contain the following six classes of compounds: saturated and unsaturated hydrocarbons, acidic hydrocarbons, halogenated compounds, sulphur compounds such as carbon disulphide and mercaptans, and inorganic compounds.[6]

Table 5.1 Summary of the Seven Landfill Sites Studied

	Site Description	Waste Types	Gas End Use
Site A	In operation since 1984; liner system mainly consists of compacted colliery shale	Trade waste (33%) and domestic waste (67%), deposited to a height of 15m	Gas extraction wells installed in 1992; ~ 300m^{3}h^{-1} gas extracted to fuel an engine for electricity generation
Site B	Valley infill; in operation since 1920; liner system mainly consists of compacted colliery shale	Trade waste (54%) and domestic waste (46%), deposited to depths of 30m	~ 1000m^{3}h^{-1} gas extracted to fuel three engines for electricity generation
Site C	Former brick pit; in operation since 1990; liner system mainly consists of in-situ compacted clays and marl	Trade waste (43%) and domestic waste (57%), deposited to depths of 30m	Gas extraction system and flare stack installed in 1992
Site D	Located at clay extraction site; in operation since 1990; liner system consists of in-situ compacted marl and shales	Trade waste (49%) and domestic waste (51%), deposited to depths of 20m	Gas extraction system and flare stack installed in 1993
Site E	Quarry infill; in operation since 1965; liner system consists of in-situ compacted clay	Trade waste (52%) and domestic waste (48%), deposited to depths of 30m	At the present time there are no gas extraction facilities
Site F	Quarry infill; in operation since 1986	Accepts both domestic (80%) and trade waste (20%)	~ 480m^{3}h^{-1} gas extracted to fuel three engines for electricity generation
Site G	Former clay extraction site; in operation since 1987	Accepts both domestic (90%) and trade waste (10%)	~ 350m^{3}h^{-1} gas extracted to fuel two engines for electricity generation

In order to assess the variation in landfill gas composition between sites and in particular the corresponding effect, if any, on the performance of the developed analytical method, seven landfill sites were visited. The sites studied are representative of the majority of modern municipal waste disposal facilities in the UK and similar in both methods of operation and construction to those in other industralised countries. Each of the sites accepted both trade and domestic waste. The latter consists of a combination of building waste and waste with a similar organic content to that of domestic waste. The exact proportions of each were unknown. None of the sites were licensed to accept toxic or industrial waste. Geographically, sites A-E are located in the midlands and sites F and G are located in south-east England. A brief description of each landfill site is given in Table 5.1.

5.2.1 Experimental Methods

The gas samples were obtained from monitoring points on existing gas extraction systems at each site using the sampling protocols developed in Chapter 4. In the case of site E, the gas samples were taken from a trial gas well that had been installed by the landfill operators to assess gas production rates. Sites B-G were visited once, with each sample being taken in triplicate. The data from site A was aquired over a 15 month period. Each sample was analysed using ATD-GC-MS under the optimised analytical conditions described in Chapter 4. Compound identification was achieved by a combination of component retention time and fragmentation pattern identification by software comparison with the Wiley/NBS database of mass spectra, which contains 130,544 spectra of 113,000 compounds.[7]

5.2.2 Results and Discussion

Over 140 compounds were identified of which over 90 were common to all seven sites. A list of the compounds is given in Table 5.2.

Table 5.2 Compounds Identified in Landfill Gas

Compound	Concentration (mgm^{-3})	Compound	Concentration (mgm^{-3})
1,1,2,2-Tetrafluoromethane	<0.5 - 4	Acetic acid-methyl ester	<0.1 - 12
Chlorodifluoromethane	<0.5 - 404	Dichloromethane	1 - 85
Propane	15 - 80	Trichlorotrifluoroethane	<0.5 - 6
1-Chloro-1,1-difluoroethane	<0.5 - 31	1-Propanol	<0.1 - 213
Oxybismethane	<0.1 - 15	1,1-Dichloroethane	<0.1 - 62
Chlorofluoromethane	<0.5 - 96	Methylpentanes	5 - 32
2-Methylpropane	12 - 76	2-Butanone	<0.1 - 191
Chloroethene	<0.1 - 87	Butanol	<0.1 - 272
Methylcyclopropane	<0.1 - 7	1,2-Dichloroethene	1 - 182
Butane	18 - 159	Hexane	<0.1 - 21
Butenes	<0.1 - 10	Acetic acid-ethyl ester	<0.1 - 100
Chloroethane	<0.1 - 8	2-Methyl-1-propanol	<0.1 - 123
Dichlorofluoromethane	<0.5 - 114	Tetrahydrofuran	<0.1 - 7
Ethanol	<0.1 - 262	1,1,1-Trichloroethane	<0.1 - 18
2-Propanone	<0.1 - 97	3-Methyl-2-butanone	<0.1 - 15
1,2-Dichlorotrifluoroethane	<0.5 - 1	Benzene	<0.1 - 7
2-Methylbutane	<0.1 - 70	Tetrachloromethane	<0.1 - 21
Trichlorofluoromethane	<0.5 - 74	Cyclohexane	6 - 30
2-Propanol	<0.1 - 127	Dimethylpentanes	4 - 14
C2-Cyclopropane	1 - 5	Propanoic acid-methyl ester	<0.1 - 9
Methylbutene	<0.1 - 8	Methylhexanes	4 - 18
Pentane	<0.1 - 36	Pentanols	<0.1 - 29
Methylbutadiene	<0.1 - 0.5	Trichloroethene	<0.1 - 152
Thiobismethane	<0.1 - 99	Dimethylcyclopentanes	<0.1 - 5
2-Methyl-2-propanol	<0.1 - 11	Propanoic acid-ethyl ester	<0.1 - 88
1,1-Dichloroethene	<0.1 -6	Acetic acid-propyl ester	<0.1 - 16

Table 5.2 (Continued)

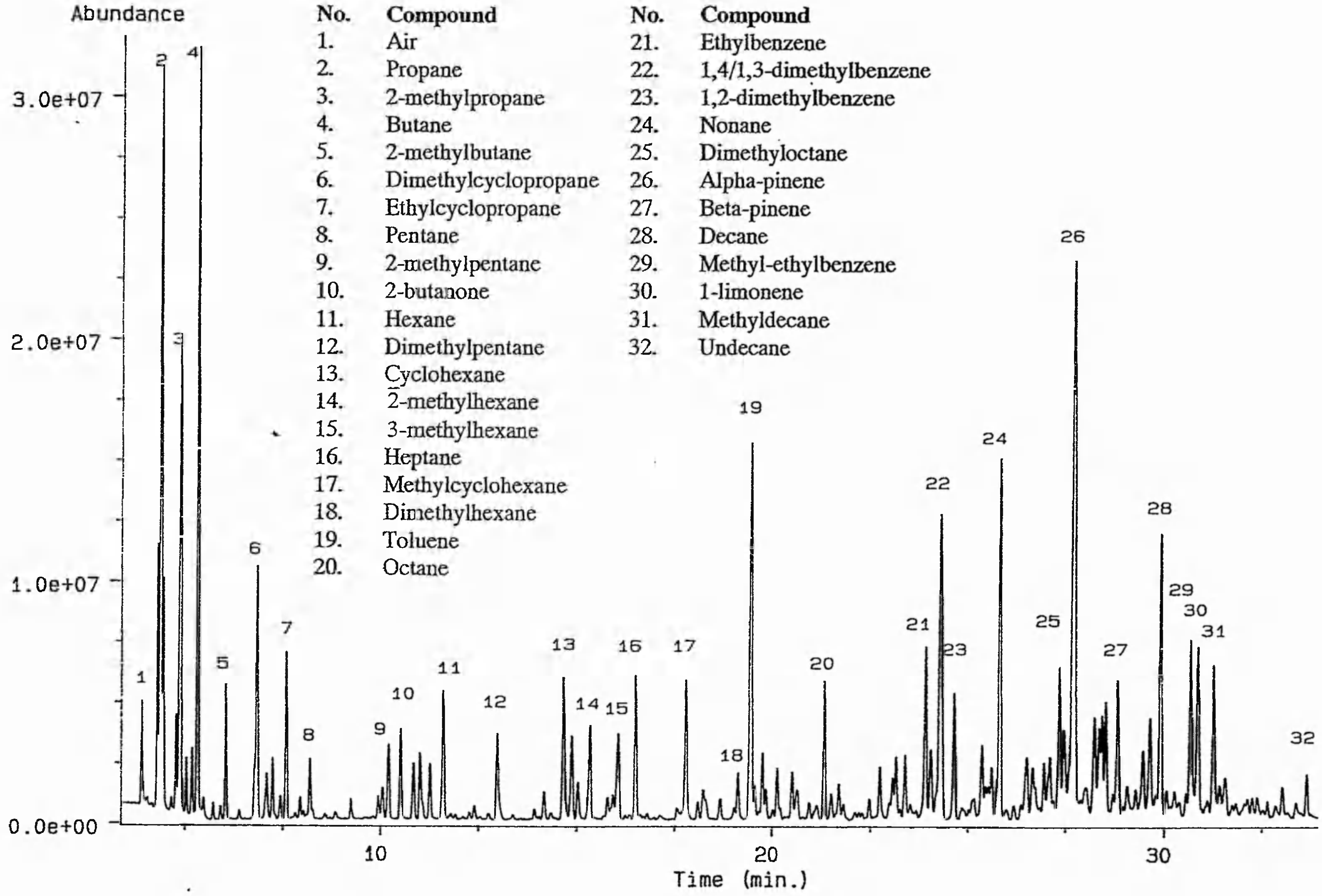
Compound	Concentration (mgm^{-3})	Compound	Concentration (mgm^{-3})
Heptane	7 - 28	Butanoic acid-propyl ester	<0.1 - 150
Butanoic acid-methyl ester	<0.1 - 54	Pentanoic acid-ethyl ester	<0.1 - 91
Methylbutanol	<0.1 - 20	C3-alkylcyclohexanes	7 - 149
4-Methyl-2-pentanone	<0.1 - 70	Nonane	14 - 217
Methylcyclohexane	11 - 45	Hexanoic acid-methyl ester	<0.1 - 27
Dimethylhexanes	2 - 16	Dimethyloctanes	10 - 157
Propanoic acid-isopropyl ester	<0.1 - 161	Thujene	<0.1 - 4
Trimethylcyclopentanes	<0.1 - 8	Alpha-pinene	24 - 285
Toluene	10 - 287	Propylbenzene	<0.1 - 130
Methylheptanes	9 - 48	Camphene	<0.1 - 28
Dimethylpentanone	<0.1 - 23	Methylnonanes	18 - 153
Butanoic acid-ethyl ester	<0.1 - 255	Hexanoic acid-ethyl ester	<0.1 - 164
Propanoic acid-propyl ester	<0.1 - 53	Beta-pinene	<0.1 - 74
Acetic acid-butyl ester	<0.1 - 70	Decane	13 - 260
Dimethylcyclohexane	<0.1 - 16	Gamma-terpinene	<0.1 - 7
C3-Alkylcyclopentanes	<0.1 - 3	Dimethylnonane	1 - 27
Octane	4 - 64	Delta-3-carene	6 - 139
Tetrachloroethene	<0.1 - 255	1-Limonene	<0.1 - 287
Dimethylheptanes	<0.1 - 47	C4-Alkylcyclohexanes	<0.1 - 33
Butanoic acid-isopropyl ester	<0.1 - 58	Methyldecanes	5 - 152
Ethylcyclohexane	<0.1 - 83	Naphthalene	<0.1 - 70
Trimethylcyclohexanes	10 - 66	Undecane	3 - 106
Hexanol	<0.1 - 59	Ethylbenzaldehyde	<0.1 - 1
Ethylbenzene	5 - 156	Dodecane	<0.1 - 23
Xylenes	36 - 440	C3-Alkylbenzenes	<0.1 - 295
Methyloctane	5 - 87	C4-alkylbenzenes	<0.1 - 294

A summary of the total concentrations of VOC's detected is given in Table 5.3. The values quoted for sites B-G refer to the range of concentrations found in triplicate samples, obtained at regular intervals over a period of 1 hour. The ranges quoted for site A summarise the variations in concentrations observed over a fifteen month period.

Table 5.3 Summary of Total Concentrations of VOC's Detected at Seven Sites (mgm^{-3})

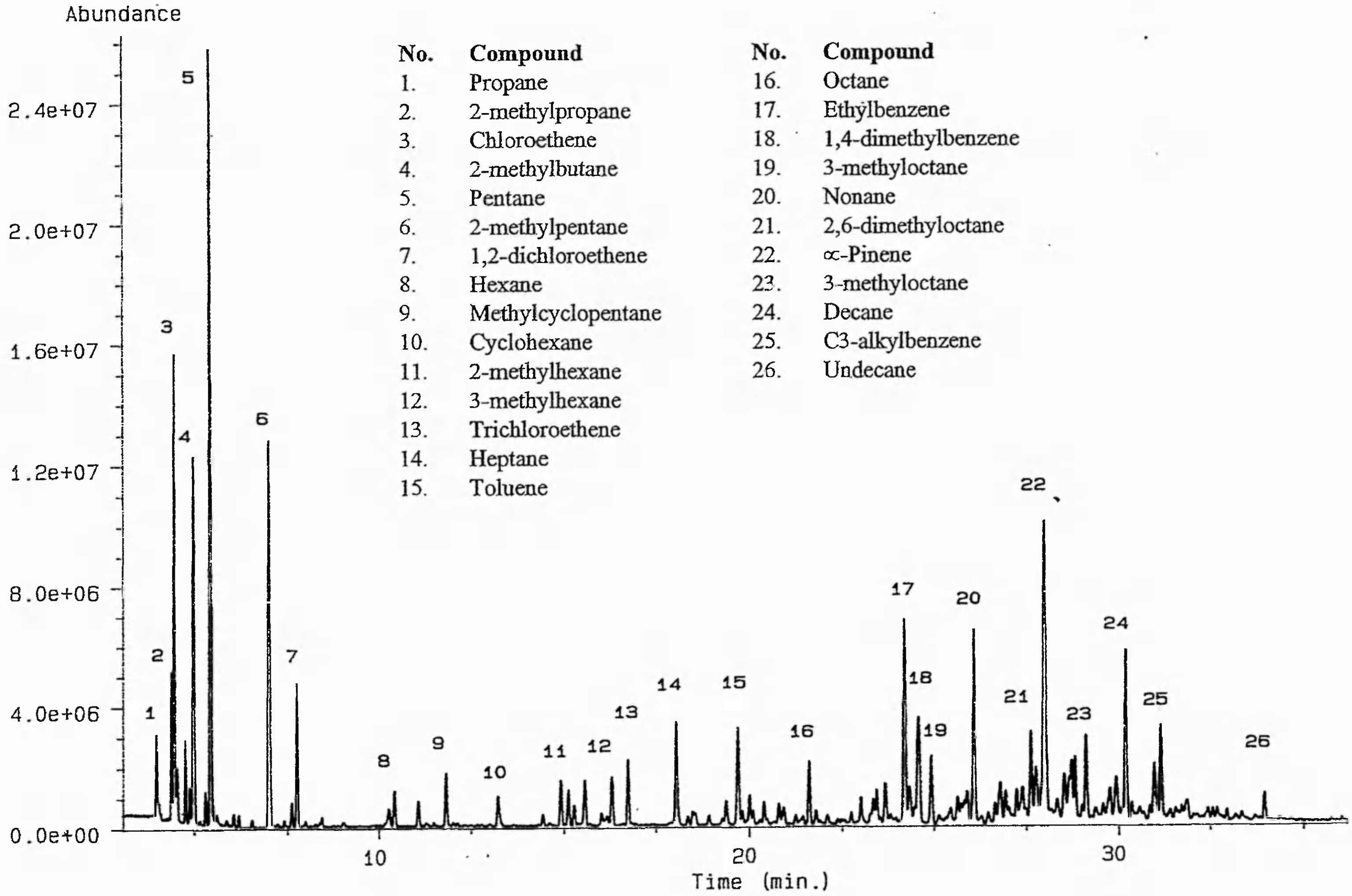
Compounds	**Site A**	**Site B**	**Site C**	**Site D**	**Site E**	**Site F**	**Site G**
Alkanes	302-503	400-523	436-537	529-810	541-621	1430-1543	639-712
C2-C5 Alkanes	140-237	62-106	165-209	407-553	133-265	119-128	106-120
C6-C12 Alkanes	150-345	383-417	271-328	122-257	275-487	1311-1415	519-607
Alkenes	8-31	25-31	19-24	12-17	18-25	18-36	<0.1-6
Alcohols and Ketones	6-51	50-84	19-25	2-4	6-11	1876-2069	689-805
Chlorinated Compds	327-739	264-270	288-348	259-345	1005-1239	957-983	341-368
Cyclic Compounds	80-208	129-143	119-131	93-135	127-194	459-487	208-234
Aromatic Compds	94-330	313-331	118-176	36-162	276-333	1741-1906	363-431
Terpenes	74-152	192-244	207-241	35-112	167-227	593-652	229-528
Acid Esters	<0.1	<0.1	<0.1	<0.1	<0.1	1240-1320	1322-1473
Bulk Gases (%)							
Methane	37-62	55	65	59	61	58	52
Oxygen	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Carbon Dioxide	24-29	37	32	30	27	40	42

Although the majority of the compounds identified were present in each of the landfill gases analysed, the relative proportions of certain classes of compounds varied considerably between sites. The latter point probably reflects differences in waste composition and the rates and mechanisms by which the waste is decomposed.



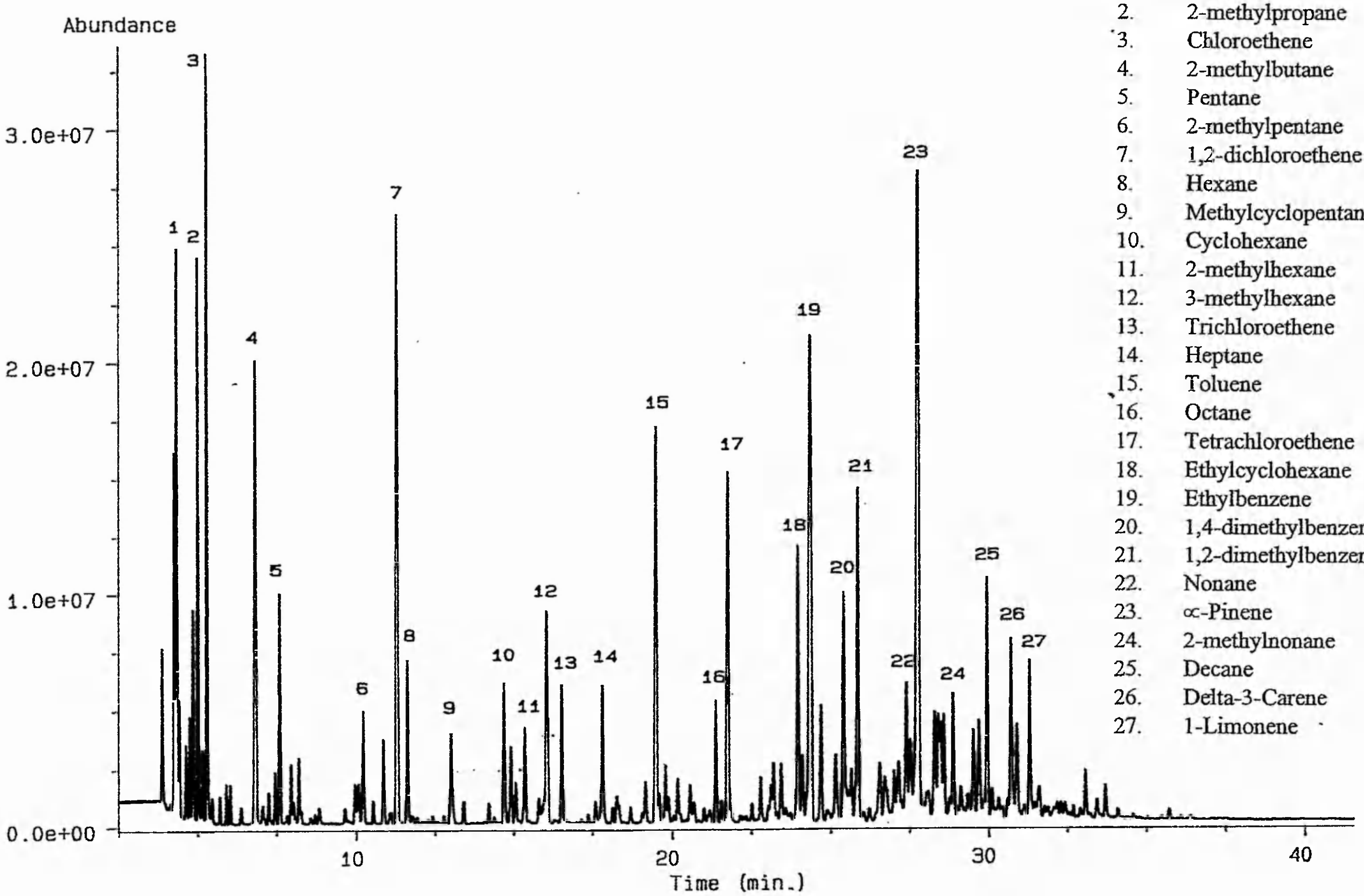
No.	Compound	No.	Compound
1.	Air	21.	Ethylbenzene
2.	Propane	22.	1,4/1,3-dimethylbenzene
3.	2-methylpropane	23.	1,2-dimethylbenzene
4.	Butane	24.	Nonane
5.	2-methylbutane	25.	Dimethyloctane
6.	Dimethylcyclopropane	26.	Alpha-pinene
7.	Ethylcyclopropane	27.	Beta-pinene
8.	Pentane	28.	Decane
9.	2-methylpentane	29.	Methyl-ethylbenzene
10.	2-butanone	30.	1-limonene
11.	Hexane	31.	Methyldecane
12.	Dimethylpentane	32.	Undecane
13.	Cyclohexane		
14.	2-methylhexane		
15.	3-methylhexane		
16.	Heptane		
17.	Methylcyclohexane		
18.	Dimethylhexane		
19.	Toluene		
20.	Octane		

Figure 5.2 Annotated Chromatogram of the VOC's in a Landfill Gas from Site A.



No.	**Compound**	**No.**	**Compound**
1.	Propane	16.	Octane
2.	2-methylpropane	17.	Ethylbenzene
3.	Chloroethene	18.	1,4-dimethylbenzene
4.	2-methylbutane	19.	3-methyloctane
5.	Pentane	20.	Nonane
6.	2-methylpentane	21.	2,6-dimethyloctane
7.	1,2-dichloroethene	22.	α-Pinene
8.	Hexane	23.	3-methyloctane
9.	Methylcyclopentane	24.	Decane
10.	Cyclohexane	25.	C3-alkylbenzene
11.	2-methylhexane	26.	Undecane
12.	3-methylhexane		
13.	Trichloroethene		
14.	Heptane		
15.	Toluene		

Figure 5.3 Annotated Chromatogram of the VOC's in a Landfill Gas from Site E.



No.	Compound
1.	Propane
2.	2-methylpropane
3.	Chloroethene
4.	2-methylbutane
5.	Pentane
6.	2-methylpentane
7.	1,2-dichloroethene
8.	Hexane
9.	Methylcyclopentane
10.	Cyclohexane
11.	2-methylhexane
12.	3-methylhexane
13.	Trichloroethene
14.	Heptane
15.	Toluene
16.	Octane
17.	Tetrachloroethene
18.	Ethylcyclohexane
19.	Ethylbenzene
20.	1,4-dimethylbenzene
21.	1,2-dimethylbenzene
22.	Nonane
23.	∝-Pinene
24.	2-methylnonane
25.	Decane
26.	Delta-3-Carene
27.	1-Limonene

Figure 5.4 Annotated Chromatogram of the VOC's in a Landfill Gas from Site F.

For example, the relative proportions of acid esters, alcohols and ketones (which included ethanol, propanol, butanol, pentanol, hexanol, propanone and pentanone) were 2-3 orders of magnitude higher at sites F and G than at sites A-E. Knox, who examined the variation in the composition of landfill gas with the age of waste material, observed that levels of alcohols were greatest in fresh refuse.[8] This observation was supported by Young and Heasman, who also noted that elevated levels of esters and alcohols were characteristic of sites with high gas production rates.[9] Dent *et al.* reported that the presence of alcohols arises from the fermentation of putresible materials such as fruit and vegetables.[10] The latter point may be of particular significance to sites F and G as a large amount of fruit is grown in south-east England. It is likely that the majority of fruit that is not suitable for sale is disposed of in landfills. Given the lack of detailed records of waste inputs and the fact that the landfill gas sampled was extracted from areas with differing waste ages, it is impossible to identify the precise reasons without further detailed investigations.

The majority of alkanes, aromatic compounds and cyclic compounds are produced during the waste degradation processes, and as a consequence, their levels in landfill gas are dependent upon both the waste composition and the stage reached in the decomposition process. The latter is influenced by a range of both physical and microbiological factors which include nutrient availability, temperature, pH, moisture content and microbiological activity. Due to the inherent complexity of these processes, however, accurate prediction of the rate of production, age and quantity of both landfill gas and trace VOC's is still not possible. A study conducted by Knox, however, suggested that the predominance of trace levels of alkanes and aromatic compounds in landfill gas is usually associated with older refuse, together with a corresponding decrease in the levels of halogenated and oxygenated compounds such as alcohols.[8] Interestingly, elevated levels of all the aforementioned groups of compounds were observed at site F. This suggests that the waste is particularly heterogeneous at this site, with the landfill gas being extracted from areas that have reached differing stages in the decomposition process.

Substantial levels of terpenes were observed at each of the seven sites studied, with the highest levels being observed at site F (593-652mg/m^{-3}). The terpenes identified included α-pinene, β-pinene, camphene, myrcene and limonene. Riemer *et al.*, who developed a method that would enable the effect of biogenic emissions of terpenes and related compounds on urban air quality to be predicted, identified α -pinene and β-pinene as being the dominant terpenes emitted together with lesser amounts of camphene, myrcene and limonene.[11] Kruschel *et al.* analysed the ambient levels of VOC's around a pine forest in Canada and identified isoprene (1.9μgm^{-3}), limonene, α-pinene (0.2μgm^{-3}) and β-pinene (0.3μgm^{-3}) as the most abundant terpenes.[12] The proportions of the latter compounds are similar in landfill gas, with limonene, α-pinene and β-pinene accounting for between 50% and 100% of the total terpene concentrations measured at each of the sites. This would suggest that the majority of the terpenes are derived from the volatisation of compounds contained in garden wastes, such as hedge clippings, shrubs and trees. Other potential sources include fragrant household detergents and air fresheners.

A summary of the halocarbons detected and their potential sources is given in Table 5.4 and 5.5 respectively. The chlorofluoro compounds (CFC's) account for up to 95% of the total chlorine measured in the landfill gases sampled at the seven sites.

Compounds	OES[1]	Site A	Site B	Site C	Site D	Site E	Site F	Site G
chlorodifluoromethane	3500	105-332	47-56	56-89	178-192	366-404	<0.5	75-87
dichlorodifluoromethane	-	116-208	67-72	120-135	28-43	111-135	221-231	96-101
1-chloro-1,1-difluoroethane	-	<0.5	11-31	13-17	14-28	<0.5	<0.5	<0.5
chlorofluoromethane	-	52-96	14-19	10-19	24-48	71-90	<0.5	<0.5
chloroethene[2]	18	4-10	4-6	2	<0.1-4	76-87	59-63	<0.1-13
chloroethane	-	<0.1-3	2-4	4-6	<0.1-3	<0.1-8	<0.1	<0.1
dichlorofluoromethane	40	<0.5-114	43-57	48-62	24-29	24-38	<0.5	<0.5
trichlorofluoromethane	-	<0.5-74	<0.1	<0.1	<0.1	<0.1-28	<0.5	<0.5
1,1-dichloroethene	-	<0.1-5	<0.1	2	1-2	<0.1-6	<0.1	<0.1
dichloromethane[2]	350	4-85	2-15	10-15	1-2	10-16	65-69	30-33
1,1,2-trichloro-1,2,2-trifluoroethane	-	<0.5-6	<0.5-1	3-5	<0.5	2-4	<0.5	<0.5
1,1-dichloroethane	810	<0.1-8	5-6	2-3	1-2	5-9	61-62	<0.1
1,2-dichloroethene	790	6-27	7-13	2-5	1-6	128-182	141-169	24-31
1,1,1-trichloroethane	-	<0.1-2	3-18	2	<0.1-1	1-6	<0.1	<0.1
tetrachloromethane	12.6	<0.1-21	2	2-5	<0.1	<0.1	<0.1	<0.1
trichloroethene[2]	535	<0.1	<0.1	<0.1	<0.1	82-91	143-152	42-47
tetrachloroethene	335	<0.1-24	12-20	4-6	<0.1	127-137	249-255	61-69
Total Chlorine	-	203.386	152-154	164-188	118-159	587-735	675-699	210-227
Total Fluorine	-	102-245	66-98	76-104	95-126	221-256	69-73	63-70
butan-2-ol	300	<0.1-13	6-12	2	1	<0.1	203-272	88-120
n-hexane	70	10-28	5	6-12	7-8	15-21	<0.1	<0.1
benzene[2]	16	2-7	4-6	2-5	1-3	3-4	<0.1	<0.1
cyclohexane	340	12-29	5-6	4-7	7-8	14-20	31	12-13
toluene	188	26-71	59-73	36-48	10-24	43-72	282-287	116-135
xylenes	434	36-112	126-140	51-63	48-94	118-153	427-440	156-180
trimethylbenzenes	123	<0.1-28	49-63	<0.1	<0.1	<0.1	48-187	<0.1

Table 5.4 Halocarbons and Components with Occupational Exposure Standards identified in Landfill Gas (mgm^{-3})

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[1] Occupational exposure standards reported as eight hour time-weighted averages (mgm^{-3}).

[2] Maximum exposure limits reported as eight hour time-weighted averages (mgm^{-3}).

Table 5.5 Potential Sources of Halocarbons Identified in Landfill Gas[6,7]

Source	Compounds
Aerosols	Chloromethane, dichloromethane, terachloromethane, dichlorodifluoromethane and trichlorofluoromethane
Paint Remover	Dichloromethane
Dry Cleaning Agents	Trichloroethene, tetrachloroethene, tetrachloromethane, and 1,1,2-trichloro-1,2,2-trifluoroethane
Dyeing solvents	1,1,1-trichloroethane, trichloroethene and tetrachloroethene
Foam Blowing Agents	Trichlorofluoromethane and dichlorodifluoromethane
Soaps, Paint and Varnish	Dichloromethane
Refrigerants	Dichlorodifluoromethane and chlorodifluoromethane

The CFC's arise from the direct volatilisation of compounds contained in plastic foam, aerosol propellants and refrigerators, and as a consequence, their concentrations are governed by the composition of the waste and are not influenced by biological decomposition processes. Given that there is a finite source of CFC's in any given landfill, one would expect their levels to decrease with time, with the highest emissions occurring during the waste deposition process. It is clear from this work, however, that the emission of substantial levels of CFC's can continue for long periods after the waste has been deposited. For example site E, where the waste was estimated to be in excess of 20 years old, has the highest levels of chlorodifluoromethane of any of the landfill gases sampled. This is thought to be due to the lack of gas extraction facilities at this site. For sites without gas extraction facilities, the loss of CFC's is governed by their rate of diffusion through the landfill cap and lining. If the rate of diffusive loss is slower than the rate of volatilisation from the waste, the levels present in the landfill gas will increase. This will continue until the two processes reach equilibrium, after which the total concentrations of CFC's will begin to fall. On the basis of the results obtained from site E, it would appear that the rate of diffusive loss is relatively slow, and as a result, substantial quantities of CFC's will continue to be present in the landfill gas for several decades. It is also clear that gas extraction rates could potentially influence the levels of CFC's in landfill gas at all landfill sites although the magnitude of this effect is difficult to predict. It should be noted, however, that the general variations in CFC's concentrations between sites is almost certainly due to differences in waste composition. An example of this is chlorodifluoromethane (HCFC 22) which, with the exception of site F, was present in all the landfill gases sampled. As the only reported use of HCFC 22 is as a refrigerant, it can be concluded that sites A-G have all been used to dispose of old refrigerators and site F has not.[13] An alternative explanation may be that the refrigeration systems disposed of at site F, have not yet had their cooling systems fractured, or have had their coolant gases removed prior to disposal. The remaining halogenated compounds detected arise from the direct volatilisation of compounds contained in domestic refuse and their concentrations in landfill gas are thus governed by the same parameters as the CFC's. Possible exceptions include tertrachloroethene, trichloroethene, 1,2-dichloroethene and chloroethene. It has been reported that 90% of the trichloroethene manufactured in the UK is used for metal cleaning and that tetrachloroethene is commonly used for both metal cleaning and dry cleaning.[13] This would suggest that both tetrachloroethene and trichloroethene were probably not derived from domestic refuse. This conclusion appears to be supported by the fact that trichloroethene was not present in the gas sampled at four of the seven sites studied and that tetrachloroethene was only present in relatively low amounts. Rettenberger and Stegmann postulated that biochemical degradation of tetrachloroethene via anaerobic hydrogen-halogen substitution can lead to the formation of trichloroethene, both cis- and trans-1,2-dichloroethene and chloroethene.[14] The results from this study seem to support this theory as sites with relatively high levels of tetrachloroethene also had elevated levels of trichloroethene, 1.2-dichloroethene and chloroethene.

A comparison between the results obtained from this study and those obtained by other authors is presented in Table 5.6. The selection of the aforementioned data was based on three considerations. Firstly, each of the papers provides a comprehensive list of the trace VOC's present in the landfill gases sampled. Secondly, all three studies used identical sampling and analytical procedures. The latter point is of importance because the observed fluctuations can be assigned to changes in the landfill gas composition and not inefficiencies in the analytical techniques used. Thirdly, in my opinion, the sampling and analytical procedures used are far more likely to provide an accurate assessment of the levels of all the trace VOC's than those employed by most of the other authors in this field. The results taken from Dent *et al.* summarise the variation in trace gas composition in the landfill gas sampled at three domestic waste disposal sites, each site being monitored over the 3-year period immediately following waste deposition.[10] All of the sites exhibited similar trends in trace gas composition: an overall decrease in the levels of all the trace gas components and a dramatic decrease in the levels of halogenated compounds and alcohols with increasing time since waste deposition. Young and Heasman examined the variation in landfill gas composition arising from fresh domestic refuse over a 6-month period.[9] They observed that almost all the trace gas constituents were common to each of the sites, although they did note that the concentrations of individual components were highly variable. The paper by Brookes and Young was primarily a discussion of the analytical methodology, and as a result, background data on the site studied was not provided.[15]

Table 5.6 Comparison of the Results Obtained from this Study with those Published by other Authors[1]

Compounds	This work	Young and Heasman[9]	Dent *et al.*[10]	Brookes and Young[15]
total alkanes	302-1543	-[2]	0.3-1738	619
C2-C5 alkanes	62-553	-	-	119
C6-C12 alkanes	122-1415	-	-	500
total cycloalkanes	80-487	-	<0.4-56	49
cyclohexane	6-30	1.1-40	-	33
methylcyclohexane	11-45	2.7-13	-	15
dimethylcyclohexanes	<0.1-16	0.5-12.5	-	<1
trimethylcyclohexanes	10-66	<0.1-5.5	-	<2
C3-alkylcyclohexanes	7-49	<0.1-21.7	-	<2
C4-alkylcyclohexanes	<0.1-33	-	-	<2
total terpenes	35-652	-	-	414
limonene	<0.1-287	3.3-269	-	240
total aromatics	36-1906	-	0.6-553	117
benzene	<0.1-7	0.6-12	-	5
toluene	10-287	18-197	-	15
xylenes	36-440	7.9-139	-	34
ethylbenzenes	5-156	3.6-49	-	14
C3-alkylbenzenes	<0.1-295	1.5-173	-	36
C4-alkylbenzenes	<0.1-294	0.1-22	-	5.8
total alcohols	<0.1-1418	-	<0.2-5053	>1052
ethanol	<0.1-262	16-1450	-	>810
propan-1-ol	<0.1-213	4.1-630	-	110
propan-2-ol	<0.1-127	1.2-74	-	>22
butan-1-ol	<0.1-238	2.3-78	-	<2
pentan-1-ol	<0.1-19	0.4-9.6	-	-
total halocarbons	264-1239	-	22-1342	-
chlorodifluoromethane	<0.5-404	<2-276	<0.1-276	4
dichlorodifluoromethane	<0.5-231	6-602	<0.1-486	10
chlorofluoromethane	<0.5-96	<0.1-110	<0.1-110	1
trichlorofluoromethane	<0.5-74	0.4-185	<0.1-185	20
dichlorofluoromethane	<0.5-114	-	0.1-602	5
chloroethene	<0.1-87	0.03-3	0.03-8.3	16
dichloromethane	1-85	7.7-490	0.1-397	140
1,2-dichloroethene	1-182	0.07-28	0.07-28	68
trichloroethene	<0.1-152	1.2-116	0.07-116	10
tetrachloroethene	<0.1-255	0.3-110	<0.1-110	250

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[1] Concentrations in mgm^{-3}

[2] - Not analysed for or concentration not quoted

It is clear from the results presented in Table 5.6 that there are significant differences in both the type of VOC's detected and their concentrations in the gases sampled. The majority of the observed variations can be readily assigned to differences in the composition of the waste, the age of the waste and the stage reached in the decomposition process. The lack of a detailed understanding of the relationship between physical, chemical and biological processes which occur within a landfill means that it is almost impossible to provide a detailed explanation of the observed fluctuations in VOC's concentrations between sites. This study has, however, highlighted several important points. Firstly, for older landfill sites, there appears to be very little variation in landfill gas composition over timescales of a year or more. This therefore means that the results from the analysis of a range of landfill gases from sites with differing types and age of waste may provide an invaluable insight into the underlying mechanisms generating landfill gas. In order to do this, however, a much larger database of information is required. Secondly, the trace gas components in the landfill gases from a wide cross-section of sites are similar, although their relative concentrations differ significantly. Thirdly, the results from this study suggest that the rate of gas extraction/loss from the landfill has a direct affect on the levels of VOC's observed. The latter point is of particular significance because in order to directly compare data between sites, the analyst should be provided with an historical record of gas extraction rates and a description of the type of site being sampled.

5.3 Environmental Impact and Health Effects of Trace Volatile Organic Compounds

It is estimated that two million tonnes of VOC's were emitted into the UK's atmosphere in 1994, of which 5% were of natural origin.[16] The main sources of anthropogenic emissions are road transport, oil refinining and distribution, the chemical industry and the manufacture and use of solvent-based paints and coatings. The generic term "VOC's", covers a diverse group of organic chemicals. As a result, their impact on both the natural environment and human health can be wide ranging. An Environment Committee, appointed by the House of Commons to addresss this problem, identified the two main areas of concern as low-level ozone formation, and other secondary pollutants associated with photochemical smog, and the carcinogenicity of a few individual substances, notably benzene and 1,3-butadiene. Both the then Minister for the Environment and Friends of the Earth considered that the most significant of these was the formation of tropospheric or low-level ozone. Although stratospheric ozone is fundamental to the chemistry of the upper atmosphere, protecting the earths surface from harmfulultravioletradiation, low-level ozone is damaging to certain plants and building materials and is harmful to human health, being an irritant to the respiratory system which can produce asthma-like symptoms, particularly in children.[17] The formation of ozone occurs by a complex series of reactions between atmospheric oxygen, oxides of nitrogen (NOx) and VOC's:[16]

$$\text{Sunlight} + NO_2 \rightarrow NO + O^{\cdot}$$

The oxygen atom then combines with a oxygen molecule to give ozone;

$$O_2 + O^{\cdot} \rightarrow O_3$$

The ozone molecule can then react with NO to form the original starting materials;

$$NO + O_3 \rightarrow O_2 + NO_2$$

Although VOC's are not directly involved in the formation of ozone, they interfere with the removal mechanism by forming competing reactants which remove NO, preventing it from reacting with ozone molecules.[16] In order to predict the potential contribution of landfill emissions to low-level ozone production, the mean annual emissions of the trace VOC's present in the landfill gases from sites A, B, F and G are given in Table 5.7.

Table 5.7 Predicted Emission Fluxes of selected Trace VOC's from Sites A, B, F and G (kg/year) if Landfill Gas was not used for Electricity Generation

Compound	Site A	Site B	Site F	Site G	Global[13]
chlorodifluoromethane	490	450	-	490	1.4×10^8
dichlorodifluoromethane	410	610	1900	300	4.5×10^8
1-chloro-1,1-difluoroethane	-	180	-	-	N/A[3]
chlorofluoromethane	180	120	-	-	N/A
dichlorofluoromethane	120	440	-	-	N/A
trichlorofluoromethane	41	-	-	-	3.5×10^8
1,1,2-trichloro-1,2,2-trifluoromethane	4	4	-	-	1.5×10^8
total CFC emissions	1245	1804	1900	790	9×10^8
chloroethene	17	44	256	28	-
1,2-dichloroethene	29	84	642	83	-
BTEX	325	1782	3011	897	-
total VOC's emissions	3800	1.3×10^4	3.6×10^4	1.2×10^4	[4]$2.1\text{x}10^{10}$

The calculated emission fluxes are based on the assumption that all of the landfill gas extracted is emitted directly into the atmosphere, without any prior treatment.

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[3] N/A Data not available (predicted to be significantly smaller than CFC's with estimated emission fluxes)
[4] Value represents estimated UK emissions for 1995[7]

The values given were calculated using the gas extraction rates to the electricity generators and do not take into account diffusive losses through the landfill cap or losses from landfill gas extraction equipment. A further limitation on the accuracy of the data is the fact that three of the four sites were only visited once, and as a consequence, the values given are based on the assumption that the composition of the landfill gas remains constant. Bearing in mind the large degree of uncertainty associated with the data, and in particular the values for sites B, F and G, it is clear that the total VOC's emissions are several orders of magnitude smaller than that of other documented sources such as motor vehicles and industry.[16] Thus their contribution to low-level ozone production is probably small. It is important to note, however, that although the majority of health effects associated with exposure to low-level ozone are observed in densely populated areas of south-east England, ozone can be transported considerable distances in air. For this reason any register of potential sources of VOC's should include landfill sites.

In terms of global air quality, the compounds of greatest concern in landfill gas are the chlorofluoro compounds (CFC's). The contribution of CFC's to stratospheric ozone depletion is well documented and, as a consequence, their use and disposal is now carefully controlled.[17] In the past, however, CFC's were widely used as aerosol propellants, foam blowing agents and refrigerants, and as a consequence, are ubiquitous in landfill gas. The potential flux of CFC's from the landfill sites studied was estimated to be of the order of 10^3kg/yr, with the best estimate of the global emission flux from all sources being 10^8kg/yr.[17] Given that there are approximately 2000 landfills in operation in the UK and assuming they all emitted similar levels of CFC's, their potential contribution to the current atmospheric concentrations would be of the order of 10^6kg/yr.

The true value is obviously considerably smaller due to the thermal destruction of VOC's in landfill gas fuelled engines and flare stacks. Speculation about the performance of flare stacks and in particular their effectiveness at the high temperatures required to destroy CFC's, however, highlights the importance of landfill gas control measures being an integral part of waste management strategy for all industrialised countries in the world.[18]

The direct risk to health associated with the exposure to the trace VOC's in landfill gas is governed by both the landfill gas composition and the rate of release of landfill gas to the atmosphere. In general, it unlikely that landfill workers or the general public will be exposed to elevated levels of landfill gas for extended periods of time. Under certain conditions, however, the exposure to landfill gas could be significant, particularly for gas engineers who install and maintain the gas migration control equipment. As a primary requirement of the Control of Substances Hazardous to Health (COSHH) regulations, 1994, employee's exposure to hazardous chemicals should be prevented, or, where this is not practicable, controlled in a responsible manner.[19] In order for employers to comply with this legislation, the Health and Safety Executive issued a list of exposure limits (EH40).[20] Two types of exposure limit were defined, maximum exposure limit (MEL), which is set at a level where there may be a residual risk to health but due to socio-economic factors this risk is considered acceptable, and occupational exposure standards (OESs), where the limit is set at a level where there is no indication of a risk to health. All exposure limits are averaged over a reference time period, usually a typical working day (8 hours). It should be noted, however, that the absence of a given substance from the list of OESs and MELs is not indicative of its safety.

Examination of the data contained in Table 5.4 indicates that landfill gas at two of the seven sites (E and F) exceed the MEL for chloroethene (vinyl chloride). Chloroethene is acknowledged as a human carcinogen and is thought to cause cancer of the liver.[21] In addition, chronic exposure to chloroethene has led to liver and spleen damage, deterioration of certain bones and circulatory defects in the hands and feet. Given that the landfill gas at sites E and F exceed the MEL by a factor of 5 an 3 respectively, it would appear that long-term exposure to the gas at both sites could be detrimental to health. Of the remaining components listed in Table 5.4, only toluene, xylene (site F), the trimethylbenzenes (site F), tetrachloromethane (on four occasions at site A) and dichlorofluoromethane (sites A-C) exceed their recommended OESs. Similar results were obtained by Scott *et al.* who identified organosulphur compounds during the early stages of waste deposition, alcohols, trimethylbenzenes, formaldehyde and a number of halogenated compounds, including dichlorofluoromethane, as being potentially detrimental to health.[22] They also concluded that the greatest risk to health was associated with waste deposition and in some cases they suggested that it may be necessary to limit access to personnel with nervous or respiratory problems. The results from this work partially contradict this statement as site E, where the waste is in excess of 20 years old, is still producing landfill gas containing significant quantities of vinyl chloride.

The use of individual OESs and MELs is not strictly adequate when considering the toxicity of complex gaseous mixtures such as landfill gas.[22] Although some mixed exposures will involve substances that act independently of each other and on different body tissue or organs or by different toxicological mechanisms, other mixtures include substances that act on the same organ. Under these circumstances it is suggested that the toxic effects are considered additive;

$$F = C1/T1 + C2/T2 + C3/T3 \ldots\ldots Cn/Tn$$

Where: F = Exposure Factor for Organ

C = Concentration of Component

T = Individual OES/MEL of Component

When the value of F exceeds unity, the toxic threshold for that particular organ or function has been exceeded, with exposure to such a mixture being potentially detrimental to health.[20] In addition to additive effects, other components may enhance the toxicity of others with the resulting effect being that the toxicity is considerably greater than the sum of the individual toxicities. Given that there are approximately 140 compounds in landfill gas and that data relating to synergistic effects is sparse, a detailed assessment of landfill gas toxicity was considered to be beyond the scope of this thesis.

5.4 Trace Volatile Organic Compounds and Corrosion

Both landfill gas and landfill sites are often seen as an unacceptable environmental burden, with waste minimisation and recycling of reusable resources being the chosen methods of dealing with the huge quantities of waste materials produced by a modern society. As a consequence, the UK governments aim is to recycle 25% of household or municipal solid waste by the year 2000.[23] The variable nature of the market for recovered materials and the fact that plastics become contaminated and paper fibres lose their strength, however, means that household waste cannot be recycled indefinitely.[23] In addition, it has been suggested that recovery of certain materials can have a greater impact on the environment than utilising fresh materials and using an appropriate disposal route for the waste.[24] An alternative approach, utilised by a number of American and European countries, is to collect the landfill gas produced during the waste degradation process and use it as a fuel for electricty generation.

The non-fossil fuel obligation (NFFO), introduced in the UK following the privitisation of the electricity supply industry in 1990, was setup to stimulate the development of renewable energy sources where it is considered to be financially attractive and environmentally acceptable.[25] The NFFO provides a guaranteed market at a premium price for electricity generated from non-fossil fuel sources. Landfill gas schemes have been the most successful of all the projects accepted by the NFFO. At the end of 1994, 42 landfill gas schemes had been awarded contracts, contributing over 80MW of renewable energy to the UK resource.[25] The use of landfill gas as a fuel, however, can be problematic. The Department of the Environment contracted a long term study of a landfill gas generation scheme installed by Shanks and McEwan.[26] The aim of the study was primarily to ascertain the technical and financial limitations of such schemes, although the project remit also included an assessment of the need for pre-treatment of the landfill gas and an environmental impact assessment. One of the findings of the report was the effect of landfill gas combustion on the TBN of the oil. TBN is a measure of the oil's alkalinity and is expressed as milligrams of potassium hydroxide equivalents per gram of oil. As the TBN falls, the oil's buffering capacity is reduced and the potential for corrosion within the engine increases. The source of the problem was identified as being the presence of halocarbons and sulphurous compounds. The combustion of the latter compounds can lead to the formation of sulphuric, hydrochloric and hydrofluoric acids. Although the problems were, for the most part, overcome by increasing the TBN of the oil at the Shanks and McEwan site, the potentially damaging effects of halocarbons were dramatically illustrated at the Braunschweigs landfill site in Germany.[27] Three internal combustion engines had been installed to power electricity generators, with the electricity produced being used at a sewage treatment works. After an operating period of only 889 hours, catastrophic failure of one of the three engines occurred. The investigation which followed revealed substantial corrosion of the connecting rod bearing shells at the crankshaft and the piston pins. Slight corrosion was also found to the piston rings, the piston heads, the piston boxes, the valve rockers, the camshaft, the crankshaft and the oil filter. Similar damage was observed in the remaining two gas engines. The cause of the corrosion was attributed to the relatively high concentrations (~ 600mgm^{-3}) of chlorinated hydrocarbons in the landfill gas. In order to keep the electricity generation plant operational, the operators found it necessary to modify the engine oil and replace certain parts within the engine with corrosive resistant materials.

At the landfill sites studied for this thesis, the manufacturer of the oils used in the landfill gas fuelled engines stipulate that the chlorine content of the gas should not exceed 250mgm^{-3} (personal communication). The results contained in Table 5.4 indicate that three sites, A, E and F, exceed this value and can thus be considered to be potentially damaging to the gas engines. Although the remaining four sites were all below the threshold value, the results obtained and the case studies discussed illustrate the need for accurate analyses of landfill gas composition prior to the installation of electricity generation equipment.

5.5 Conclusions

A number of conclusions can be drawn from this study. Firstly, the results of the long-term monitoring programme at site A indicate that if the site is operating under normal conditions with both landfill gas extraction and production rates being in a state of equilibrium, a single analysis dataset can provide a fairly accurate estimate of the typical levels of VOC's. Ambient conditions, such as pressure and temperature, were observed to have a minimal effect. Secondly, although the majority of the components identified were present in each of the landfill gases sampled, the relative proportions of certain compounds varied considerably between sites. This was thought to be due to differences in the waste composition and the stage reached in the decomposition process. Thirdly, emission of landfill gas was found to be potentially detrimental to both ambient air quality and the landfill operatives health, although further studies are required to determine the magnitude of this effect. Fourthly, the results presented in this thesis were similar to those obtained by other authors.[9,10,15] The main benefit of this work over other reported methods, however, is the reduced analysis time. Landfill gas analysis using the latter authors method took in excess of a day. Sample analysis using the method developed for this thesis took approximately 1.5 hours. Given the current market pressures for laboratories to reduce sample turn-around times without affecting analytical quality, this time saving is of particular significance.

5.6 References

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Chapter 6

Remote Monitoring of the Trace Volatile Organic Compounds in Landfill Gas

6.0 Research Aims

To design, develop and evaluate a system for on-site analysis of trace VOC's in landfill gas.

6.1 Introduction

In sharp contrast to universal concerns over air and water pollution, contaminated land has, until recent times, received little publicity. The worlds first recognised pollution incident arising from a contaminated site occurred in the 1970's at Love Canal, America.[1] The resulting adverse publicity and subsequent identification of a range of similar sites across the United States led the American Government to set up the "Comprehensive Environmental Response Compensation and Liability Act (CERCLA)", now known as Superfund. Superfund was used to finance the identification, investigation and remediation of contaminated sites.

The need for legally defensible data together with the complex cocktail of pollutants identified at the sites resulted in the developent of a range of sophisticated analytical methods together with exacting quality control standards and supporting documentation. The strict adherance to these protocols resulted in laboratory turnaround times being of the order of 30 days. It soon became clear that there was a need for fast, cost-effective screening methods which would allow on-site personnel to obtain an overview of the site under investigation in real time. The US EPA responded to this need by providing a framework of three levels of investigative analysis.[1] Level I was used to ascertain the total levels of contaminants present (ie. total VOC's) to a precision of ±10%, an accuracy of ±50% and typical detection limits of 1000ppm or better. Level II screening was then used to determine the identity and relative concentrations of the analytes present to a precision of ±10%, an accuracy of ±15% and detection limits of the order of 10ppm. The final level, III, was carried out within the existing laboratory framework to litigation standards. The resultant need for sensitive, robust, portable field instruments led to the development of a range of analysers and field test kits. In the case of organic pollutants, these range from simple hand-held photoionisation detectors to portable gas chromatographs.

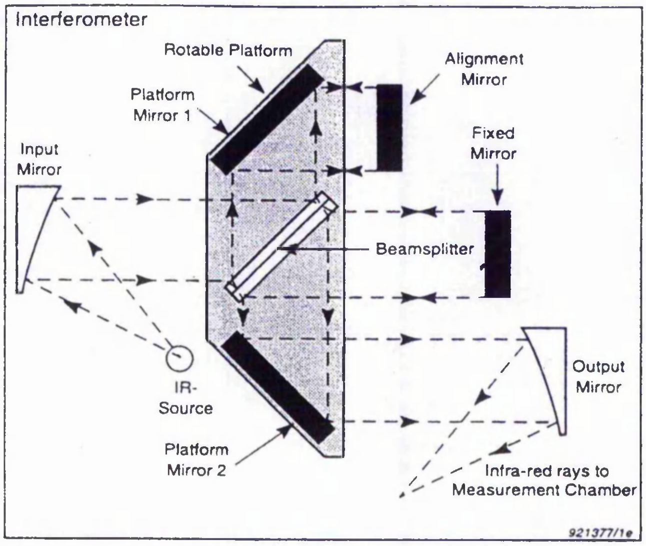
From the outset, one of the aims of the work described in this thesis was to provide a sound basis for the development of a remote landfill gas monitor. The ability to provide on-line analysis of the trace VOC's in landfill gas is important for two reasons. Firstly, the effects of commissioning new landfill gas wells on overall landfill gas quality can be immediately assessed. The latter is of particular importance for landfill gases with elevated levels of halogenated compounds, which can be potentially detrimental to both the landfill operatives health and the gas handling equipment.[2-4] Secondly, continuous analysis of the trace gas composition may provide a valuable insight into waste degradation processes. Thirdly, as the analytical equipment is in-situ, landfill workers can operate the instrumentation themselves, thus reducing analysis costs.

Whilst developing the method for the ATD-GC-MS, described in Chapters 3 and 4, every effort was made to simplify both the sampling and analytical procedures, whilst ensuring that an acceptable level of accuracy and robustness was maintained. The results from the field trials, discussed in Chapter 5, indicate that this was achieved. Although an ATD-GC-MS could be installed on site and thus be used for remote monitoring, it is clearly not a cost effective option as each system would cost in the region of £80-100k. In addition, the site operatives would need specialist training which is both time-consuming and expensive. As a consequence an alternative option was considered, based upon US EPA Type I and II screening methodology, using adsorbent preconcentration followed by thermal desorption and Fourier transform photoacoustic detection (FTPAS).

6.2 Bruel and Kjaer 1301 Gas Analyser (FTPAS)

One of the major disadvantages of conventional infra-red spectroscopy is it's inherent slowness. This is due to the measurement process which involves making consecutive discrete measurements across the infra-red spectrum, with the resultant signal being monitored and recorded. This process can take in excess of ten minutes. Clearly, if the spectrum only contains one or two regions of interest, the majority of this time is spent recording background noise. The system employed in the Bruel and Kjaer FTPAS gas analyser, however, utilises Fourier transform spectroscopy, which allows the simultaneous and almost instantaneous acquisition of the whole spectrum, resulting in a 10-100 fold reduction in scan time.[5] Central to this process is the modified Michelson Interferometer, illustrated in Figure 6.1. A conventional Michelson interferometer consists of a beam splitter and two mirrors, one fixed and the second moveable. The beam splitter is constucted from a plate of transparent material (eg. potassium bromide) coated so as to transmit 50% of the radiation to the first mirror and reflect the remaining 50% to the second moveable mirror. The radiation reflected from the two mirrors is then recombined to a single beam at the beam splitter and refocussed onto the measurement chamber. The recombined beam exhibits both destructive and constructive interference. The magnitude of the latter effects is governed by the relative path lengths of the first fixed mirror and the beam splitter and the second moveable mirror and the beam splitter.

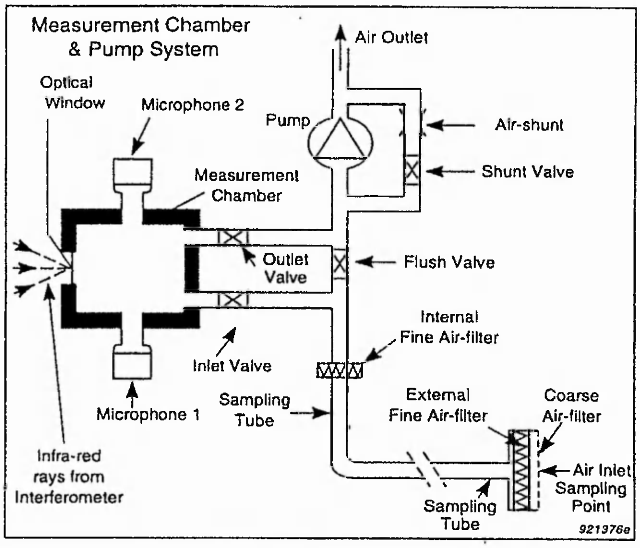
Figure 6.1 Bruel and Kjaer Interferometer



As the moveable mirror traverses backwards and forwards, the radiation received by the detector fluctuates in intensity. If the recombined beam is directed through a sample before reaching the detector, sample absorptions will show up as gaps in the frequency distribution. By applying the Fourier transform process, which essentially solves a series of simultaneous equations used to describe the complex variations in frequency intensity and distribution, a conventional absorption spectrum can be obtained.[6,7] The main difference between a conventional Michelson interferometer and that employed in the FTPAS is that the beamsplitter and both mirrors are fixed to a single platform which rotates over an angle of 1° relative to the IR source. This process, which takes approximately 13 seconds, continuously varies the path length of the beam and thus produces the interferogram.[8] The main reason for adopting this approach is that the optics are far more stable in the latter configuration and as a consequence, less susceptible to external disturbance from vibration or impacts during transit and analysis.

A schematic diagram of the FTPAS measurement chamber and pumping system is illustrated in Figure 6.2. A small internal pump is used to draw the gas sample from the sampling point, through two air filters and into the measurement chamber which is then hermetically sealed by closing two gas-tight valves. The IR light reflected from the interferometer is then selectively absorbed by the sample within the measurement chamber, causing the temperature of the gas to fluctuate. This in turn produces a corresponding fluctuation in pressure and thus an acoustic signal. The magnitude and wavelength of the acoustic signal, which is measured by two microphones mounted on the chamber wall, depends upon both the wavelength of the radiation absorbed and the amount of sample present.

Figure 6.2 Schematic Diagram of the Measurement Chamber and Pumping System



The resulting signal is filtered, converted from an analogue to a digital signal and then Fourier transformed to produce the absorption spectrum. A fully integrated data handling system then automatically compensates the recorded signal for fluctuations in input pressure and temperature and also normalises the spectra for small variations in the intensity of the infra-red light.

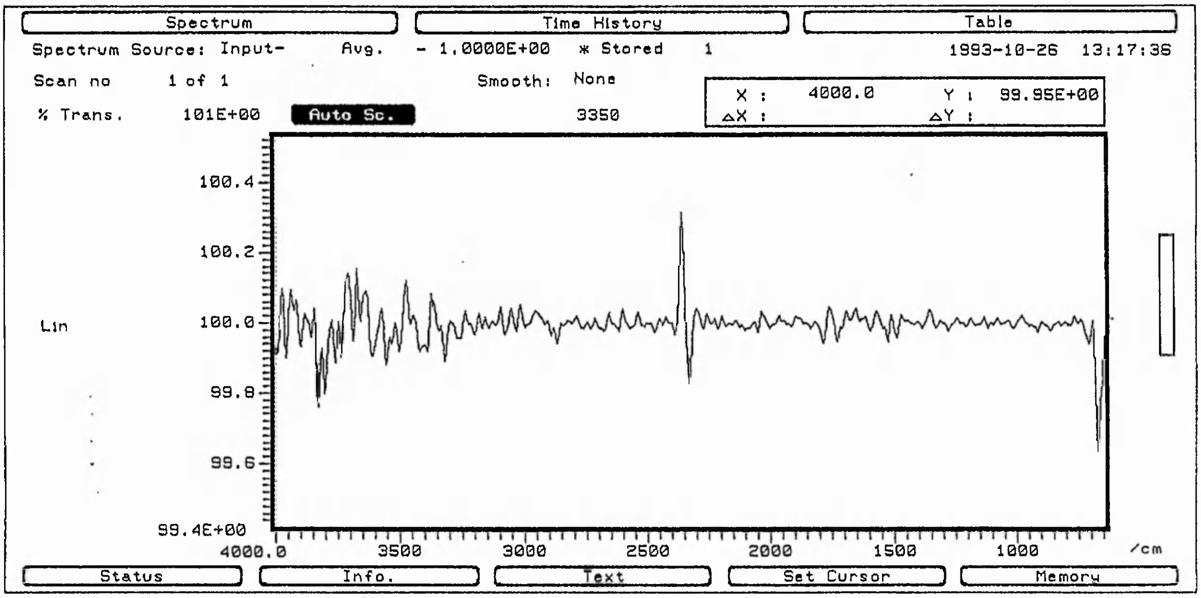
6.3 Optimisation of FTPAS Sensitivity

The main advantage of photoacoustic detection over conventional semi-conductor detection systems is it's enhanced sensitivity.[9-14] Transmission spectroscopy relies upon the measurement of minor changes in a large background signal. As a consequence, relatively small deviations in the measurement of the background signal can lead to huge uncertainties in the predicted analyte concentration. By contrast, photoacoustic detection measures small flutuations in the pressure of the absorbing species from an almost negligible background signal. By careful design of the measurement chamber, background noise is kept to a minimum, resulting in a much more stable, and as a consequence sensitive, detection system. As with all Fourier transform instruments, the FTPAS also utilises computer averaging techniques to further enhance sensitivity gains. This process essentially works by storing discrete data points in separate channels. The process can then be repeated several times, with each set of data being added to that previously obtained. Although in any one scan a weak analyte signal may not be visible above the baseline noise, after n summed scans the signal will be n times larger in each channel. By contrast the noise, which is random in nature, will sometimes be additive and sometimes negative and as a consequence will make less of a contribution to the overall magnitude of the signal. It has been shown that the net gain to the signal to noise ratio of this process is $n^{1/2}$ where n is the number of scans.[5] It is clear therefore, that sensitivity can be increased by increasing the scan number. In the case of the FTPAS, however, there are several processes which act in the opposite direction.[8] The manufacturers have found that after a certain period of time the gases can diffuse out of the measurement chamber. In addition, they have also noted that gases from previous samples can be released from the internal spaces within the measurement chamber walls and microphones. Furthermore, given that it takes 18 seconds to obtain a spectrum and that the S/N ratio only improves with the square root of time, it can be an inefficient use of analysis time. The aim of the work described in this section, therefore, was to ascertain the optimum scan number.

6.3.1 Experimental

In order to maintain the composition of the sampled gas, the baseline stability studies were conducted on a sample of laboratory air stored in a 10 litre bell jar fitted with a dual arm adaptor which was sealed with an inert rubber septum. 3mm I.D. teflon tubing was connected to both the inlet and outlet ports on the FTPAS and inserted into the bell jar through the two glass arms. The connectors between the glass arms and teflon tubing were sealed using gas-tight teflon compression fittings. This effectively formed a closed system, with the analysed gases being returned to the bell jar and then resampled. Sample homogeneity was maintained by pushing the exhaust (outlet tubing) from the FTPAS to the bottom of the bell jar. In order to accurately determine the stability of the photoacoustic signal in the presence of carbon dioxide and water vapour, an average background signal was obtained by repetitively sampling and scanning the laboratory gas. This signal was then subtracted from all subsequent spectra. In total, fifteen samples were taken and the effect of increasing the scan number from 1 to 15 assessed.

Figure 6.3 FTPAS Spectrum obtained from Subtracting an Average Background Spectrum of Laboratory Air from a Single Scan Spectrum of the Same Sample.



Spectrum Source: Input- Avg. - 1.0000E+00 * Stored 1 1993-10-26 13:17:36

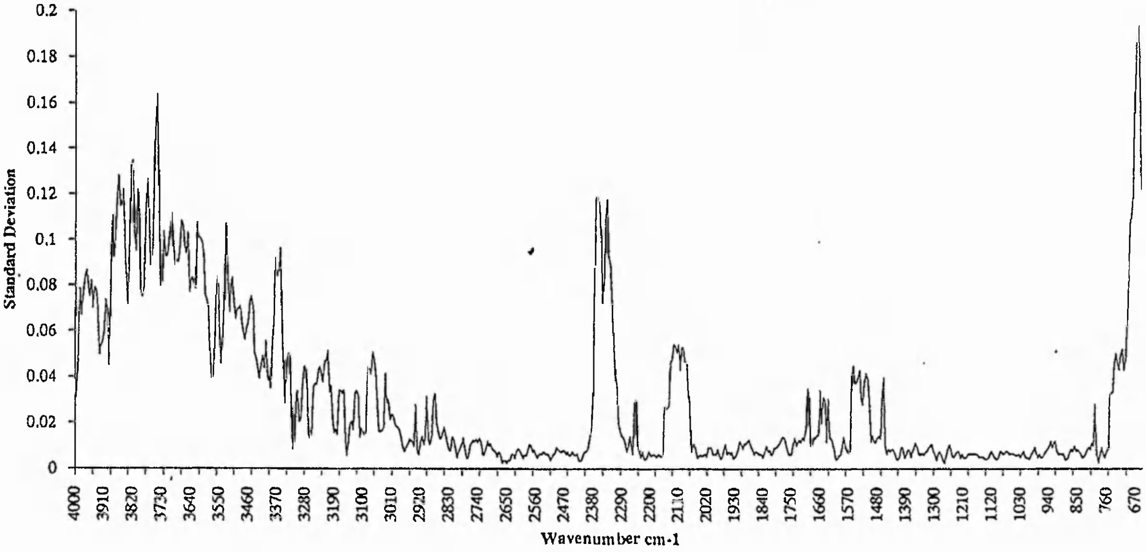
Scan no 1 of 1 Smooth: None

% Trans. 101E+00 3350

X : 4000.0 Y : 99.95E+00

ΔX : ΔY :

Figure 6.4 Variation in Standard Deviation with Wavelength for a Single FTPAS Scan of 15 Spectra.



6.3.2 Results and Discussion

Examples of the results obtained are illustrated in Figures 6.3 and 6.4. As nitrogen and oxygen are not infra-red active, the two regions of interest are the carbon dioxide and water vapour absorption bands. Water vapour absorbs strongly in the regions 1400-1800cm^{-1} and 3400-4000cm^{-1} and carbon dioxide, 2250-2400cm^{-1}. Examination of both the spectra and the statistical data indicate that the largest deviations in baseline stability occur within these regions. The particularly intense bands at approximately 2350 and 670cm^{-1} are due to the antisymmetric stretch and bending vibrations of the carbon dioxide bonds.[5] Given that landfill gas contains percentage levels of both carbon dioxide and methane, these regions of the spectra should, wherever possible, be avoided when selecting filter limits for quantitative purposes. As would be expected, the overall accuracy of the data improves with increasing scan number. For example, increasing the scan number from 1 to 15, results in a two-fold reduction in the standard deviation of the baseline signal and thus the detection limit. Conversely, the analysis time increases from approximately 20 seconds to nearly 5 minutes. It is clear therefore, that selection of a suitable scan number will essentially be a compromise between analytical quality and measurement time. Overall, a scan number of 8 was considered acceptable and was thus used for all subsequent investigations.

6.4 Quantitative Analysis of Methane

The FTPAS operating system, which includes a database of spectral information, allows the determination of 100 different gases of which seven can be analysed simultaneously.[8] The measured results are based directly on the amount of infra-red light absorbed by the gas sample. Quantitation is achieved by integrating the peak areas between predefined filter limits. The latter are usually selected so as to encompass the main absorption bands of the component of interest. The manufacturers claim that the relatively high degree of accuracy and low drift means that calibration is not usually required more than four times a year. The following sections summarise the results obtained from the quantitative analysis of methane.

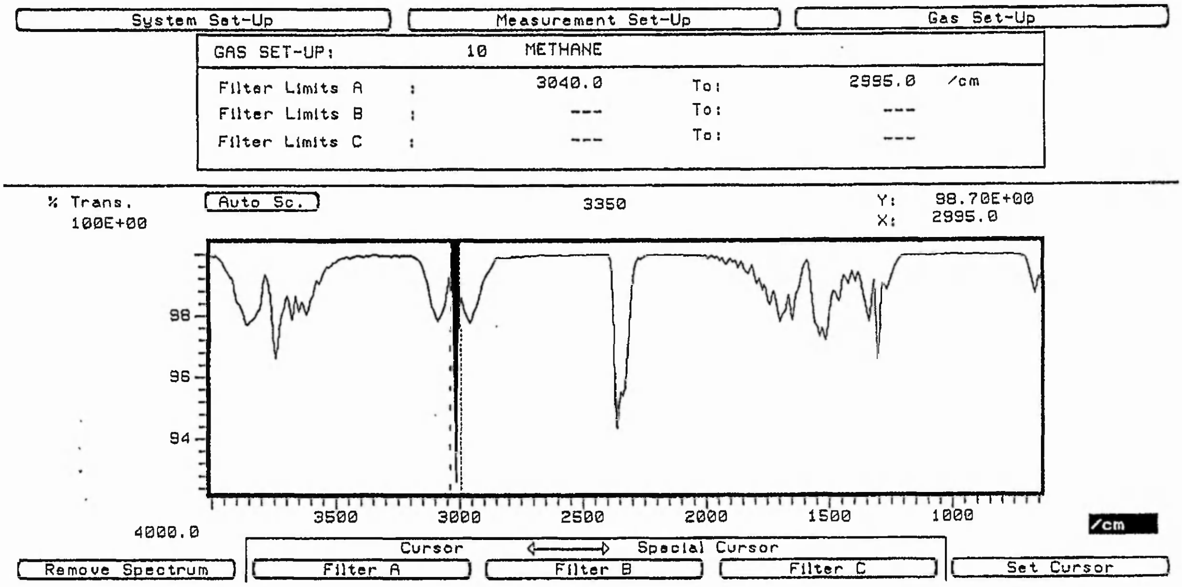
6.4.1 Experimental

A sample of town gas was taken directly from the laboratory supply and stored in a Tedlar gas sampling bag obtained from Alltech, Carnforth. Using the experimental set up described in section 6.3.1, a known volume of gas was injected into the bell jar through the inert rubber septa using either a 1, 5, 10 or 100ml Hamilton gas syringe. The FTPAS pump was then used to recirculate the mixture for ten minutes prior to the measurement of the absorption spectra. The mixture was then repeatedly analysed until the integration results stabilised. The methane concentration was corrected for impurities using information supplied by Transco.

6.4.2 Results and Discussion

The methane absorption spectra consists of three main bands, an intense absorption centred at approximately 3025cm^{-1}, together with two broad, weaker features between 3200cm^{-1} and 2800cm^{-1}. As a consequence, two sets of filter limits were assessed, one utilising the sharp absorption band (2995-3040cm^{-1}) and the second covering all three absorption bands (2845-3100cm^{-1}). The latter are illustrated in Figures 6.5 and 6.6 respectively. The resultant calibration plots are illustrated in Figures 6.7.

Figure 6.5 An FTPAS Spectrum of Methane Illustrating the Narrow Absorption Band Filter Limits (2995-3040cm^{-1}).

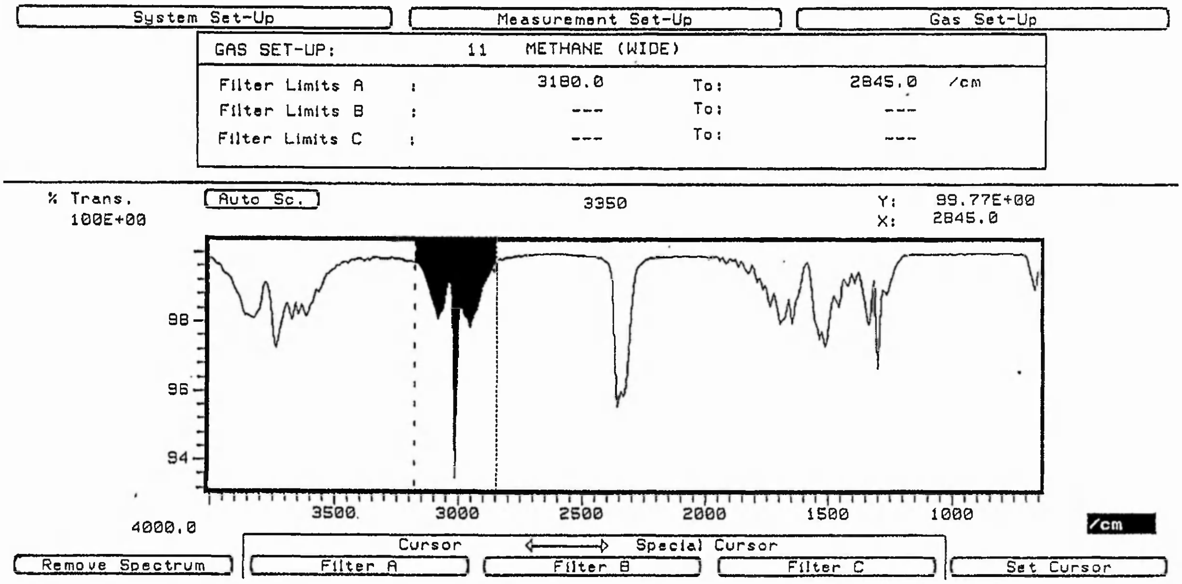


GAS SET-UP: 10 METHANE

Filter Limits A	:	3040.0	To:	2995.0	/cm
Filter Limits B	:	---	To:	---	
Filter Limits C	:	---	To:	---	

Y: 98.70E+00
X: 2995.0

Figure 6.6 An FTPAS Spectrum of Methane Illustrating the Wide Absorption Band Filter Limits (2845-3100cm^{-1}).



GAS SET-UP: 11 METHANE (WIDE)

Filter Limits A	:	3100.0	To:	2845.0	/cm
Filter Limits B	:	---	To:	---	
Filter Limits C	:	---	To:	---	

Y: 99.77E+00
X: 2845.0

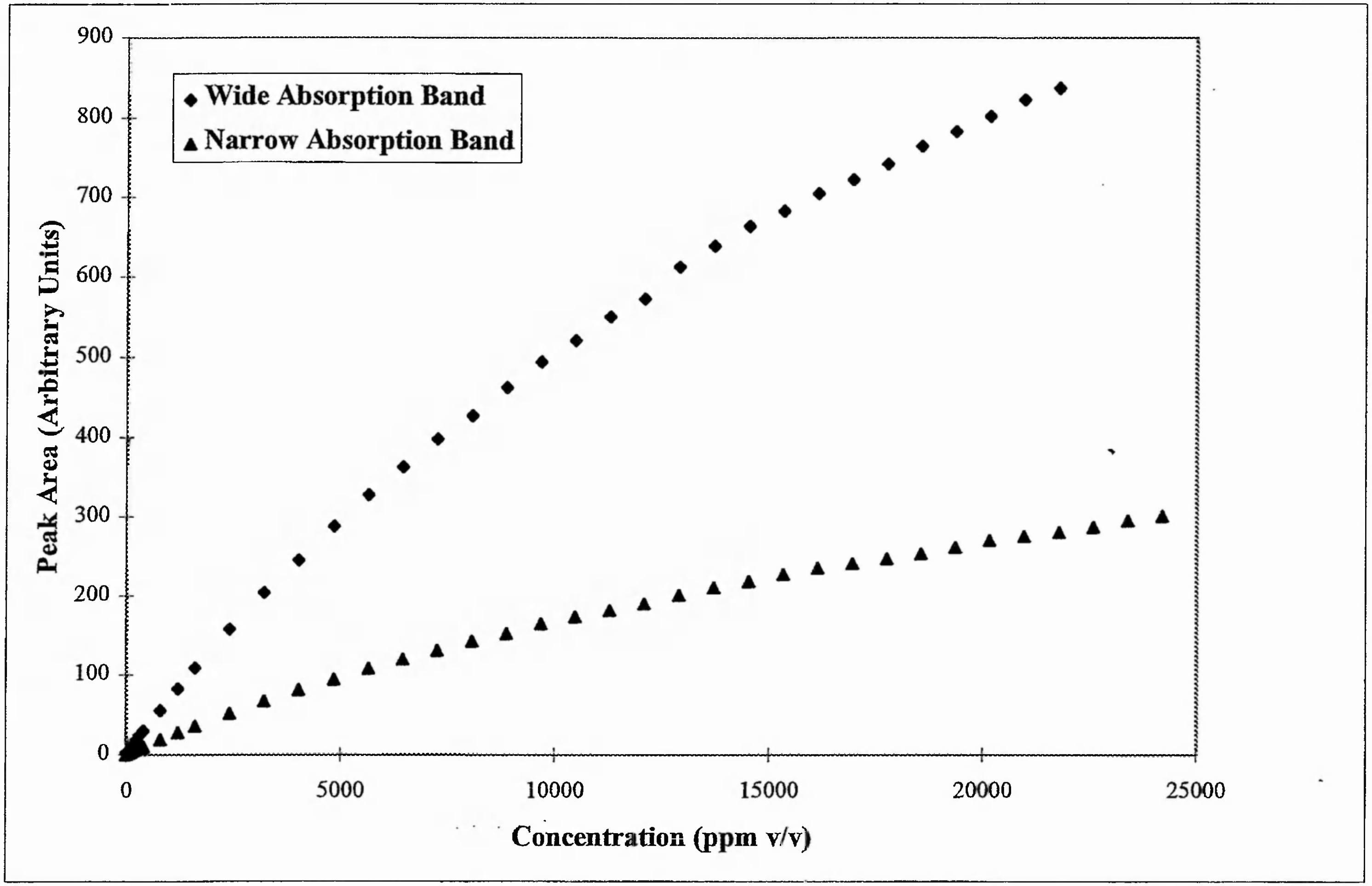


Figure 6.7 FTPAS Calibration Curves for the Wide (2845-3100cm^{-1}) and Narrow (2995-3040cm^{-1}) Methane Absorption Bands.

The narrow filter band calibration plot was found to be linear to 500ppm v/v and the broad filter band, to 300ppm v/v. Above the latter values, the detector response was found to be non-linear. The detection limits for both calibration procedures were calculated as follows;

For the narrow band filter limit:

Standard deviation of background noise = 0.17 (n=6)

Average detector response of 20ppm v/v standard = 0.74 (n=6)

Detection Limit = 3 x Standard Deviation from the baseline noise/Unit Response of Detector

= (3 x 0.17)/(0.74 / 20) = 14ppm v/v

For the broad band filter limit:

Standard deviation of background noise = 0.32 (n=6)

Average detector response of 20ppm v/v standard = 2.78 (n=6)

Detection Limit = (3 x 0.32)/(2.78/20) = 7ppm v/v

Several conclusions can be drawn from this study. Firstly, the overall reproducibility and sensitivity of the detector is good, with detection limits being of the order of 10ppm v/v and the linear working range being approximately two orders of magnitude. Secondly, in order to maximise sensitivity, the filter bands should be selected so as to encompass the majority of the absorption bands of the component of interest and not just the most intense. In the case of methane, this was found to result in a two-fold reduction in detection limit.

6.5 A Preliminary Assessment of the Specificity and Selectivity of the FTPAS

It has been shown that linear molecules have 3N-5 fundamental vibrations and non-linear molecules 3N-6, where N is the number of atoms in the molecule.[5] Each of these vibrations involves displacement of all or nearly all of the atoms within the molecule. In some modes all the atoms may undergo approximately the same displacement whilst in others, the displacement of a small group of atoms may be much greater than those of the remainder. As a consequence, the normal modes of vibration are divided into two categories; skeletal vibrations, which involve all the atoms to much the same extent, and characteristic group vibrations, which involve only a small portion of the molecule. Skeletal frequencies usually occur in the range 1400-700cm^{-1} and arise from linear or branched chain structures within the molecule.[5] Group frequencies are usually independent of the structure of the molecule as a whole and generally arise in the IR regions above and below those of the skeletal modes. Their absorption bands are highly characteristic and as a consequence can be used for qualitative and quantitative analysis of mixed analytes.[5] Given the large number of VOC's in landfill gas, it is clearly not possible to detect and quantitate each individual compound. As a consequence, the group frequencies of each class of compounds will be used and if possible, discrete frequencies selected so as to differentiate between alkanes, aromatic, oxygenated and chlorinated compounds.

6.5.1 Experimental

Using the experimental set up described in section 6.2.1, a selection of individual VOC's, obtained from Sigma-Aldrich, Poole, were injected into the bell jar through the inert rubber septa and allowed to vaporize. The FTPAS pump was then used to recirculate the air for five minutes prior to the measurement of the absorption spectra. Following analysis, the bell jar and FTPAS were thoroughly flushed with clean air prior to injection of the next component.

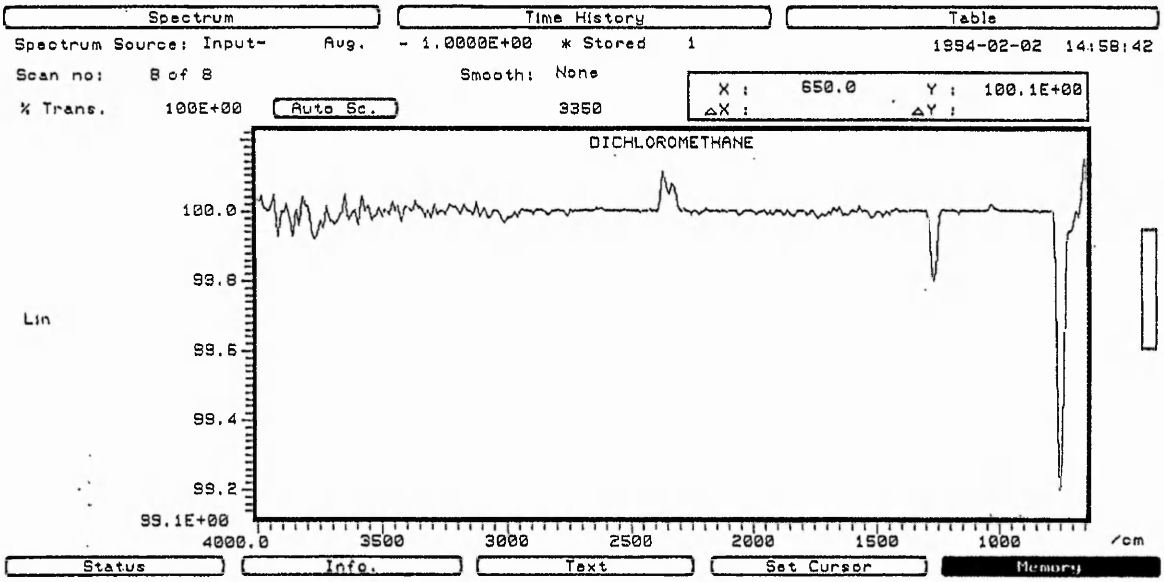
6.5.2 Results and Discussion

Examples of the absorption spectra obtained are illustated in Figures 6.8 and 6.9. A summary of the main absorption bands are given in Table 6.2.

Table 6.2 Characteristic Absorption Bands of Selected Volatile Organic Compounds

Compound	Strong Band (cm^{-1})	Medium Band (cm^{-1})	Weak Band (cm^{-1})
n-Pentane	2970	2885	2850
n-Hexane	2970	2935	2880
n-Heptane	2970	2935	2875
2,2,4-trimethypentane	2960	2910	1370 / 1475
iso-Octane	2965	2905	1370 / 1475
n-Nonane	2935	2965	2870
n-Dodecane	2935	2965	2870
Cyclohexane	2930	2865	-
Benzene	670	3050	3095
Toluene	730	3040 / 2935	1495 / 1610
Dichloromethane	755	1270	-
Chloromethane	795	-	-
1,1,1-Trichloroethane	725	1090	-
Trichloroethylene	850 / 940	-	780
n-Butanol	2995 / 2890	-	1060
Acetone	1740	1365 / 1220	-
Ethyl Acetate	1245 / 1765	1050 / 1380	2995

Figure 6.8 FTPAS Absorption Spectrum of Dichloromethane.



Spectrum Source: Input- Avg. - 1.0000E+00 * Stored 1

1994-02-02 14:58:42

Scan no: 8 of 8

Smooth: None

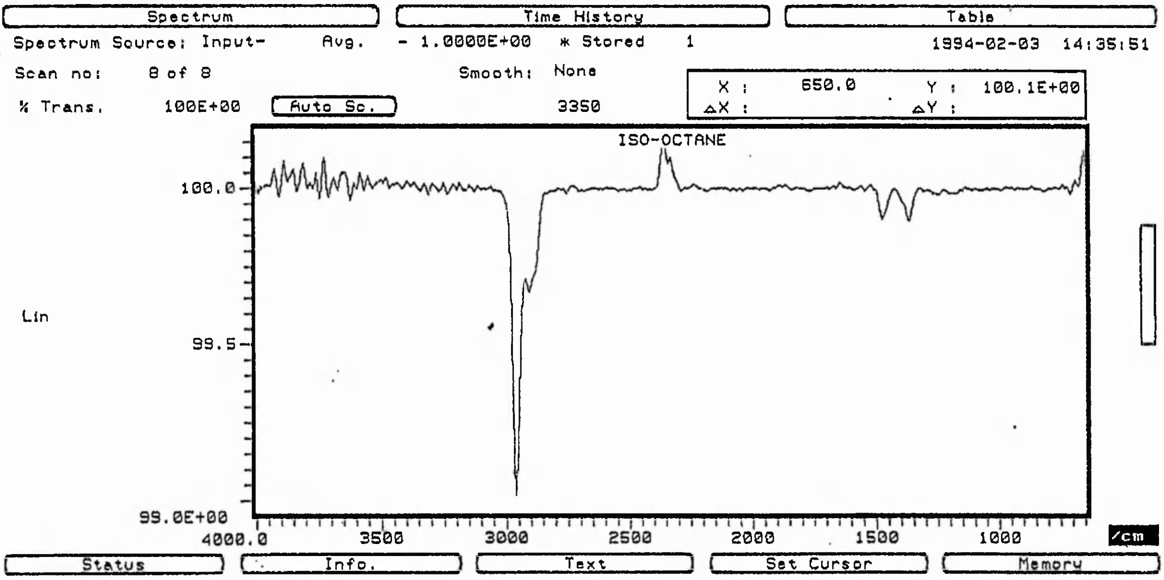
% Trans. 100E+00

3350

X : 650.0 Y : 100.1E+00

ΔX : ΔY :

Figure 6.9 FTPAS Absorption Spectrum of iso-Octane.



Spectrum Source: Input- Avg. - 1.0000E+00 * Stored 1

1994-02-03 14:35:51

Scan no: 8 of 8

Smooth: None

% Trans. 100E+00

3350

X : 650.0 Y : 100.1E+00

ΔX : ΔY :

Inspection of both the spectra and data contained in Table 6.2 indicates that quantitation of the individual groups of VOC's is likely to be problematic. As would be expected, the main alkane absorption bands, which occur between 2935cm^{-1} and 2970cm^{-1} and are characteristic of the CH_2 and CH_3 stretching frequencies, coincide with the main absorption band of methane.[5] Given that methane levels in landfill gas are several orders of magnitude higher than those of the longer chain-length alkanes, it is clear that the preconcentration device must be designed in such a way as to eliminate all of the methane prior to desorption and analysis. Perhaps of greater concern, however, is the degree of overlap between the main groups of interest, the chlorinated compounds and the aromatic compounds, which all absorb in the region 650-800cm^{-1}. The latter compounds are important because of their inherent toxity and potentially detrimental effect on gas handling equipment.[2-4] It was originally hoped that two filter bands would be used to define each of the main C-Cl and aromatic group frequencies. Given the variation in frequency of the absorption bands for the four halocarbons investigated and the fact that one of the main absorption bands of the substituted aromatic compounds lies in the same region, it is clear that for quantitative purposes, a number of narrow filter limits will need to be set-up for each of the halogenated and aromatic compounds identified. Although this is not a fundamental problem, it does, however, mean that there will be some manual manipulation of the data prior to reporting. Alternatively, a computer programme could be designed to automatically process the data. It is also clear that a more comprehensive study of the absorption bands of a wider group of compounds is required before the FTPAS can be used for quantitative analysis of the trace VOC's in landfill gas.

6.6 Design and Construction of a Remote Landfill Gas Monitor

The original aim of this work was to produce a fully operational portable landfill gas monitor. However, due to a fire within the Department of Chemistry and Physics and the subsequent damage to the FTPAS, this was not achieved. As a result, the following sections are limited to a brief description of the proposed system, together with a discussion of potential inefficiencies and suggestions for future development.

6.6.1 Preconcentration Device

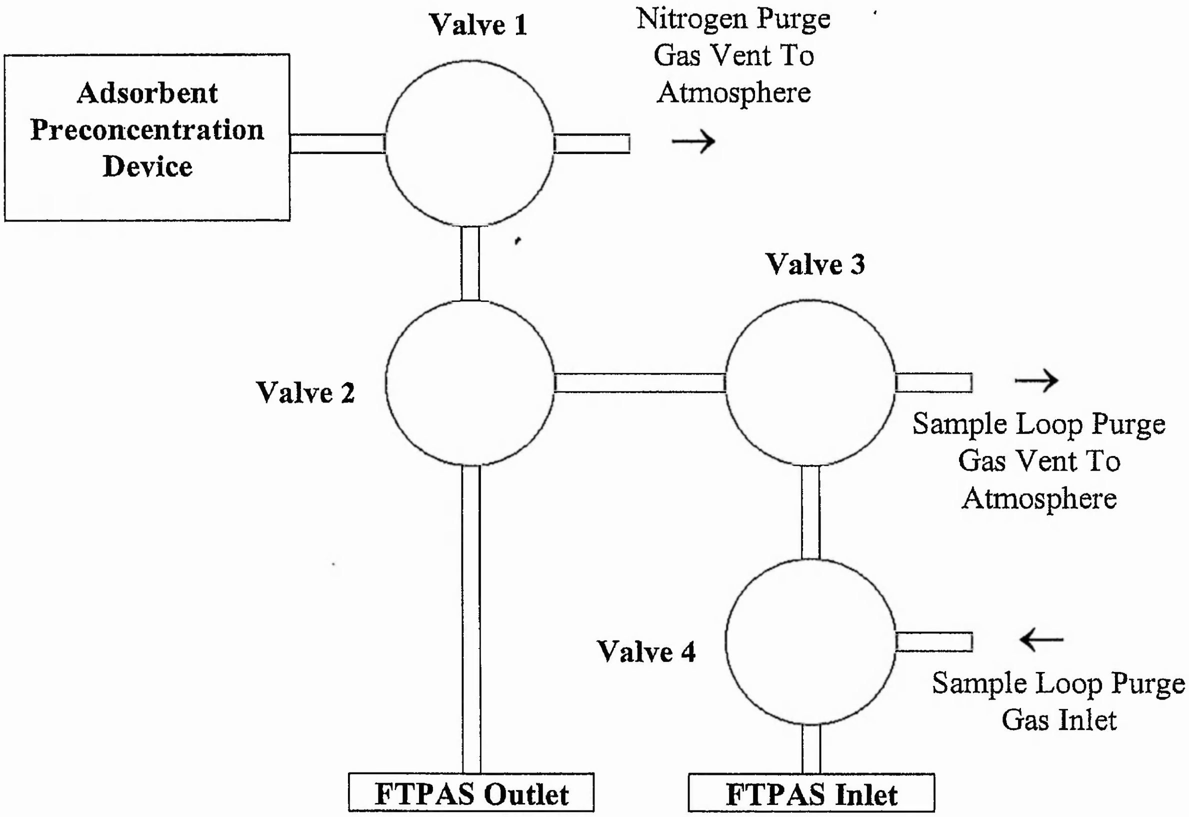
The original design for the preconcentation device consisted of three main components; an adsorbent trap, a pressurised nitrogen supply and a Gilian pump (model number PN800518) fitted with a constant low-flow module, supplied by Quantitech, Milton Keynes. The pump was to be used to draw the landfill gas through the adsorbent trap during the preconcentration step and the pressurised nitrogen supply to elute the analytes during thermal desorption and analysis. The adsorbent trap consisted of a 1/4" stainless steel U-tube, approximately 2cm in length, packed with Tenax TA. The trap was sandwiched between two Peltier effect heat pumps, supplied by RS. Peltier effect heat pumps operate on the priciple that the passage of current through the junction of two different conductors can either heat or cool this junction depending on the direction of the current, with the rate of heat adsorption or generation being proportional to the magnitude of the current and also the temperature of the junction.[15] As a result, they provide a simple, compact means of both cooling the adsorbent trap during sampling and rapidly heating it during desorption and analysis. The latter factors also governed the choice of adsorbent. The fairly weak retention characteristics of Tenax TA mean that thermal desorption of all the trace VOC's can only be achieved at relatively low temperatures (Chapter 3). In addition, as the analytes are only weakly retained, the desorption volume is relatively small thus increasing overall system sensitivity. An additional benefit of using Tenax TA is the fact that it will effectively eliminate interference from methane as it is not retained by Tenax TA at the temperatures required to adsorb the trace VOC's in landfill gas.

The only modification to the original design was the inclusion of a membrane separator to exclude interference from water vapour. The separator, which was supplied by Bruel and Kjaer, was to be used to remove water vapour as the landfill gas was sampled, thus preventing condensation within the adsorbent trap. No information was available from Bruel and Kjaer on the performance of the separator and in particular it's effect on trace gas composition. As a result, the system should be fully evaluated within a controlled environment prior to undertaking field trials.

6.6.2 Design and Construction of the FTPAS-Preconcentration Device Interface

The design of the interface between the preconcentration device and the FTPAS was based upon three considerations. Firstly, as elevated pressures are potentially damaging to the FTPAS microphones, it must be capable of reducing the higher pressures required to desorb the analytes from the adsorbent trap to near ambient pressure. Secondly, in order to maximise sensitivity gains, it's internal volume should be kept to a minimum. Thirdly, as the system is portable, it should be robust and compact. A schematic diagram of the final design is shown in Figure 6.10.

Figure 6.10 Schematic Diagram of the FTPAS-Preconcentration Device Interface.



As the interface is based upon a sample loop, it can be considered to be analogous to a conventional liquid chromatographic injector, with the single multi-port valve used in the latter system being replaced by four three-way selonoid valves (Part Number: LYFA1219010H) supplied by LEE Products Ltd, Gerrards Cross. LEE valves were selected because they are chemically inert and have a low internal volume. During sampling the interface and FTPAS are isolated from the preconcentration device using valve 1, which is positioned to vent the exhaust gas from the adsorbent trap to atmosphere. Following preconcentration of the VOC's, the adsorbent trap is then isolated by closing valve 1. In order to minimise the desorption volume, the trap is then preheated and the analytes flushed off the Tenax TA using pressurised nitrogen. Solenoid valves 1 and 2 are then instantaneously switched to allow the analytes to enter the sample loop. The pressure within the sample loop is reduced to atmospheric by simultaneously venting the purge gas within the sample loop through valve 3. After a predefined period of time, valves 1, 2 and 3 are switched to isolate the sample loop and FTPAS. The internal pump in the FTPAS can then be used to recirculate the gases through the interface until a stable reading is obtained from the analysis of the gases. Following sample analysis, the FTPAS pump is then used to draw a supply of clean nitrogen through valve 4, with the analysed gases being flushed out of the sample loop and measurement cell and vented to atmosphere through valve 3. The initial aim was to use a breathing apparatus style supply-demand valve coupled to a pressurised nitrogen cylinder to control the flow of nitrogen to the FTPAS. However, due to their prohibitive cost, a 55 litre cali-5 bond gas sampling bag filled to atmospheric pressure was used as a nitrogen reservoir.

Clearly, as it was not feasible to test the system, there is still a large amount of development/evaluation to be done. This includes optimising the sample loop size, optimising the desorption volume and flow required to elute all of the trace VOC's from the adsorbent tube and identifying the FTPAS sampling time required to produce a homogeneous gas mixture within the sample loop and measurement chamber prior to analysis. In addition, as the FTPAS can be operated by a PC through an RS-232 interface, a suitable software package needs to be written to remotely control both the interface solenoid valves and the FTPAS.

6.7 Conclusions

Due to a fire within the Department of Chemistry and Physics, the original objective of producing a fully operational remote landfill gas monitor was not achieved. As a result it is difficult to predict the performance of the system as developed. The results from the preliminary investigations, however, have highlighted a number of inefficiencies in the proposed design, the most significant being the lack of specificity of the technique. For the gas monitor to be of any practical use, it must be capable of accurately determining the total levels of chlorinated and aromatic compounds in landfill gas. Initial studies suggest that this may not be possible as the main aromatic and chlorinated alkane group frequencies overlap. Further development work is required to fully assess the magnitude of this problem.

6.8 References

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Chapter 7

Conclusions and Suggestions for Future Work

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The primary aim of the research described in this thesis was to develop, optimise and evaluate a method for the analysis of all the trace volatile organic compounds (VOC's) in landfill gas using automated thermal desorption-gas chromatography-detector. The first stage of this work was to identify a suitable adsorbent(s) for the preconcentration of the VOC's prior to analysis. A review of published properties indicated that no single adsorbent could be used to analyse all of the VOC's identified in landfill gas because of their differing volatilities. As a consequence, a multiple-adsorbent sampling tube was developed. It was prepared by filling 6.4mm I.D. x 89mm stainless-steel tubes with approximately 100mg of each of the following adsorbents packed in series; Tenax TA (80/100 mesh) / Chromosorb 102 (80/100 mesh) / Carbosieve SIII (60/80 mesh). In order to exploit their differing retention characteristics, the adsorbents were arranged in order of increasing adsorptive strength. The two "primary" adsorbents, Tenax TA and Chromosorb 102, essentially act as filters, removing the less volatile trace components which would otherwise be irreversibly adsorbed by the Carbosieve SIII. Carbosieve SIII was required to trap the highly volatile components such as the chlorofluoro compounds (CFC's). The main advantages of this approach are that it is a highly efficient, flexible and robust method of sampling a wide range of trace VOC's. The latter point is significant because the developed method will be used to sample a variety of landfill sites, each having different waste inputs and, as a result, differing landfill gas compositions. In addition, existing methodology involves the use of a dual-tube system, with the second sample tube being cooled to -80°C using solid carbon dioxide during sampling and transit to the laboratory. The multi-layer approach described in this thesis eliminates the need for sub-ambient cooling and thus greatly simplifies the sampling process. Furthermore, as only a single sample tube is analysed, analysis times are greatly reduced.

The retention characteristics of five adsorbents, Chromosorb 102 and 106, Tenax TA, Porapak Q and HayeSep Q, were assessed by examining the breakthrough volume data derived from discrete injection of individual components and the continuous injection of a sample of landfill gas. The information acquired was then used to assess the adsorbents suitability for use as a primary adsorbent in conjunction with Carbosieve SIII for the preconcentration of all the trace volatile organic compounds (VOC's) in landfill gas. Both studies indicated that the adsorptive strength (BTV) increased in the order; Tenax TA << Chromosorb 102 < Porapak Q < HayeSep Q < Chromosorb 106. The retention characteristics of the latter four adsorbents were all found to be similar. The final choice of adsorbents for use in the mutiple-adsorbent tube was therefore somewhat subjective. The criteria for the selection of the primary adsorbent(s) were their desorption efficiencies for the less volatile trace compounds and their thermal stability. Desorption efficiency was assessed by carrying out multiple analyses of a landfill gas sample, and thermal stability, by analysing a batch of clean, freshly conditioned adsorbent. Of the adsorbents studied, Tenax TA and Chromosorb 102 were confirmed to be the most appropriate. Chromosorb 106 was discounted because the desorption efficiencies of undecane, dodecane and certain substituted aromatic compounds were found to be unacceptably low (less than 75%). HayeSep Q and Porapak Q were discounted for two reasons. Firstly, both exhibited relatively low thermal stability which led to artifacts in their blank chromatograms. The artifacts arise from partial degradation of the polymer matrix at elevated temperatures and thus cannot be completely eliminated. Secondly, given that only 500ml of landfill gas is required for VOC's analysis, Chromosorb 102 was chosen in preference to Porapak Q and HayeSep Q because of its lower breakthrough volumes and hence desorption volumes of the less volatile substituted aromatic compounds and alkanes. As an additional safeguard, Tenax TA was selected to trap the least volatile of the trace VOC's, such as the larger substituted aromatic compounds.

The optimum analytical conditions were found to be as follows; for the Perkin-Elmer ATD50, an overall split ratio of 200:1 was selected together with a cold trap high and low of 300°C and -30°C respectively. The desorption temperature and time selected were 250°C and 15 minutes. Following desorption, the GC conditions were as follows; the column temperature was maintained at 35°C for five minutes and then programmed to ramp at 5 °C/minute to 180 °C, which was then maintained for 15 minutes. The capillary column selected was a non-polar 60m Restek RTX-1®. Two methods of detection were assessed, flame ionisation and mass selective. The latter was chosen in preference to flame ionisation detection because of it's lack of specificity, and in particular, the poor response of the FID to CFC's. The accuracy and precision of the calibration procedure, which involved the direct injection of known amounts of a range of compounds directly onto an adsorbent tube, was found to be comparable to the Hewlett-Packard autosampler. Quantitative accuracy, which was assessed by analysing a certified gas standard of dichloromethane, was found to be less than 1%.

The performance of the Gilian® Personal Air samplers was found to be excellent, with the contribution of the pump to the overall error in the sampling process being predicted to be less than 1%. Once adsorbed, the analytes on both sample and calibration tubes were found to be stable for in excess of 14 days. By contrast, the storage of landfill gas in two commercially available gas sample bags was found to significantly effect the measured landfill gas composition, with the concentration of some of the analytes being reduced by 100%. It was thought that this was due to adsorption of these compounds onto the gas sample bag surfaces. As a consequence, it is recommended that all landfill gas samples should be stored on tightly capped adsorbent tubes in an air-tight container.

As a result of continuous improvements in analytical instrumentation, a number of modifications could be made to the method described above. The Hewlett-Packard mass selective detector used for the work described in this thesis is now obsolete, with it's replacement offering higher scan rates and increased sensitivity. For certain compounds, the increase in sensitivity is as much as two orders of magnitude. This allows smaller landfill gas volumes to be sampled and as a consequence, reduces sampling time. In addition, improvements in computer processing power has allowed the development of a much more sophisticated and versatile data handling system. One of the main problems encountered during the duration of this work was accurately assigning baselines to partially resolved peaks. The Hewlett-Packard software upgrade allows the total ion chromatograms to be reconstructed using selected ion/ions. This allows the analyst to select ions which are characteristic of the target analyte and not present in the co-eluting compound, effectively eliminating resolution problems.

Field trials of the developed method were conducted at seven UK landfill sites. Over 140 compounds were detected, of which more than 90 were common to all seven sites. The groups of compounds and concentrations observed were alkanes (302-1543mgm^{-3}), aromatic compounds (94-1906mgm^{-3}), cycloalkanes (80-487mgm^{-3}), terpenes (35-652mgm^{-3}), alcohols and ketones (2-

2096mgm^{-3}) and halogenated compounds (327-1239mgm^{-3}). The results from a long-term monitoring programme at one of the sites indicated that if the site was operating under normal conditions, with both landfill gas extraction and production rates being in a state of equilibrium, a single analysis dataset can provide an accurate estimate of the typical levels of VOC's. Ambient conditions such as temperature and pressure were found to have a minimal effect on the levels of VOC's. The observed variations in landfill gas composition were largely attributed to differences in the waste composition and decomposition processes at each of the sites. Three sites were found to have total chlorine concentrations , derived from the organochlorine compounds in the gas, of above 250mgm^{-3}. Chlorine contents of this level were considered to be potentially damaging to gas fuelled engines used for electricity generation. Chloroethene (<0.1-87mgm^{-3}) was identified as being the most abundant toxic component. Chloroethene levels in the landfill gases sampled from two of the sites studied were found to be in excess of the UK maximum exposure limit by a factor of five and three. In terms of global air quality, the chlorofluorocarbons (CFC's) are perhaps the most important group of compounds identified. The potential emission flux of CFC's from four of the sites visited was estimated to be of the order 10^3 kg/year. The true value was considered to be somewhat smaller due to the thermal destruction of VOC's in flare stacks and landfill gas fuelled engines. The potential environmental impact of landfill gas release does, however, highlight the importance of landfill gas control measures being an integral part of waste management strategy for all industrialised countries in the world.

Although the results from the field studies highlighted a number of important issues, it is clear that in order to accurately assess the environmental implications of landfill gas emissions, a much larger database of information is required. This could be achieved by implementing a number of studies which should include; a study of a wider cross-section of landfill sites and gases, an assessment of the flux of VOC's through landfill caps and the quality of ambient air adjacent to operational landfill sites. In addition, very little is known about the thermal destruction efficiency of both flare stacks and landfill gas fuelled engines, particularly at the high temperatures required to destroy CFC's and HCFC's. Given that a large proportion of the gas generated at the sites studied was either burnt in a flare stack or in a landfill gas fuelled engine, it is clear that analysis of the exhaust gases may provide the most accurate assessment of total landfill gas emissions.

From the outset, one of the main aims of the work described in this thesis was to develop a remote landfill gas monitor. Due to a fire within the University's Chemistry Department, the programme of research outlined to address this only reached the preliminary design and development stage. The system consisted of a sample introduction device, based upon adsorbent preconcentration and thermal desorption, and Fourier Transform Photoacoustic detection (FTPAS). The development of the sample introduction device was largely driven by inefficiencies in the FTPAS. These include a lack of specificity and sensitivity, particularly for the chlorinated and aromatic compounds, and perhaps more importantly, the need to eliminate interference from the bulk matrix gases, water, carbon dioxide and methane, which all absorb strongly in the infrared region. The preconcentation device consists of four main components; a membrane separator to remove water vapour from the landfill gas as it is sampled, an adsorbent trap, a pressurised nitrogen supply and a Gilian pump fitted with a constant low-flow module. The pump was to be used to draw the landfill gas through the adsorbent trap during the preconcentration step and the pressurised nitrogen supply to elute the analytes during thermal desorption and analysis. The adsorbent trap consisted of a 1/4" stainless steel U-tube, approximately 2cm in length, packed with Tenax TA. The trap was sandwiched between two Peltier effect heat pumps, which were used to cool the adsorbent trap during sample preconcentration and heat it during sample desorption. The fairly weak retention characteristics of Tenax TA mean that thermal desorption of all the trace VOC's can be achieved at relatively low temperatures. In addition, as the analytes are only weakly retained, the desorption volume is relatively small thus increasing overall system sensitivity. An additional benefit of using Tenax TA is the fact that it will effectively eliminate interference from methane as it is not retained by Tenax TA at the temperatures required to adsorb the trace VOC's in landfill gas.

As a fully working system was not constructed and as a consequence field tested, there is still a large amount of development work to be done for both the preconcentration and detection/quantitation processes. In my opinion, however, the range of problems encountered during the initial design and development stages suggest that the FTPAS is probably not suitable for this application and as a result, alternative detection systems should be considered. For example, Chrompack's Micro GC, which is fitted with a thermal conductivity detector, weighs only 10kg and is the size of a small briefcase, is capable of carrying out complex separations in a matter of seconds. In addition, it can also be configured to be dual channel, with the second channel being used for confirmation of the target analytes or, by adapting column stationary phases and film thickness, as a means of simultaneously determining a wider range of compounds to those on the first channel. The main disadvantage of this type of instrument, however, is the lack of resolution. In general, portable GC's have a limited oven temperature range and size. As a result, column choice is restricted to short (usually less than 10m), thin film capillary or packed columns. Consequently, for universal detectors, such as FID's and TCD's, quantitation of individual components can be problematic due to co-elution of non-target analytes. The latest development in on-site monitoring instrumentation, Inficon's HAPSITE, eliminates this problem. Weighing only 16kg and having dimensions of 46cm x 43cm x 18cm, the Inficon system is the first truly portable mass spectrometer. With a mass scan range of 1-300AMU, a scan rate of 1000AMU/second and a 70eV ionisation source, the HAPSITE GC-MS offers all the advantages of a conventional benchtop GC-MS. These include unequivocal structural information, a library matching facility and target analyte analysis using selected ion monitoring. The latter function is of particular relevance to landfill gas analysis as it would allow individual classes of compounds, such as the CFC's, to be monitored without interference from other trace species with similar retention times. Although the purchase cost is somewhat prohibitive (~ £65k), any future study of on-site monitoring techniques for the analysis of trace VOC's in landfill gas should include a full appraisal of this instrument.

APPENDIX 1

OPTIMISED CONDITIONS FOR THE ANALYSIS OF THE TRACE VOLATILE ORGANIC COMPOUNDS IN LANDFILL GAS

Perkin-Elmer ATD50

Mode: 2

Oven Temperature: 250°C

Desorb Time: 15 minutes

Transfer Line Temperature: 150 °C

Cold-Trap Low: -30 °C

Cold-Trap High: 300 °C

Trap Adsorbent: Tenax TA (60/80 mesh)

Outlet Split: 19ml/min

Inlet Split: 27ml/min

Hewlett-Packard 5890 GC-MSD

GC Column: RTX®-1; 60m; 1.5µm; 0.32mm ID

Oven Temperature Program: 35°C for 5mins, ramp at 5°C/min to 180 °C

Carrier Gas: Helium

Linear Velocity: 21cm sec^{-1}

Detector Temperature: 250°C

Detector Mass Range: 20-250 amu

Sampling

Pump: Gilian Personal Air Sampler fitted with a constant low-flow module

Sample Flow Rate: 50ml/min

Landfill Gas Volume Sampled: 500ml

Adsorbent Sampling Tube: 100mg each of Tenax TA (80/100 mesh), Chromosorb 102 (80/100 mesh) and Carbosieve SIII (60/80 mesh).