REFERENCE

The Study of Volatile Organic Compounds in Urban and Indoor Air

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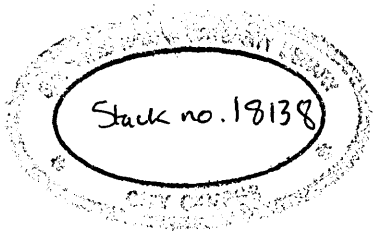
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Abstract

Chapter 1 is a review of the literature concerning the study of volatile organic compounds in the atmosphere. It examines the basic chemistry of the atmosphere and the roles that organic compounds play in it. Also investigated are the methods of sampling and analysing the volatile organic compounds in the air, paying particular attention to the role of solid phase sampling. Chapter 1 also examines the role of volatile organic compounds on air quality.

Chapter 2 describes the experimental procedures that were employed during the course of this research project.

Chapter 3 examines a multi-method approach to the study of volatile organic compounds in urban and indoor air. The methods employed were capillary electrophoresis, high performance liquid chromatography and gas chromatography. Although good results were obtained for the various methods that were investigated Chapter 3 concludes that a more unified analytical approach is needed to the study of the air.

Chapter 4 investigates the possibilities of using a unified approach to the study of VOC's. This is achieved by the development of an air sampling method that uses solid phase extraction cartridges. By investigating many aspects of air sampling mechanisms the results show that a simple yet efficient method for the sampling of VOC in air has been developed. The SPE method is a reusable, yet reliable method that by using sequential solvent desorption has been shown to exhibit some degree of selectivity. The solid phase that gave the best results was styrene-divinyl benzene however other phases were also investigated.

The use of a single gas chromatography method was also investigated for the purpose of confirmatory identification of the VOC's. Various detection systems were used including MS and AED. It was shown that by optimising the GC's it was possible to get complimentary results.

Also investigated was the possibility of compound tagging in an attempt to confirm the identity of several of the compounds found in the air.

Chapter 5 is a theoretical discussion of the ways presenting the data obtained experimentally in an easy to understand way. Instead of targeting 7 or 8 compounds as being representative of air quality it is argued that by using a technique such as Air Fingerprinting, it is possible to show data that is indicative of the whole air sample. Using

actual data it is possible to show the origin of the air sample in a simple yet effective way using air fingerprints.

Also discussed is the Individual Component Air Quality Index, this is a method of quantifying air quality. By taking into account compound toxicity, atmospheric lifetime and UV exposure, the ICAQI, it is argued, is a technique that presents a more accurate picture of air quality.

Chapter 6 concludes the thesis by drawing together the themes and issues that were raised.

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Preface

Volatile organic compounds and air quality have long been linked yet, for all the work it seems we have achieved little in way of understanding. Examining the vital, yet often unacknowledged, roles that these compounds play in the life of the atmosphere it is found that the composition of the atmosphere is a dynamic mixture, in a constant state of motion.

It is also found that there are many ways of measuring the compounds in the air, and that each method has it's own followers. It was found, though, that for all the work on new methods, little was achieved in understanding of the air. Yet after all that, it is often found that the people who require them does not understand the results we produce.

The work contained within this thesis, then, is the result of a journey: a journey through science. To study volatile organic compounds in urban and indoor air requires the knowledge and use of many aspects of science: From environmental chemistry to physics to analytical science to medicine. It was a journey to understand what is happening in the air, to determine how to measure it efficiently and simply and then to present it in a way for all to understand. It is with these three aims in mind that we started our work:

The Study of Volatile Organic Compounds in Urban and Indoor Air.

Acknowledgement

I would like to acknowledge the following: my main supervisor Professor Mike Cooke who allowed me the freedom to develop my ideas and my thoughts into reality, although crazy at times some of them worked! To my second supervisor Dr Malcolm Clench, who though remaining in the background, was a useful source of information when asked. I would also like to acknowledge the assistance of Dr David Crowther, for help and encouragement, especially in the latter stages of the project. To Dr Pete Drew for the friendly advice, especially on the environmental stuff. And to the technical expertise of Mrs Joan Hague, overworked and underpaid, who through thick and thin would always pull the instruments through.

And finally to John Andrews, Alan Jeffs and the leaders of Rotherham New Life Christian Centre who have allowed me to use church equipment in the preparation of this thesis.

Thank you.

Author's Declaration

The results and opinions described within this thesis are those of the author, other material used in the discussion has been attributed to the works author in the reference section at the end of this document.

Chapter 1

Introduction

1.1 The Atmosphere and the Earth

1.1.1 The Biosphere

The Earth is unique in our solar system, in having an oxidising atmosphere. With this type of atmosphere most compounds are oxidised, and it is expected that the most predominant oxidised species should be NO*x*, SO*x* and CO*x*. However dioxygen and dinitrogen are the predominant atmospheric molecular species, with a geochemical balance being maintained at approximately 78% dinitrogen and 20% dioxygen.[1] (Figure 1-1)

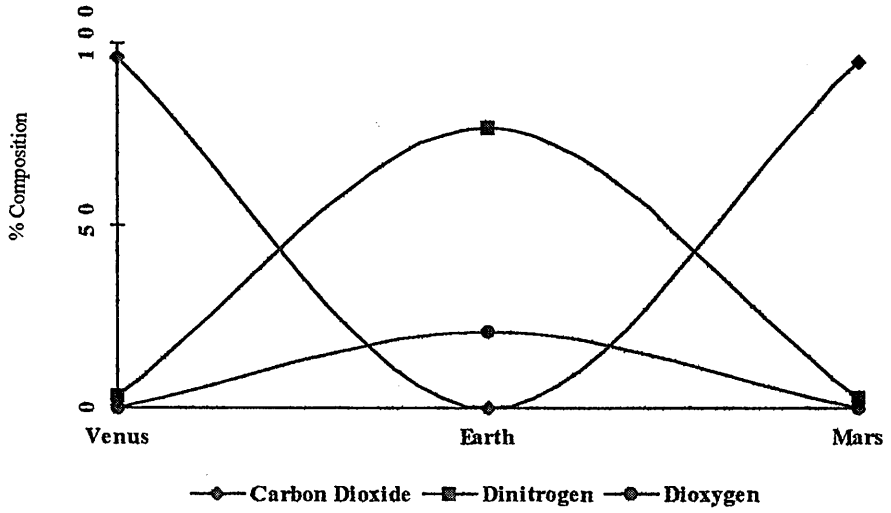


Figure 1-1 - A Chart Showing the Comparison of Planetary Atmospheres

Unlike Venus and Mars, which have oxidised atmospheres, Earth is special, and special for one reason. It has life. Without life the atmospheric gases would tend towards equilibrium, with the atmospheric dinitrogen being oxidised, and the dioxygen reduced.[2] The maintenance of this disequilibrium is through the actions of living organisms. The majority of the 10^{18}kg of dioxygen present in the atmosphere originates from photosynthesis in plants, whereas the dinitrogen is present from the actions of nitrogen fixing bacteria.[3]

The atmosphere of Earth at present contains concentrations of O_2 and CH_4, that resemble a combustible mixture, whereas Venus and Mars, possess atmospheres that resemble the products of combustion.[4]

Life allows the elements of carbon[5], nitrogen[3] and oxygen[6] to be cycled through the many different sinks and sources that comprise the biosphere.[7] The cycling of these elements

is an important concept in understanding how the planet, and specifically the atmosphere, functions.

Lovelock and Margulis [2] suggested in their Gaia hypothesis that the whole biosphere can be treated as a living organism. By examining the Earth in this way, it can be assumed that any reduced organic compounds that are present in the atmosphere will be oxidised back to carbon dioxide as part of the biospheric cycles, in a way that is similar to the traditional definition of life. Simultaneously, the carbon dioxide is being reduced to produce more complex organic compounds, and the cycle continues. As a result it can be seen that Earth's chemistry and composition is more complicated and delicately balanced than is often assumed. The Gaia theory assumes that all life is interdependent. This treatment, however, does not consider the effects the cycles have on humans or, more importantly, the effects we humans have on the biospheric cycles.

1.1.2 Biospheric Cycles

Oxygen, nitrogen, and carbon are the key elements that are cycled through the biosphere. The carbon cycle[5] is of greatest interest when considering the role of organic compounds in the Earth's atmosphere. At present the energetics of the biosphere depend on the reduction of carbon dioxide to organic compounds and dioxygen through the action of photosynthesis. This process takes the general form:

$$n\mathrm{CO_2} + 2n\mathrm{H_2A} + \mathit{ENERGY} \rightarrow (\mathrm{CH_2O})n + n\mathrm{A_2} + n\mathrm{H_2O} \quad \textbf{(1.1)}$$

Where A can be either oxygen(O) orin the case of sulphur photosynthesising bacteria(S). Geochemically, photosynthesis produces the oxidised part of the biosphere, specifically the atmosphere and oceans, with the more reduced part being in the bodies of organisms and their decomposition products.

The key point to note is that in the biosphere there is a continual oxidation of the reduced part, through respiration, decomposition or by the action of atmospheric oxygen to produce carbon dioxide and energy.

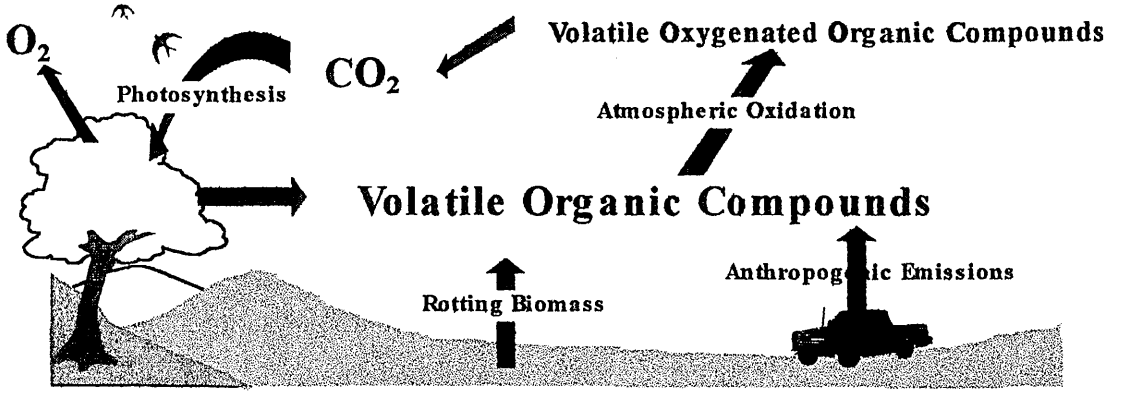


Figure 1-2 - The Carbon Cycle

Since the industrial revolution this balance has been altered by an excessive increase in emitted volatile organic compounds and atmospheric carbon dioxide. The result of the increase in atmospheric carbon dioxide and the subsequent increase in global temperature is known as the greenhouse effect and is the topic of both political and scientific debate.

Besides the issue of climate change, the increase in anthropogenic emissions has brought the issue of air quality to the attention of the public and the scientific communities.

Understanding air quality, the carbon cycle and climate changes are all dependent on knowledge of how the atmosphere functions at a molecular level. The chemistry of the atmosphere is not dissimilar to any other chemistry, but due to the abundance of radical reactions, tends to be held at arms length by many scientists. In understanding the sources and sinks of compounds in the atmosphere we, as scientists, can be more specific in what we investigate.

1.1.3 Atmospheric Chemistry

The atmospheric chemistry of organic compounds is a wide and complicated field, embracing both organic and physical chemistries. As already stated, the atmosphere of the earth is oxidising, so the organic compounds take a route through the atmosphere from reduced to oxidised form.

A simple example of the oxidation of an organic compound is shown below. (Figure 1-3) Although the initial step is energetically unfavourable in the atmosphere, such a scheme illustrates the wide variety of organic compounds than can, potentially, be formed.

$$\underset{-4}{CH_4} \longrightarrow \underset{-1}{CH_3OH} \longrightarrow \underset{0}{CH_2O} \longrightarrow \underset{+3}{HCOOH}$$

Figure 1-3 - Oxidation States of Carbon

There is a wide body of research into the atmospheric oxidation of organic compounds. These studies range from kinetic data[8] to detailed mechanisms and atmospheric routes.[9] [10]

The chemistry of the atmosphere is a combination of photochemistry, free radical chemistry and covalent chemistry. Of the three it is free radical and photochemistry that dominate the majority of the free radical reactions or chemistry.

1.1.3.1 Photochemistry

The energy required for the photochemistry that takes place in the atmosphere originates with the Sun. The Sun emits a wide spectrum of electromagnetic energy, but only the visible and ultra-violet regions are of any real importance when considering photochemistry.

The basic principle that drives photochemical reactions is the adsorption, by a molecule, of a photon of energy that leads to the electronic excitation of that molecule. This may be expressed as: -

$$AB + h\nu \rightarrow AB^* \quad \textbf{(1.2)}$$

Where AB is an atmospheric molecule, $h\nu$ is a photon of energy and AB^* represents the molecule in an excited electronic state. The excited molecule, AB^*, can then become de-excited in a variety of ways, the outcome of which determines the overall type of reaction. The main de-excitation pathways are fragmentation, luminescence, energy transfer, quenching and reaction.

Fragmentation of the excited molecule can follow two paths, (i) dissociation and (ii) ionisation. Dissociation occurs when the energy provided by the photon is, simply, too great for the molecule. The molecule becomes unstable and splits in two.

$$AB + h\nu \rightarrow AB^{*} \rightarrow A + B^{(*)} \quad \textbf{(1.3)}$$

Any excess energy remaining from the bond breaking might be transferred to one of the fragments, leaving it in an excited state.

For ionisation to occur the excited molecule must lose an electron, thus becoming de-excited. This type of reaction is most prevalent in the upper atmosphere, and is rarely seen in the chemistry of the troposphere.

Luminescence is when the photon is re-emitted from the molecule. This is represented in the form

$$AB + h\nu \rightarrow AB^{*} \rightarrow AB + h\nu \quad \textbf{(1.4)}$$

In the atmospheric photochemistry of organic compounds, there are two reactions that are of primary importance. These are the photolysis of ozone and the photolysis of formaldehyde.

In the photolysis of formaldehyde, the molecule dissociates to produce a hydrogen radical, $H^{\cdot}$ and the formyl radical, $HCO^{\cdot}$.**(1.5)** The formyl radical, independent of temperature, reacts rapidly with atmospheric dioxygen to produce carbon monoxide and a hydroperoxy radical, $HO_2^{\cdot}$.**(1.6)**[9] Another hydroperoxy radical is formed with the reaction of atmospheric dioxygen and the hydrogen radical.**(1.7)**

The reaction scheme is completed with the formation of the hydroxyl radical, $OH^{\cdot}$, as the hydroperoxy radicals react with atmospheric nitric oxide, NO. **(1.8)**

$$CH_2O + h\nu \longrightarrow {}^{\cdot}HCO + {}^{\cdot}H \quad \textbf{(1.5)}$$

$${}^{\cdot}HCO + O_2 \longrightarrow {}^{\cdot}HO_2 + CO \quad \textbf{(1.6)}$$

$${}^{\cdot}H + O_2\,(+M) \longrightarrow {}^{\cdot}HO_2\,(+M) \quad \textbf{(1.7)}$$

$${}^{\cdot}HO_2 + NO \longrightarrow NO_2 + {}^{\cdot}HO \quad \textbf{(1.8)}$$

The other major photochemical reaction to be discussed is the photolysis of ozone. The action of UV light of wavelengths between 240 and 330 nm on ozone breaks the ring structure to produce dioxygen and an energetically excited oxygen atom. **(1.9)**

$$O_3 + h\nu \longrightarrow O_2 + O^{\ddagger} \dashrightarrow O_2 + O \quad (1.9)$$

$$O^{\ddagger} + H_2O \longrightarrow 2HO^{\bullet} \quad (1.10)$$

Where $O^{\ddagger}$ represents an excited oxygen atom. The energetic state of the oxygen atom formed has been examined at a quantum level[11], from which the important point to note is that $O^{\ddagger}$atom is more reactive than the ground state O atom and thus reacts with atmospheric water to produce two hydroxyl radicals. **(1.10)**

1.1.3.2 The Hydroxyl Radical

As shown by the two examples above the hydroxyl radical is an important atmospheric species. It can be formed by a large number of different photochemical reactions, with the two most important already being discussed. The photolysis of formaldehyde is the dominant source of hydroxyl radicals in polluted air whilst the photolysis of ozone is dominant in clean air.[12]

The hydroxyl radical undergoes reactions with most atmospheric species, leading to secondary pollutants being formed which, as will be discussed, can often be more physiologically harmful and more environmentally harmful than the primary pollutants.

1.1.3.3 Reactions of Aromatics

Benzene, toluene and the xylenes (BTX) are considered to be priority primary pollutants and as such are monitored at their emission sources. Reactions, primarily with the $HO^{\bullet}$ radical, NO*x* and ozone, cause the photooxidation of BTX to secondary pollutants. According to the literature toluene is the most abundant non-methane hydrocarbon in the urban atmosphere.[13] Bearing this in mind the degradation products and chemistries are of vital importance in understanding the atmospheric behaviour of aromatic compounds.

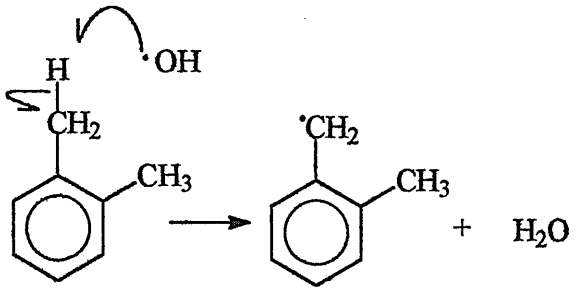
Research by Dumdei and O'Brien[13] has shown that toluene, under simulated atmospheric conditions can degrade to at least 27 identifiable compounds. Amongst the by-products of the degradation, phenol, cresol, and formaldehyde phenol, cresol and formaldehyde which are all considered as priority pollutants. The reaction mechanisms involved are not fully understood for all the compounds found.

The hydroxyl radical can react in two possible ways: abstraction or addition. The compounds that are formed are dependent on the pathway followed. Gery *et al.*[14], studying

the hydroxyl radical radical reactions with *ortho-* and *meta-* xylenes have found that both addition and abstraction are taking place simultaneously.

1.1.3.3.1 Abstraction

In abstraction the hydroxyl radical attacks a methyl hydrogen yielding a methylbenzyl radical and water. **(1.11)**



(1.11)

Methylbenzyl Radical

Figure 1-4 - Radical Abstraction

Under atmospheric conditions, oxygen will react rapidly with the methylbenzyl radical to form the appropriate methylbenzylperoxy radical. Subsequent reactions yield tolualdehydes, methylbenzyl nitrates and nitrites. (Figure 1-4.) The rapid photolysis of methylbenzyl nitrites means that their atmospheric chemistry can be considered unimportant. Further reactions of the tolualdehydes are thought to lead to nitrated methyl phenols and benzoquinones.

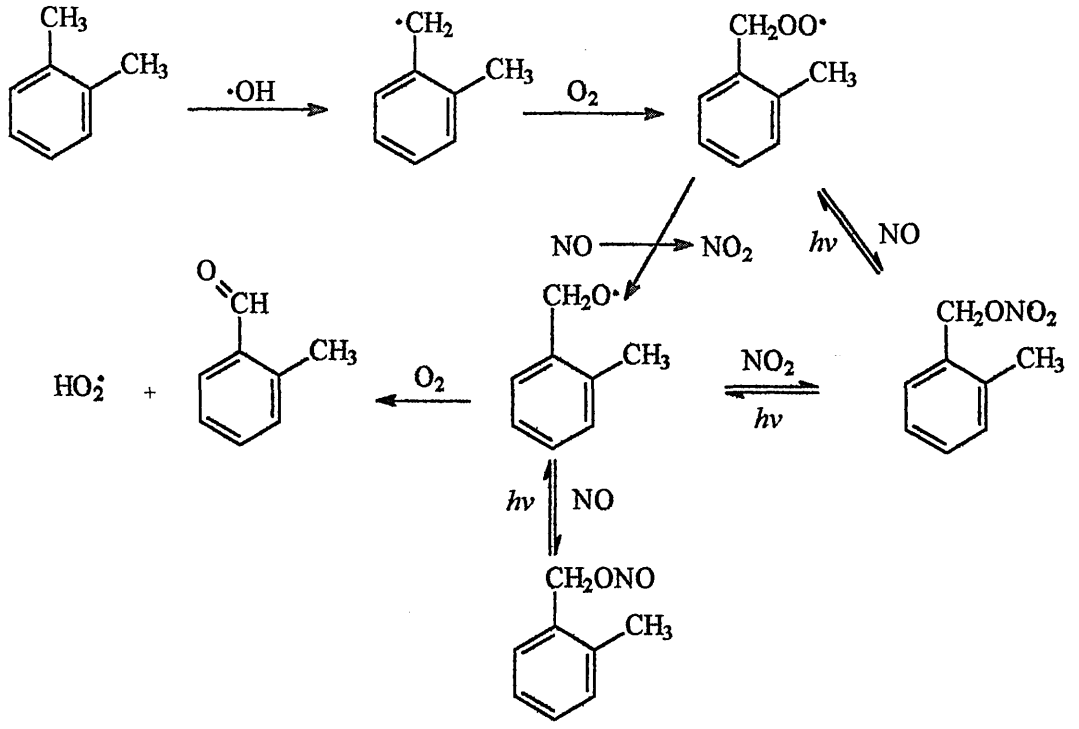


Figure 1-5 - A Diagram Showing the Photochemical Oxidation of Xylene

Leone and Seinfeld[15] have shown that analogous reaction mechanisms occur for the atmospheric decomposition of toluene following the abstraction pathway.

1.1.3.3.2 Addition

The free radical addition to the aromatic system can occur at a variety of sites around the ring leading to two main mechanisms, phenol formation and ring cleavage.

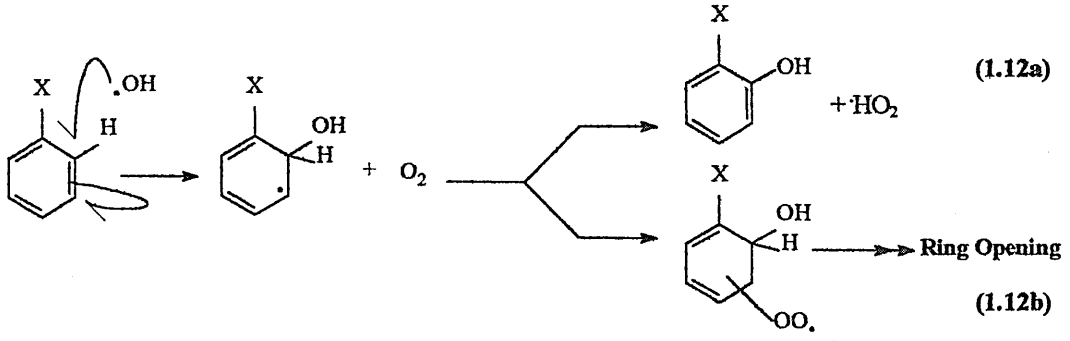


Figure 1-6 - A Diagram Showing the Simplified Hydroxyl Addition Mechanisms for Toluene

After addition of HO·, the displacement of a hydrogen, through reaction with atmospheric dioxygen, can lead to the formation of the appropriate phenol, either methyl or

dimethyl depending on the original aromatic compound.**(1.12a)** It is also suggested that both mono- and di-nitrophenols are formed. The ring cleavage yields smaller molecules, such as carbonyls, dicarbonyls and alkenes.**(1.12b)** [9] Figure 1-7 shows a full mechanism for the oxidation of toluene through the action of free radicals.

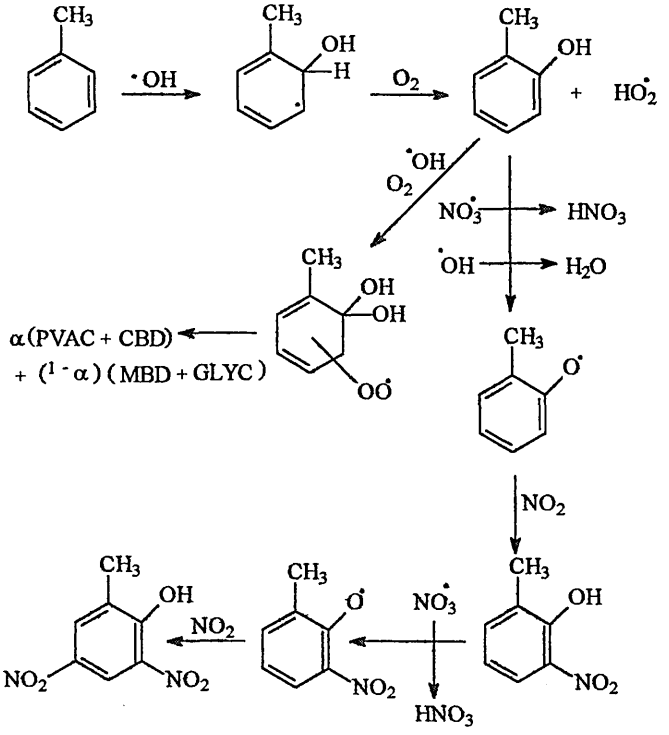
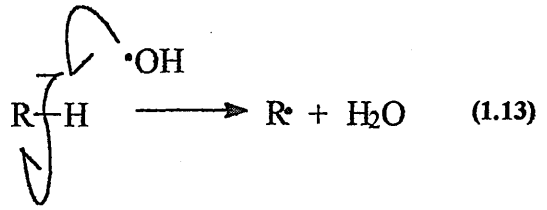


Figure 1-7 - A Diagram Showing the Photochemical Oxidation of Toluene

1.1.3.4 Reactions of Aliphatics

1.1.3.4.1 Alkanes

It has been established that the only significant gas phase sink for alkanes in the atmosphere is reaction with hydroxyl radicals.[16] In this process the hydroxyl radical abstracts a proton from a C-H bond. **(1.13)** The alkyl radical that is formed then rapidly reacts with atmospheric dioxygen to form an alkyl peroxy radical.**(1.14)**



$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet} \qquad (1.14)$$

An important reaction of the alkyl peroxy radical is with NO_x. The alkyl peroxy radical can react with both NO and NO_2. **(1.15-1.17)**

$$^{\bullet}RO_2 + NO_2 \rightleftharpoons ROONO_2 \qquad (1.15)$$

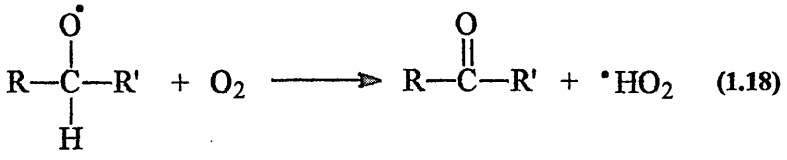
$$^{\bullet}RO_2 + NO \longrightarrow {}^{\bullet}RO + NO_2 \qquad (1.16)$$

$$^{\bullet}RO_2 + NO \longrightarrow RONO_2 \qquad (1.17)$$

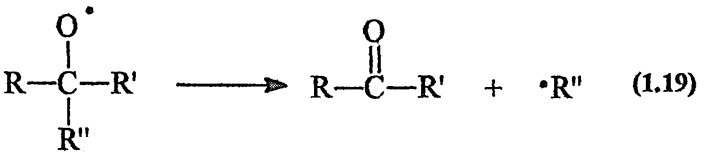
As the alkyl peroxynitrates formed through the reaction with NO_2 **(1.15)**, thermally decompose[17] to their parent compounds, it is only the reactions with nitric oxide **(1.16 & 1.17)** that are a significant net sink for alkyl peroxy radicals.

Reaction **(1.17)** is a radical terminating reaction that also removes atmospheric NO. Reaction **(1.16)**, on the other hand, is radical and NO_2 propagating. The route through which a particular alkyl peroxy radical reacts with nitric oxide is dependant on the size of the alkyl chain and the kinetics of the reactions. In general, smaller alkanes tend toward reaction **(1.16)**. Consequently, the reactions of the alkoxy radicals formed in reaction **(1.16)** are of major importance to the atmospheric chemistry of alkanes.

Alkoxy radicals can react through three different modes. The first is through the abstraction of an α-hydrogen by atmospheric dioxygen to form the hydroperoxy radical and a carbonyl compound. **(1.18)**

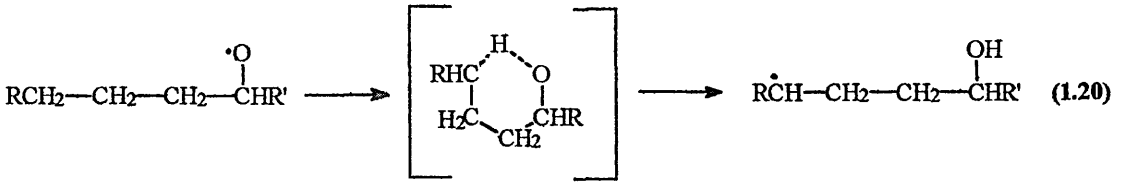


Except for ($CH_3O^{\bullet}$) most alkoxy radicals can undergo fragmentation through β-scission to form smaller alkyl radicals and carbonyl compounds. **(1.19)** The alkyl radical formed in the fragmentation reacts in the same way as the parent alkyl radical formed in the initial reaction.(Reaction **(1.13)**)



(1.19)

The final mode to be discussed is isomerisation. This occurs with longer chain alkoxy radicals by way of cyclic transition states to form hydroxy-substituted alkyl radicals, which can also add O_2 and react further. Research into the thermodynamics of such reactions suggests that the most favourable process is a 1,5-H shift through a six membered ring transition state. **(1.20)**

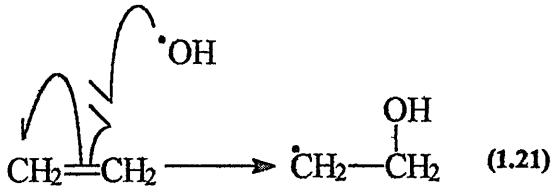


(1.20)

This process will, where possible, generally dominate over competing reactions of the alkoxy radical. This isomerisation is therefore an important process in the oxidation mechanisms of higher n-alkanes.

1.1.3.4.2 Alkenes

Reactions between alkenes and the hydroxyl radical are dominated by addition across the C=C double bond to form a β-hydroxy radical.**(1.21)** As the chain length increases H-abstraction starts to play a more significant role in the overall oxidation process.



(1.21)

The hydroxyl radical can add to either carbon across the double bond though it has been reported that for propene the terminal carbon is favoured 65% of the time[18].

The β-hydroxyalkyl radicals then rapidly react by the addition of O_2 in a similar way to that shown in reactions **(1.13-1.20)**

Subsequent reactions and decompositions can occur but these are beyond the scope of this thesis.

1.1.3.5 Reactions of Ozone

Ozone reacts directly and indirectly with a whole variety of organic compounds in the atmosphere, [10] and, as such, plays an important role in the chemistry of the atmosphere. Ozone, in the troposphere, is one product of photochemical air pollution and is considered to be something of a health risk. In the early 1970s it was recognised that, in unpolluted air, ozone contributes to the formation of the hydroxyl radical. **(Reactions (1.9-1.10))** Tropospheric ozone is formed through the following photochemical reaction sequence.

$$NO_2 + h\nu \rightarrow NO + O^{\ddagger} \qquad \textbf{(1.22)}$$

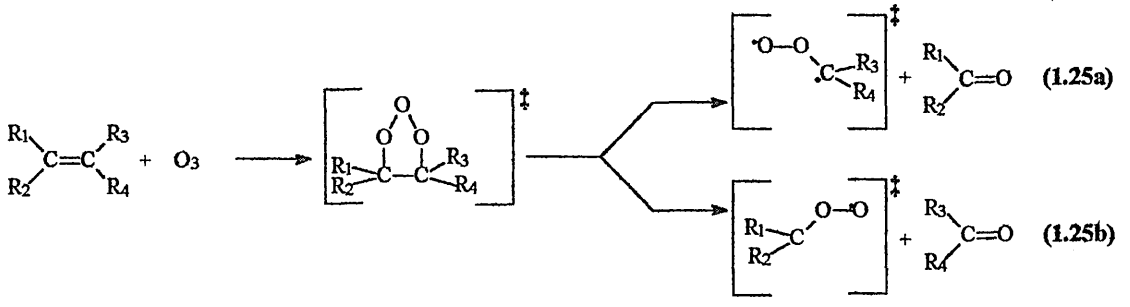
$$O^{\ddagger} + O_2 + M \rightarrow O_3 + M \qquad \textbf{(1.23)}$$

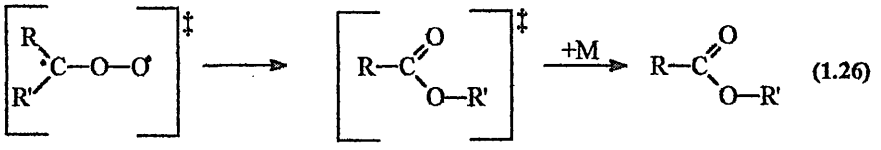
$$NO + O_3 \rightarrow NO_2 + O_2 \qquad \textbf{(1.24)}$$

As ozone is photochemically active it can also contribute to the removal of organic compounds, especially alkenes, from the atmosphere. Because of this the reaction of ozone with alkenes is considered of primary importance in atmospheric chemistry.[19]

The initial step in the reaction of ozone with alkenes is the formation of a "molozonide". This energy rich intermediate rapidly decomposes to a carbonyl and energy rich biradical, called the Criegee intermediate. **(1.25)**

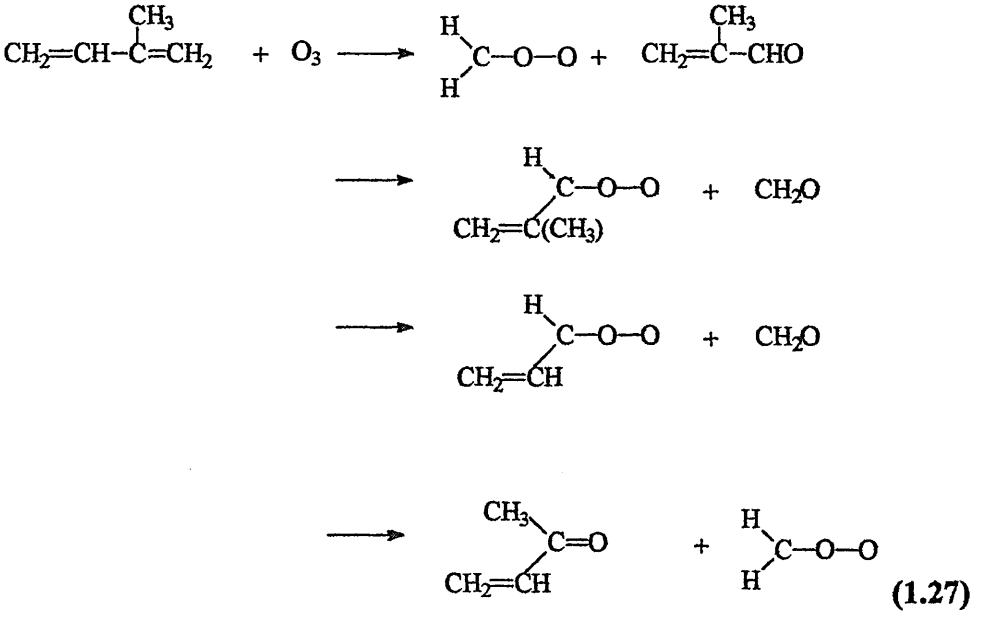
The Criegee intermediate can either be stabilised and undergo subsequent bimolecular reactions **(1.26)** or undergo unimolecular rearrangement and fragmentation.





The reaction of ozone with other alkenes will, of course, produce different products. Propene, for example, would produce formic acid, acetaldehyde, and eventually acetic acid.

Another source of organic acids will be from the reaction of natural products with ozone, through a similar mechanism to that shown below. The basic building block for terpenes is isoprene, or 2-methyl-1,3-butadiene and will, therefore, react with ozone to produce a carbonyl, methacrolein (an aldehyde), methyl vinyl ketone, and the Criegee intermediate that produces formic acid. The methacrolein can be oxidised to form an organic acid or can react with the Criegee intermediate to eventually produce methyl vinyl ketone and formaldehyde.



(1.27)

There are many possibilities for the compounds that could be formed by such reactions. The kinetics of the reaction, though, determine the type and the atmospheric lifetimes of the compounds formed in the atmosphere. [8]

1.2 The Role of Organic Compounds in the Atmosphere

Many organic compounds or, more specifically, classes of compound appear in one or more of the reaction schemes shown above. In trying to understand the role that one class of compounds, e.g. organic acids, plays in the environment we find that we have to take into consideration a whole range of other compounds, including n-alkenes, terpenes, toluene and ozone. This complex maze of organic reactions and routes is analogous to the metabolic

pathways found within living organisms, and lends weight to the arguments of Lovelock[4], for the treatment of the biosphere as a complex living organism.

It can be seen that the organic chemistry of the atmosphere is as important as that of the inorganic chemistries of nitrogen and oxygen, although these tend to be given a more prominent role in the pollution and air quality debate. The public, due to poor education in schools and the sensationalism of the popular press, tend to relate organic compounds in the environment directly to anthropogenic pollution. Generally misunderstood is that there are natural sources for organic compounds in the atmosphere, from both marine and terrestrial vegetation, and that these can also act as natural sinks for organic compounds.

Most organic compounds that are found in the atmosphere are termed *pollutants*. But one can ask the question: Is a compound that is naturally occurring a pollutant? Although, it is convenient to use phrases such as *"...biogenic pollutants..."* this is often misleading to non-scientific readers. This use of the word, pollute, may be behind public misconception on many environmental issues. How the public perceives a subject or an issue, such as air quality, will be discussed in Chapter 5.

The compounds that appear most frequently in the atmospheric cycles discussed earlier are carbonyls and carboxylic acids. These are highly oxidised forms of organic compounds and have a significant role to play in the atmospheric cycles of most other organic compounds. Hence their role in the atmosphere will now be discussed in detail.

1.2.1 Carbonyl Compounds

The sources of atmospheric carbonyl compounds are varied. In the troposphere they appear in many of the atmospheric pathways mainly as intermediates but also as end products of the photochemical oxidation of organic compounds in air. Carbonyl compounds also have many biogenic sources namely direct emission from vegetation and biomass burning.[20] Anthropogenic sources such as the incomplete combustion of fossil fuels and waste incineration also add to the atmospheric carbonyl flux.[21]

Dawson and Farmer[22], describe formaldehyde as a "*"funnel" through which much of the carbon flux passes in the course of oxidation to CO and CO_2.*" From this statement we can see that formaldehyde plays a central role in the carbon cycle.

Carbonyl compounds are photochemically active and produce radical species that are responsible for the atmospheric oxidation of hydrocarbons. Due to the complexity of the

atmospheric role of carbonyl compounds there is no one scheme which can be said to be dominant. Of all the carbonyl compounds that are found in the atmosphere it is, however, the simplest ones which are of most importance e.g. formaldehyde, acetaldehyde and acetone.

The extent of the role that is played by formaldehyde in the chemistry of the atmosphere has not been fully understood. On a technical level as analytical techniques are being improved it is becoming possible to determine formaldehyde at much lower levels than has previously been possible. Furthermore, it is now being found that formaldehyde plays an important and integral role in many different atmospheric reactions.

1.2.1.1 Sources and Sinks of Atmospheric Carbonyl Compounds

Formaldehyde is a compound that is naturally occurring within the atmosphere. Formaldehyde is, however, toxic to humans when present in high concentrations. In examining the sources and sinks of carbonyl compounds in the air I will be paying particular attention to formaldehyde.

Formaldehyde is the simplest of all the carbonyl compounds, having a relative molecular mass of just 30 amu. Regardless of the compound's simplicity its importance in atmospheric cycles cannot be overstated.

Formaldehyde has both atmospheric sinks and sources. The primary sink for atmospheric formaldehyde is through photolysis, which is one of the fundamental reactions in atmospheric chemistry. This occurs at $\lambda < 338$nm to produce two radical fragments. *Equation (1.5)* These radicals then react further. *Equations (1.6 - 1.8).*

Formaldehyde is also removed from the atmosphere through radical oxidation processes. The aqueous phase oxidation is a slow process requiring the hydroxyl radical. [23] [24] [25] **(1.28)**

$$CH_2(OH)_2 + {}^{\bullet}OH \longrightarrow {}^{\bullet}HO_2 + HCOOH \quad (1.28)$$

The gas phase oxidation of formaldehyde to produce formic acid is a more complicated scheme. **(1.29 - 1.33)**. This requires the hydroperoxy radical and atmospheric oxygen. Both of the mechanisms require free radicals to proceed. [19] [26]

$$HO_2 + HCHO \longleftrightarrow (HOOCH_2O) + OOCH_2OH \quad (1.29)$$

$$HO_2 + OOCH_2OH \longrightarrow HOCH_2OOH + O_2 \quad (1.30)$$

$$OOCH_2OH + OOCH_2OH \longrightarrow 2(OCH_2OH) + O_2 \quad (1.31)$$

$$\longrightarrow HCOOH + HOCH_2OH + O_2 \quad (1.32)$$

$$OCH_2OH + O_2 \longrightarrow HCOOH + HO_2 \quad (1.33)$$

The atmospheric sources of carbonyls in general and formaldehyde specifically are complex and varied. It has been shown that different hydrocarbon precursors produce a wide range of carbonyl compounds upon photochemical oxidation.

shows a selection of hydrocarbons and the carbonyls that they produce.[27]

Table 1-1 - Carbonyl Compounds and their Sources

1° Compound	Carbonyl Compounds Identified
Methane	Formaldehyde
Ethane	Formaldehyde, Acetaldehyde
n-Butane	Methylethylacetone, acetaldehyde
Propane	Acetone
Isobutane	Acetone
Pentane	2-Pentanone, 3-Pentanone
Ethylene	Formaldehyde, acetone
Isoprene	Methyl-2-acrolein, 2-butene-2-one, Formaldehyde
1-Pentene	Butanol, formaldehyde
Toluene	Benzaldehyde, formaldehyde
o-Xylene	Glyoxal, biacetyl, propanalone
m-Xylene	Glyoxal, propanalone, formaldehyde
p-Xylene	Glyoxal, propanalone
Methanol	Formaldehyde
Styrene	Benzaldehyde, formaldehyde

Calvert and Madronich[28] suggest that the carbonyls formed as initial products have atmospheric lifetimes of under 1 day, except acetone (12 days). Calvert and Madronich also show that the atmospheric concentration of other reagents such as NO_x and O_3 are important

in determining the composition of the carbonyls in the atmosphere. In smog chamber studies they show that, as the concentration of NO_x increases, so does the proportion of aldehydes produced.

Background or ambient levels of formaldehyde are observed in the range between 0.22-11 ppb/v($\mu g\ L^{-1}$). In polluted air the levels increase dramatically, with concentrations reported in the 10-150 ppb/v($\mu g\ L^{-1}$) range for formaldehyde. [27]

The short atmospheric lifetimes reported by Calvert and Madronich in theoretical studies were confirmed by Schulam *et al.*[29], in both urban and rural air. They observed variation of between 0.8-2.6 ppb($\mu g\ L^{-1}$) for formaldehyde and 0.2-0.8 ppb($\mu g\ L^{-1}$) for acetaldehyde.

Harley and Cass[21], showed that carbonyl emissions from petrol engines comprise between 1.96% and 3.40% by weight of the total volatile organic compounds released in the exhaust, (of which ~70% is formaldehyde[30]). They also show data to suggest that, for Southwest California, there are daily emission of 29 x 10^3kg of formaldehyde, 9.1 x 10^3kg of acetaldehyde, 4.6 x 10^3kg of acrolein and 14 x 10^3kg of methyl isobutyl ketone.

Hanst *et al.*[31], using a long path infra red spectrometer studied various hydrocarbon compounds in Los Angeles smog. Included in the study was formaldehyde.

Figure 1-8 shows a plot of atmospheric formaldehyde levels against time. Hanst *et al.*, showed that it was possible to correlate the rise in formaldehyde concentration with the observed rise in ozone and other hydrocarbons. They go on to conclude that formaldehyde, although emitted directly from petrol exhausts, is formed *in situ* mainly through the photochemical ozonolysis of ethene and other unsaturated compounds.

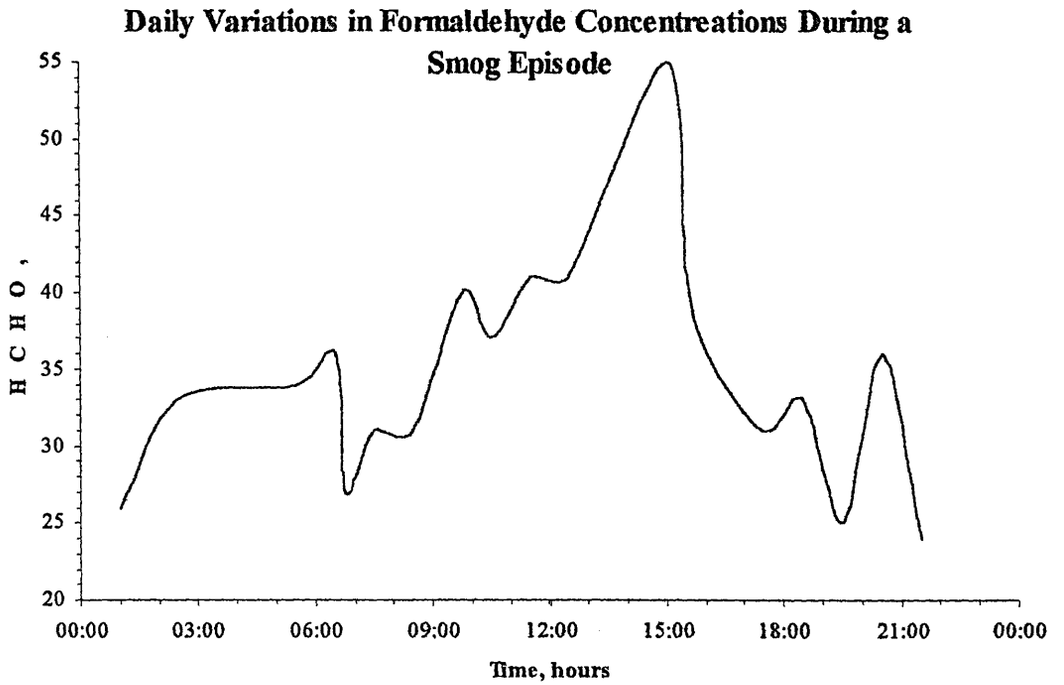


Figure 1-8 - Chart Showing Daily Formaldehyde Variations during a Smog Episode

Although the data plotted in Figure 1-8 was recorded during a smog episode, similar daytime variations in formaldehyde concentrations have been observed by Arlander *et al.*[24] As well as these 24 hour variations it has also been observed that there are seasonal variations in the sources of atmospheric carbonyl compounds. Possanzini *et al*[32], also showed a correlation between O_3 concentration and the ratio of formaldehyde to ethene during the summer that was not present during the winter. Also the summer maximum was twice that of the winter. These results suggest two different sources for tropospheric carbonyls. During the summer the carbonyls are present as secondary products from certain atmospheric processes, such as ozonolysis. This is indicated by the correlation of ozone with formaldehyde/ethene. However, during the winter, when the photochemical oxidation of hydrocarbons produces less ozone, it is thought that direct emission from motor vehicles is the dominant source. Possanzini *et al.*, further suggest that, with the increase in use of catalytic converters, the levels of directly emitted carbonyls will drop over the coming years.

1.2.2 Organic Acids

Organic acids are ubiquitous in the atmosphere, and have long been considered to play an important role in its chemistry. As far back as 1960 it was suggested that these organic compounds may contribute significantly to the ionic composition of rain.[33] It was not until the 1980s, however, that there was any significant research into the role of organic acids in the atmosphere. As the analytical and sampling techniques have improved, data has been provided that allows the role of organic acids in atmospheric cycles to be understood more fully. [34 35]

1.2.2.1 Atmospheric Sources

There is some uncertainty of the sources of organic acids in the atmosphere. It is suggested that the aqueous-phase oxidation of aldehydes with peroxides or hydroxyl radicals may be one source of organic acids. [23–25] These reactions are proposed to occur in clouds or rain water. *Equation (1.28)* The aqueous phase formic acid can either be transferred to the gas-phase through evaporation or be further oxidised in solution. Analogous reactions forming higher acids are too slow to be a significant source. As aqueous phase reactions cannot account for all the organic acids present in the atmosphere, gas-phase reactions must be a major source.

As already discussed the ozone-alkene reaction represents a significant sink for alkenes from both anthropogenic and biogenic sources. As a consequence various organic acids are produced but the dominant product is formic acid. This reaction is considered to be the main atmospheric source of formic acid.

Grosjean calculated the daily yields of organic acids from their individual alkene precursors.[36] These data are shown in Table 1-2. Grosjean states that the *in situ* alkene-ozone reaction produces more formic acid than acetic acid, with ratios of 2.5 and 8.0 for day and night production, respectively. Furthermore, Grosjean compares these data to that for the direct emission of formic and acetic acids, where there are higher levels of acetic acid.

Table 1-2 - Organic Acid Prescursors

	Organic Acid production rate (metric tons d^{-1})			
	Day		Night	
Alkene	**Formic**	**Acetic**	**Formic**	**Acetic**
Ethylene	9.1	-	24.6	-
Propene	3.3	1.8	3.5	1.9
3-Methyl-1-pentene	2.9	-	1.7	-
1-Pentene	2.6	-	1.5	-
2-Methyl-2-butene	-	2.6	-	0.1
1,3-Butadiene	2.1	-	0.7	-
2-Methyl-1-butene	1.4	-	0.3	-
1-Butene	1.6	-	1.7	-
cis-2-Butene	-	2.6	-	0.8
trans-2-Butene	-	2.5	-	1.0
Isobutene	0.8	-	0.1	-
3-Methyl-1-butene	0.7	-	0.4	-
2,3-Dimethyl-1-butene	0.4	-	0.05	-
cis-2-Pentene	-	0.3	-	0.4
trans-2-Pentene	-	0.2	-	0.1
trans-3-Methyl-2-pentene	-	0.1	-	-
1-Hexene	0.04	-	0.0	-
2-Ethyl-1-butene	0.03	-	0.0	-
Total	**25.0**	**10.1**	**34.5**	**4.3**

Another proposed source of organic acids proceeds through the oxidation of non-methane hydrocarbons and aldehydes. (*Equations 1.29-1.33* and this was discussed briefly in section 1.1.2.1.)

Ehalt *et al.*[37] discussed the role of alkanes in the formation of organic acids. As discussed earlier formaldehyde is produced in the gas-phase oxidation reaction of alkanes. The formaldehyde can be oxidised to formic acid through the routes discussed above.

Unlike the biogenic sources of atmospheric organic acids that have a widespread distribution across the planet, this is not so for the anthropogenic sources. As *Homo sapiens* have evolved into the twentieth century person he has aggregated himself into relatively small pockets of habitation, i.e. cities. A city gives a well defined, if excessively large, point

source of pollution. The effect of these sources on the biosphere as a whole is becoming more apparent, with damage to the ozone layer being very topical, but most pollutants are removed through *natural* atmospheric sinks within a short distance from their source.

One major biogenic source of organic acids is from the natural product, isoprene. This dialkene is the building block for terpenes and is emitted from plants. Isoprene photochemically decomposes to formic, methacrylic and pyruvic acids. However, results show that due to the amounts of isoprene emitted, this mechanism can only account for a third of the total formic acid found in the atmosphere. [35] This data suggests that there are other sources of atmospheric formic acid, especially primary emissions from vegetation, soils and from Formicine ants. [35 38]

The oxidation of isoprene is one of two recognised sources of atmospheric pyruvic acid. The other being the oxidation of *o*-cresol, though this can only be considered significant in highly polluted urban areas. [39 40] A major source of atmospheric acetic acid has been observed in Amazonia to originate, naturally, from vegetation and soils[41].

1.2.2.2 Atmospheric Sinks

Rapid photochemical sinks for pyruvic and methacrylic acids control their atmospheric concentrations. Formic and acetic acid, however, do not undergo any gas-phase reactions that significantly alter their atmospheric concentrations.[42] This being the case, these compounds must be removed by deposition, both wet and dry. At any given static sampling site, ventilation, or the movement of the air mass past the site must also be taken into consideration.

Therefore formic and acetic acids are removed from a point either by deposition or ventilation. The combination of the rates of these two mechanisms gives a daily figure for atmospheric removal. In a closed system a steady state would be achieved between source and sink. For formic acid this steady state gives an atmospheric lifetime of approximately 2.5 days.

1.2.2.3 Atmospheric Trends

There has been an observed diurnal behaviour to the atmospheric concentrations of both formic and acetic acids. [34] This diurnal behaviour is caused by the action of the atmospheric sources and sinks. In the preceding sections it has been the chemical processes

that have been discussed. In the environment there are also physical processes that are occurring that, when combined with the chemical mechanisms, affect the overall levels of the organic acids in the air. There are several possible sources for atmospheric acetic and formic acids, as already described. These are biogenic and photochemical production as well as anthropogenic emission. Talbot *et al.*[34] also suggest that due to the atmospheric lifetimes of formic and acetic acids, the re-entrainment of old boundary layer air should provide another source. They also arise from the revolatilisation of formic and acetic acid after precipitation. However, this is dependent on the meteorological conditions and the type of surface from which the revolatilisation is occurring.

Observations have shown that the concentrations of formic and acetic acid are lowest just before sunrise. This fall is thought to result from gaseous dry deposition. Talbot *et al.*[34], suggest that the dry deposition is the dominant mechanism hence the rapid decrease in the mixing ratio, shown in Figure 1-9.

Chart Showing Daily Variations in the Formic/Acetic Acid Ratio

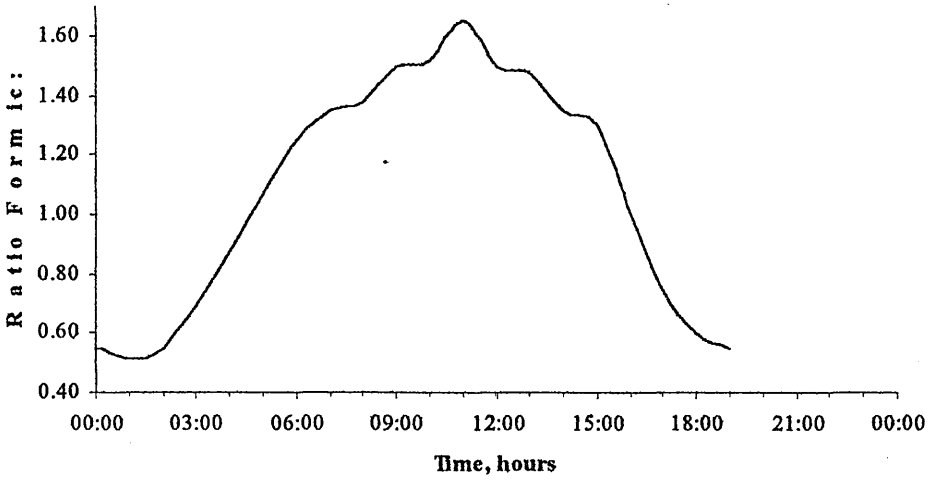


Figure 1-9 - Chart Showing Daily Formic:Acetic Acid Ratio Variations

From early morning the ratio of formic to acetic acid rises steadily untill midday, where there the levels plateau, except for a spike at around 4pm. The major anomaly in these results is the continuance of this plateau into the early hours of the evening. Talbot suggests two possible reasons for this phenomenon.

The first is that the sampling site was downwind of a small town, suggesting that the vehicle emissions are partly responsible for the elevated levels of organic acids. The second reason suggested is the nocturnal shrinking of the boundary layer. This has the effect of trapping these emissions closer to the surface.

Another physical feature that is thought to affect the atmospheric concentrations of formic and acetic acids on a diurnal basis is the evaporation, from plant surfaces, of early morning dew.[43]

Seasonal trends have also been observed in the levels of atmospheric organic acids. The emission of organic acids, and their hydrocarbon precursors, from plants has been seen to increase rapidly during the growing season of March to September (Mid-latitude temperate site).

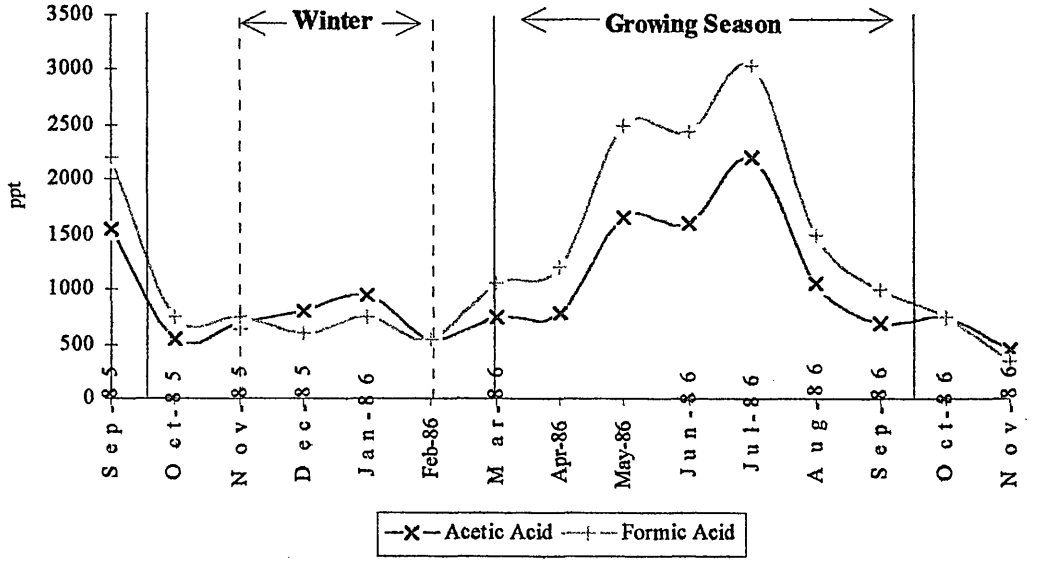


Figure 1-10 - A Chart Showing the Seasonal Formic and Acetic Acids Variations

Figure 1-10, above, shows the variation in formic and acetic acid levels throughout the year that Talbot *et al.* [34] observed. The data shown is from 1985-6. It can be seen that during the growing season there is a good correlation between the two acids, with formic acid having the greater concentration. At the end of the growing season there is a marked decrease in the concentration of both acids, with acetic acid having the higher concentration throughout the winter period. This data has led Talbot to conclude that there are annual changes in the relationship between the sources and sinks of both formic and acetic acid. It is hypothesised that the relative increase in the level of acetic acid during the winter period is

from direct emissions from motor vehicles and from the combustion of biomass. These results mirror those of Grosjean[36], in which he also observed higher levels of acetic acid from direct emissions.

Talbot also reports that, during certain high-pressure weather conditions, increased levels of organic acids in the order of 3-4ppb(μg L^{-1}), were found.

1.2.2.4 Transport of Organic Acids

Due to the location of Talbot's site and the fact that there appears to be no long range atmospheric transport of organic acids it can be assumed that in localised areas biogenic sources of organic compounds are more significant than anthropogenic sources. Hence, the quality of urban air is largely determined by two factors: the weather and the motor car.

Results of studies suggest that the primary sources of organic acids in the atmosphere, both in gaseous and aqueous phases, are natural. Sampling at both remote terrestrial sites and rural sites within industrialised regions give similar results. This tends toward the hypothesis that there is very little long range transport of organic acids within the atmosphere, and that the levels of acids are localised. [34]

1.2.2.5 Anthropogenic Sources

Grosjean *et al.* [44] found formic and acetic acid concentrations in the ranges 1-20 and 1-13ppb(μg L^{-1}) respectively for a sampling site at Claremont, California. This site is downwind of Los Angeles, so could be expected to have slightly elevated levels. Grosjean *et al.* also found that a Palm Springs site which was impacted by the Los Angeles urban plume, showed levels of formic and acetic acids similar to those generally found in urban areas. To interpret these results fully the geography of this sampling area needs explaining. Palm Springs is at the eastern end of a densely populated conurbation that stretches approximately 30 miles from Los Angeles in the west. As the plume moves eastward it is continually being added to. Therefore if long range transport was occurring the organic acid levels in Palm Springs would be considerably higher than the results that were obtained. This again suggests that there is very little long range transport of organic acids and that deposition occurs within an area close to the source.

The major source of anthropogenic pollution is exhaust emissions from motor engines. Formic and acetic acid levels of 9 and 32 ppb($\mu g\ L^{-1}$) respectively have been found in the exhaust gases of petrol engines. Other higher organic acids were also found, along with benzoic acid. These direct emissions are translated into the urban atmosphere, at more diluted but still significant levels, and in similar ratios. Up to 4ppb($\mu g\ L^{-1}$) of acetic and 3ppb($\mu g\ L^{-1}$) of formic acids were monitored in urban Los Angeles air.[45] The presence of these organic acids in the exhaust is suggested by Kawamura *et al.* [45], to be from the incomplete combustion of the fuel. Since 1985, however, there has been a gradual introduction of catalytic converters and this should lead to a reduction in the levels of anthropogenic organic acids.

Samples taken in Rio de Janeiro, Brazil, where ethanol is used as a primary motor fuel, revealed elevated levels of acetic acid. Concentrations in the range of 1-18ppb($\mu g\ L^{-1}$) are attributed to the incomplete combustion of the fuel.

The study of organic acids in indoor air has received very little attention as an area for research. The organic acids found in indoor air are present either by direct emission or as an effect of external air. As part of the previously mentioned study by Grosjean *et al.*, air samples were taken from an office building in Ventura, California. Levels of formic and acetic acids were found in concentration ranges 1-4 and 1-3 ppb($\mu g\ L^{-1}$) respectively.

1.2.2.6 Dicarboxylic Acids

Dicarboxylic acids have been reported in snow, rain and aerosols in both the urban[46] [47] and remote[48] atmospheres. Due to their highly polar nature they readily dissolve in atmospheric water thus their gas phase impact will be limited. They are derived from primary emissions from motor exhausts and also secondary reactions from anthropogenic hydrocarbons such as cyclic alkenes.

Dominant dicarboxylic acids include oxalic, malic and succinic acids. Also observed are ketoacids including pyruvic and glyoxylic acids.

Kawamura *et al.* [48] reports that there is a seasonal variation in the long range transport of the diacids in a study carried out of the polar sunrise (Mar-May). At the arctic site levels peaked around April, after which they steadily decreased down to background levels, after which time there was also little evidence of south-north transport in the

atmosphere. The rapid increase is thought to originate from the secondary photochemical reactions brought on by polar sunrise. The results of this experiment suggest that photochemical production of dicarboxylic acids should be considered as a major source.

1.3 Sampling Methods for Volatile Organic Compounds in Air

1.3.1 Introduction

"The results from an analysis are only as good as the sample"

This quote is or should be drilled into analytical scientists from the very beginning of their training, but its importance is often missed until it is too late. The ideal sample is one that is totally homogeneous, and thus representative of the whole. However the atmosphere is a dynamic system with dynamic sources and sinks, hence the results of analysis can be difficult to interpret objectively.

One of the major problems with air sampling is that there isn't much of it. Although air is everywhere on this planet it has a very low density. On a molar level, one mole of air has a volume of 22.4L (at STP), compared with an aqueous sample where one mole occupies 18mL. This difference in concentration (~1.3×10^3) is not appreciated until we understand that the analytical techniques are analyte and not sample dependant. Thus in order to obtain a sample that is of a similar molar concentration to one of water, we either need to use much larger volumes of sample in our determination procedures or we need more efficient sampling techniques to provide sufficient concentration.

1.3.1.1 Sampling Techniques

There are numerous ways in which air samples can be taken. Each technique is, generally, specific for the particular analytes being collected. Initially air sampling can be sub-divided into two types: active and passive. Passive sampling techniques are where the sample is collected without any mechanical assistance. Active sampling is where a volume of air is mechanically drawn through the sampling system, through either positive pressure or vacuum pumping.

1.3.1.1.1 Passive Samplers

Passive or diffusive samplers are used for a variety of different classes of compounds. The main usage for such samplers is in workplace monitoring. Levin and Lindahl [49] discuss several approaches to the passive sampling of reactive compounds, using sorbent, liquid or filter based devices. Aldehydes can be determined readily using 2,4-dinitrophenylhydrazine doped sorbents[50] [51] and filters.[52] Other compounds discussed by Levin and Lindahl include amines[53] [54], diisocyanates[55] and reactive inorganics such as nitrogen dioxide, NO_x.

Other reactive inorganic compounds have also been determined using passive sampling techniques. Koutrakis *et al.*[56], used a nitrite coated filter to determine ozone. Over a period of eleven months they obtained results that were comparable with those collected concurrently from a UV photometric based system.

Grosjean *et al.*[57], also used passive samplers to determine ozone as well as other reactive inorganic compounds. Using colourimetric reagents they determined parts per billion levels of photochemical oxidants in the atmosphere.

Brown *et al.*[58], used a Tenax TA packed tube to perform long term diffusive sampling of volatile organic compounds. The results showed, that the sample uptake is compound dependant. The compounds of higher volatility having a lower rate of uptake as would be expected.

1.3.1.1.2 Active Sampling

Active sampling techniques can again be sub-divided into three general methods. These are grab, sparging and sorbent. Within these three groups all active air sampling methods can be classified.

Grab techniques are where a unit of air is collected and then taken back to the laboratory for analysis.[59] This is the simplest of all the active techniques however it does have its drawbacks. The primary disadvantage is that there is no sample pre-concentration. Therefore the type of analytes that can be determined from this technique is limited to those found in high concentrations or those that can be determined under extreme experimental conditions i.e. large volume injection or cryogenic trapping.

Denha *et al.* [59], used Tedlar gas bags for the determination of methane in city centre air. The results were determined by GC-FID using 1cm^3 gas injections. Values obtained for

the methane concentrations were in the 4.5-6.5 ppm (mg L^{-1})range. Evacuated 500mL glass pipettes were used for the determination of hydrocarbons in the Sydney Harbour tunnel by Duffy and Nelson[60], determining both aromatic and aliphatic hydrocarbons of concentration range 2-175ppbv(μg L^{-1}). Several workers have reported the use of polished stainless steel canisters: Bayer[61] for monitoring VOC in indoor air, Sweet and Vermette[62] for determining toxic VOC in Urban Illinois, Moschonas and Glavas[63] for the determination of atmospheric C_3-C_{10} hydrocarbons in Athens air. All of the reported methods required a cryogenic trapping step before analysis. This pre-concentration step was necessary to allow adequate sensitivity for the determinations.

Sparging techniques[64 65 66] are where the air sample is passed through a liquid into which the analyte is dissolved. The liquid used is dependent on the analyte under investigation. For the determination of carbonyls, 2,4-dinitrophenylhydrazine solution has been reported. This allows the *insitu* derivatisation of the analytes.[67] Also for the determination of carbonyl compounds Shi and Johnson[68] used a solution of $NaHSO_3$ and ribose.

Sorbent sampling techniques are where the air is passed over a solid media, which traps the compounds from the air. The mechanisms for the trapping will be discussed later. Due to the versatility of solid sorbents and the range of sorbent media commercially available this type of technique is used for most air sampling applications today. Before examining the types of sorbent, consideration needs to be given to the type of extraction or desorption methods that are commonly used.

Thermal Desorption

Thermal desorption as the name implies uses heat to remove the analytes from the sorbent material.[69 70] The sorbent material is heated (~ +250°C) over a period of several minutes, allowing the analytes to be vaporised from the sorbent. The heat can be generated either by a traditional heater element or as more recently reported by a microwave generator.[71 72] However the majority of workers report the use of the traditional technique. The analytes are then cryofocussed by use of a "cold trap" (~ -100°C). After the desorption period has ended the cold trap is rapidly heated causing the rapid desorption of the analytes into the gas phase and onto the GC column. Using cryofocussing, the narrowest possible band of analyte is passed onto the GC column. Thermal desorption is a "one-shot" method

allowing only one analysis per cartridge, meaning that for further analysis a fresh sample is required. After the initial desorption period the sorbent is effectively clean, and can be reused. Thermal desorption is a rapid and simple technique.

Thermal desorption is a commonly used technique for the sampling of VOC. Bayer[61] used thermal desorption as a compliment to grab in techniques described earlier insection 1.3.1.1.2.. Ciccioli *et al.*,[73] determined in excess of 120 compounds in air samples taken in Italy and in the Himalayas. Lewis *et al.*,[74] used a programmable temperature injector to allow the thermal desorption of natural products. Karpe *et al.*[75], used thermal desorption as a sample introduction technique for an elaborate detection system involving mass spectrometry, flame ionisation detection and a "sniffer" device for the determination of odorous volatile organic compounds in air. Yamashita *et al.*[76], have demonstrated that thermal desorption can be used with a range of GC detection systems. Use of such detectors as flame ionisation and atomic emission have all been reported.

With thermal desorption the choice of sorbent material is critical. Cao and Hewitt[77] found that some analytes are degraded on certain sorbents even at relatively low desorbing temperatures. An example is of α- and β-pinene decomposing on Carbotrap at 220°C. Multisorbent beds have been used when trapping compounds that have a wide range of physcial properties. Heavner *et al.*[78], showed that it was possible to sample aliphatic, aromatic and polar compounds from tobacco smoke in cartridges comprised of Tenax TA and Carbotrap 20/40 mesh.

Solvent Extraction

The alternative to thermal desorption is solvent extraction. There are a multitude of different approaches that have been reported that fall into the category of solvent extraction. Each has its merits and drawbacks. In solvent extraction the analyte is desorbed from the sorbent by means of dissolution into a solvent. The solvent that is used can be aqueous, organic or supercritical. The analytical method being used tends to determine which type of solvent is used.

The simplest method of solvent extraction requires the bringing together of sorbent and solvent. The extraction occurs rapidly and can be aided by shaking or the use of

ultrasonification. This form of solvent extraction is rapid and uses minimal amounts of solvent.

Cleghorn *et al*[79], extracted the sorbent in 3mL of ice cold dichloromethane for 30 minutes, for the determination of phenol, cresols and xylenols in air. Henriks-Eckerman[80] used a series of solvents, extracting with 2mL of each, to assess the efficiency of XAD-2 for use in determining VOC's in air. Koo *et al*[81], used a 2mL ethanol/6mL benzene mixture to extract PAH from particulates on filters. The process was aided by ultrasonification and the particulates removed by centrifugation. Kawamura *et al*[82], extracted organic acids from KOH impregnated filters using pure water. They used three 5mL aliquots of water and were aided by ultrasound.

However as the sorbent and solvent are in constant contact throughout the extraction procedure it is possible for the analyte to re-adsorb back onto the surface of the sorbent material. This effect can be minimised by using multiple aliquot extractions.

Soxhlet Extraction

A technique that separates the extracted analytes from the sampling media is the Soxhlet system. The Soxhlet extractor is a piece of glassware that allows the continuous washing of a solid sample by a set amount of hot solvent. A water cooled condenser keeps the solvent refluxing within the system. After extraction the analyte is removed from the sorbent. This prevents an equilibrium being achieved between the analyte and the sorbent. Soxhlet extraction uses large amounts of solvent, energy and is very time consuming.

Chuang *et al*[83], used both a single step dichloromethane (DCM) extraction (for 16h) and a two step DCM (16h) extraction followed by an ethyl acetate extraction (for 8h) for the determination of nicotine and polynuclear aromatic hydrocarbons in indoor air.

Soxhlet extraction has several drawbacks which need to be addressed. Primarily the length of the extraction procedure does not allow for rapid analysis of the sample, and can also be seen as wasteful of energy (for the heating mantle) and water (for the condenser). These are operational considerations that need bearing in mind in the light of the current economic climate and diminishing water resources. The Soxhlet method also requires large volumes of extracting solvent (~100mL) for each extraction. This is then reduced either by rotary vacuum evaporation or by simple evaporation to atmosphere under nitrogen. This can also be considered wasteful of resources and importantly can be a source of error in the

analysis. In sample reduction of this kind there is the possibility of loss of volatile samples through evaporation.

Microwave Assisted Extraction

Another process that is available is microwave-assisted extraction. A conventional microwave oven is used as a heat source for the extraction process. Lao *et al.*[84], suggest that this technique offers similar recoveries to the equivalent Soxhlet technique, but with a shorter extraction time (*c.* 2.5mins). Again, however, the methodology suggests the use of large quantities of solvent and a blow-down reduction step. Commercially available dedicated instruments use smaller volumes of solvents in pressurised vessels. This in principle is similar to accelerated solvent extraction (ASE) using a microwave instead of a thermal energy source.

Accelerated Solvent Extraction

Accelerated solvent extraction is a comparatively recent innovation (*c.*1995). Developed by the Dionex Corporation, ASE is marketed as an alternative to supercritical fluid extraction. Although its use has so far been limited to soil samples, it is worth noting the potential offered by ASE for the extraction of solid phase sampling media. The principle behind ASE is that the solid sample and solvent are kept heated and under pressure for the duration of the extraction procedure. Dean has reported extraction times of 10 minutes[85]. It has been used for extraction of both polar and non-polar compounds from soil.[86 87 88]

Supercritical Fluid Extraction (SFE)

Supercritical fluid extraction is a technique that bridges the gap between ordinary solvent extraction techniques and the more powerful accelerated solvent extraction. Supercritical fluids have similar physical properties to liquids and, as such, have comparable extraction efficiencies to many liquid extraction systems. However, the time required for supercritical fluid extractions is considerably shorter. SFE uses carbon dioxide at 78 atm and 31°C as the solvent. Because of the comparatively low temperature, thermal degradation and pyrolysis of the sample is avoided. Solvent modifiers are often added to alter the polarity of the supercritical fluid.[89 90]

Unlike ASE the use of SFE with air sampling media has been reported. Wong *et al.*[91], describe the use of SFE to desorb volatile and semi-volatile mutagens from various solid adsorbents. They report recoveries of between 60-90% for a range of aromatic

compounds. Hansen *et al.*[92], report recoveries of 70-105% for a series of alcohols and organic acids compared with 0-30% for thermal desorption.

1.3.1.1.3 Sampling Media

There is a wide range of sorbent materials reported in the literature for use in air sampling. The choice of sorbent is dependant on the analytes, the preparative steps and the analytical procedure being used. There are five main types of sorbent that are routinely used. These are polymers, foams, filters, charcoal or the carbon-based materials, and silica.

Polymer based sorbents are the most common type of materials used for air sampling. They are used in both thermal and solvent desorption systems. Common materials that are used are Tenax and XAD. Each has different physical and chemical properties that can be exploited during sampling. They are obtained in particulate form of varying sizes dependant upon the end usage.

Tenax is the general trade name for sorbents based on the 2,6-diphenyl-*p*-phenylene oxide polymer. (Figure 1-11) It is generally used for thermal desorption work due to its high thermal stability but also its insolubility to polar solvents.

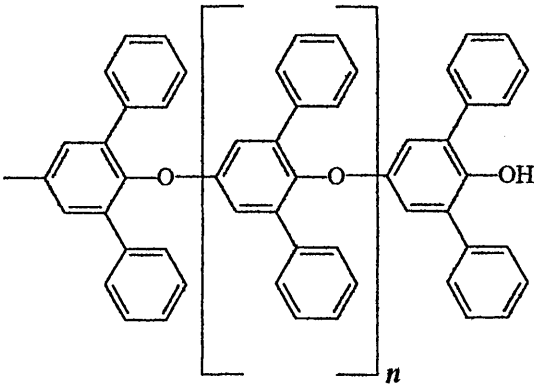


Figure 1-11 - A Diagram Showing the Structure of Tenax

As a sorbent, Tenax has been studied widely.[93] [94] De Bortoli *et al*, have suggested that Tenax is suitable for trapping both polar and non-polar VOC's with good reproducibility and low blanks. They also suggest that the polymer is stable for "*hundreds of sampling-desorption cycles.*"[93] Tenax has been reported to decompose in the presence of oxides of nitrogen, although the work of Hanson *et al.*[94], was performed using high levels of NO_x, it is still worth noting.

Lewis *et al*[74], used a combination of Tenax TA and Carbosieve S-III, a carbon based sorbent, for the sampling of isoprene, methacrolein and methyl vinyl ketone. Fung and Wu[95] used Tenax GR for the determination of VOC in air, reporting levels of aromatics and halocarbons with linear working ranges of between 3.2 $\mu g\ m^{-3}$($ng\ L^{-1}$) and 770mg m^{-3}($\mu g\ L^{-1}$) Ekberg[96] used Tenax for the determination of total VOC's in office buildings. Results were in the 0.16 to 0.35mg m^{-3} ($\mu g\ L^{-1}$) range.

Oliver *et al*[97], used Tenax GR, as well as Carbotrap and Carbosieve S-III, in a multisorbent trap. Their automated system was used for the assessment of ozone precursor compounds. They achieved detection limits of between 0.06 and 2.4 ppbv($\mu g\ L^{-1}$) over a range of 56 aliphatic and aromatic hydrocarbons.

Another type of polymer that is commonly used is XAD. This is the trade name for several polymers based on styrene-divinyl benzene (SDB). Styrene-divinyl benzene is more resistant to solvent than Tenax and is therefore more associated with solvent desorption sampling systems. Like Tenax, however, SDB does have a tendency to decompose through reactions with NO_x. Hanson *et al*[94], reported the presence of 17 dichloromethane soluble decomposition products, some of which were thought to produce a mutagenic response in a *Salmonella* assay.

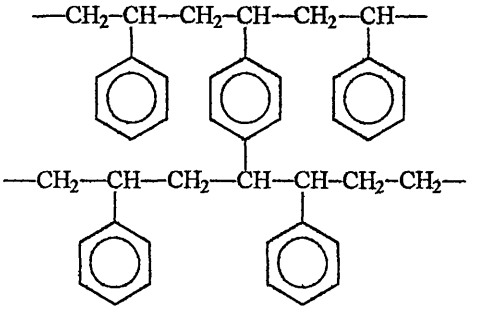


Figure 1-12 - A Diagram Showing the Structure of XAD

Polynuclear aromatic hydrocarbons and nicotine have been determined using XAD-2 and XAD-4[83]. The difference between the two polymers is pore size and hence active surface area. Chuang *et al.*, found that by using XAD-4, which has the larger surface area, it was possible to trap both PAH and nicotine whereas XAD-2 failed to achieve this. Hedge *et al.*[98], also used XAD-4, for the determination of nicotine, obtaining a detection limit of 0.56 $\mu g\ m^{-3}$($ng\ L^{-1}$) for a 180L sample.

For the determination of workplace phenolic compounds, Cleghorn *et al.*[79], used pre-packed XAD cartridges. Impurities in the polymer gave low precision and accuracy in the analyses. They did conclude however that XAD may be used to sample specifically for phenolic compounds.

The sampling efficiency of XAD systems for aliphatic and aromatic hydrocarbons was studied by Henriks-Eckerman[80]. In a glass fibre-XAD system he showed that humidity, sample flow rate and organic dust had very little effect on the sampling efficiency. He also showed that compounds of different polarities could be collected using XAD.

The use of polymeric synthetic foams has been reported in the literature. Polyurethane foam (PUF) has one main advantage over loosely packed polymer particles, and that is its structure. Polymeric foams are tough and durable materials that can be used in systems that require high flow rates[99] such as sampling for trace levels of pesticides[100] and polyhalogenated compounds[101]. Atmospheric phenols[102], have also been sampled using polyurethane foams. Wagel *et al.*[101], used a PUF-Tenax sampling system for the sampling of large chlorinated molecules such as polyhalogenated dibenzo-*p*-dioxins and polychlorinated biphenyls. Sampling flow rates in excess of 200L min^{-1} were used. Nerín *et al.* [100], used a PUF-Tenax system for the determination of pesticides in air samples. Using a low flow rate they sampled for 12 hours. Zaranski *et al.*[103], studied the use of PUF-Tenax systems for the sampling of volatile organic compounds. They found that the limiting factor for the types of compound that were trapped was vapour pressure. This suggests that there are only weak interactions between the PUF and the analytes.

Other polymeric materials that have been used include polyimide[104] and polysiloxane[105].

Inorganic materials, such as silica, have been used for the sampling of polar compounds in air. Silica gel is used as a drying agent because of its hygroscopic nature. The same mechanism that allows water to be trapped also allows the trapping of polar compounds such as organic acids and alcohols. Silica is readily commercially available in bulk. However, there is now a tendency to use silica that is pre-packed into fritted syringe bodies. This makes it easy to handle and robust. Furthermore there is potential for the reuse of the sampling media. Hekmat and Smith[106] used silica gel air sampling tubes for the

determination of low molecular weight organic acids as did Zhang *et al.*[107], in their study of indoor air organic acids.

Silica is readily surface derivatised. This is seen in many HPLC column packing materials. Due to steric hindrances, however, complete derivatisation is not possible, so there will be some inherent polarity. Zhang *et al.*[108], studying organic acids in indoor air used alkaline impregnated C_{18}-silica packed in solid phase extraction cartridges. Samples were collected at 1.0-2.0 L min^{-1}. Grosjean *et al.*[44], have used alkaline impregnated C_{18}-Silica cartridges for the determination of organic acids in various atmospheres and Zhang *et al.*, have determined aldehydes using 2,4-dinitrophenylhydrazine impregnated C_{18}-silica SPE cartridges. The use of 2,4-dinitrophenylhydrazine impregnated C_{18}-Silica SPE cartridges has been widely reported in the literature for the determination of carbonyls.[118, 119 121, 126] Lehmphul and Birks[109] used C_{18}-Silica packed cartridges impregnated with 2,4,6-trichlorophenylhydrazine for the determination of carbonyls.

Perhaps the most studied adsorbing material, as far as physical chemists are concerned, is charcoal. Charcoal is a carbon-based material that has a high surface area and therefore a high potential for adsorbing gases. A comparison of charcoal and Tenax-TA shows that charcoal has a surface area of 500-2000m^2 g^{-1} compared with 35m^2 g^{-1} for Tenax[91]. Wong *et al.*[91], suggest that materials like charcoal with large surface areas trap the more volatile compounds quantitatively. However the use of charcoal has now diminished following the development of the polymer based adsorbent materials discussed earlier in this section.

Grob et al.[110], used charcoal as the absorbent in an open tubular trap system for the analysis of air and headspace samples. The charcoal traps were thermally desorbed in the injector of the gas chromatograph. Other workers have used various forms of carbon based molecular sieves for the sampling of volatile organic compounds in air[111].

The use of glass fibre and paper filter papers is generally limited to the sampling of airborne particulates. However, Kawamura *et al.*[82], used alkaline impregnated filter papers for the determination of organic acids in motor engine exhaust gases. Using both primary and secondary filters they managed to trap ~99% of the organic acids in fumes.

To understand the choices of sampling media and technique it is necessary to understand the physical and chemical processes that are occurring at the gas-solid interface.

1.3.2 Sorbent Air Sampling Mechanisms

Adsorption, or sorption, is used to describe the phenomenon of gas uptake by solids. This occurs when a gas and a "clean" solid surface are brought together, and some of the gas becomes attached to form an adsorbed layer on the surface of the solid. Any solid is capable of adsorbing a certain amount of gas. The extent of the adsorption, however, is dependent on temperature, the pressure of the gas, the surface area of the sorbent and the chemical nature of the surface of the sorbent.

It follows, therefore, that the most important sorbents, are highly porous solids, notably charcoal and silica gel, and finely divided powders. Charcoal and silica gel have internal surface areas of *c.*1000 $m^2 g^{-1}$.

The imbalance of attractive forces which exists at a surface and the surface free energy, are reduced by adsorption. When adsorption takes place the motion of the gas molecules is restricted, to just two dimensions. This adsorption process results in a decrease in entropy and also a decrease in free energy. From the thermodynamic relationship:

$$\Delta G_{abs} = \Delta H_{abs} - T\Delta S_{abs} \qquad 1.34$$

it can be determined that ΔH_{abs} must be negative, as bond formation is occurring, and that the adsorption of gases onto a solid surface is always an exothermic process.

The enthalpy of adsorption can be used to determine what type of adsorption process is occurring. There are two generic processes that can occur. Chemisorption processes which involve chemical attachment to the sorbent surface have, in general, large enthalpies, i.e.≥150kJ mol^{-1}. Physical adsorption, or physisorption, involves low energy molecular interactions. These interactions are of the order ≥50kJ mol^{-1}. In air sampling it is the low energy molecular interactions that are of maximum importance.

1.3.2.1 Molecular Interactions

To examine intermolecular forces it is necessary to look at the fundamentals of these interactions. The initial work done on such forces was applied to gases. By examining these mechanisms it is possible to apply them to both the sorbate(gas) and sorbent(solid).

Clapyeron's equation of, $PV = nRT$, is commonly known as the ideal gas expression. This equation relates Boyle's and Charles', 17th and 18th Century gas laws to

Amadeo Avogadro's hypothesis of 1812. It mathematically summarises the relationship between the number of molecules in a given gas sample, temperature, pressure and volume. There are several assumptions that are made for ideal gases. These are: (i) the particles are in a state of continuous random motion, (ii) the volume of the particles is negligible compared with the total volume of the gas, (iii) the attractive forces between the particles are negligible and (iv) that the collisions between particles of the gas are perfectly elastic.

In real gases, however, there is a deviation from ideal behaviour which is caused by substantial intermolecular attractions because the molecules occupy a finite volume. These observations led J.D. van der Waals to propose modifications to the ideal gas equation. In 1873, he added two new terms to produce the equation:

$$\left(P + \frac{a}{V^2}\right)(V - b) = nRT \qquad \textbf{1.35}$$

where a and b are constant for a particular gas. The term of $(V - b)$ takes into account the volume of the molecules in the gas and (a/V^2) compensates for any intermolecular forces.

There are four types of intermolecular interactions that need to be examined when considering gas phase air sampling. These are the non-polar dispersion forces, and the specific forces of hydrogen bonding, dipole-dipole and dipole-induced dipole interactions.[112]

1.3.2.1.1 Dispersion Forces

There are two competing forces active on a molecule as it approaches another molecule. These are attractive and repulsive. Both forces are described in the van der Waals equation. Further derivations of the van der Waals equation lead to the forces being combined in the Lennard-Jones Potential Function:

$$U_{(r)} = 4\varepsilon_{LJ}\left[\left(\frac{\sigma_{LJ}}{r}\right)^{12} - \left(\frac{\sigma_{LJ}}{r}\right)^{6}\right] \qquad \textbf{1.36}$$

Where ε_{LJ} is Lennard-Jones' measure of attraction, σ_{LJ} is the size of the molecule and r is the intermolecular distance. The plotting the Lennard-Jones function shows how both the attractive and repulsive forces are linked through the term $U_{(r)}$.

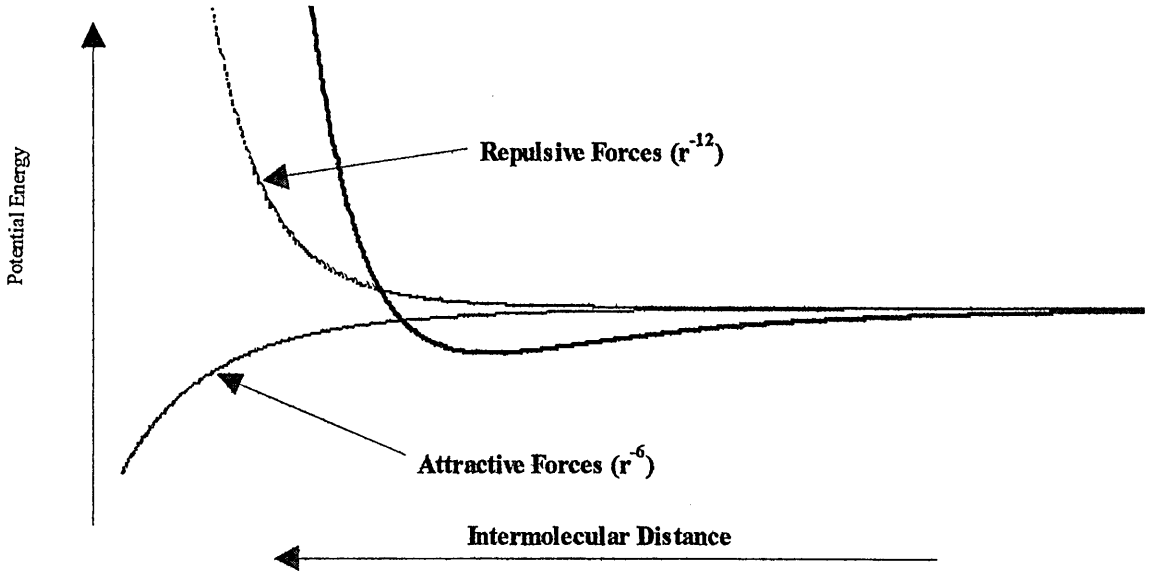


Figure 1-13 - A Lennard-Jones Plot for Molecular Repulsion/Attraction

Dispersion forces are the weakest of the four interactions being discussed. They occur because of the random movement of electrons within the molecule in question. At any instant, the electrons can assume an instantaneous, temporary charge separation. A transitory dipole is created in one molecule that will briefly polarise the electrons in an adjacent molecule, creating a temporary dipole in the second molecule. The two temporary dipoles are then momentarily electrostatically attracted to one another.

Dispersion forces are most effective at small intermolecular distances. This is shown by the r^{-6} function.(Figure 1-13) As the two molecules approach the r^{-12}, the repulsive force function, dominates. The enthalpy of bonding for dispersion forces is low, meaning that the bonding or attractive effects are weak, i.e. physisorption. In chemisorption we find that there is enough energy present in the system to overcome the repulsive forces and bond formation occurs.

There is a second equation which describes the energy of the dispersion attraction, $E_{1,1}$, between two adjacent atoms of the same kind, in terms of polarisability of an atom, the ionisation potential and intermolecular distance. This is shown as:

$$E_{1,1} = -\frac{3\alpha_1^2 I_1}{4 r_{1,1}^6} \qquad 1.37$$

Here α_1 is the polarisability of an atom of type 1, and I_1 is its ionisation potential and $r_{1,1}$ refers to the distance separating the two adjacent atoms. As the chain length of a molecule increases, the number of interacting atoms will also increase. It can be seen from this equation that the strength of the interaction is dependent on the chain length, or effective area of interaction, of one or both of the molecules involved. This type of electrostatic attraction is only really significant in long chain hydrocarbons, e.g. C_{18}.

By using a derivative of this equation that takes into account the dispersion energies from two dissimilar atoms, e.g. sorbent and sorbate, it is possible to determine the contribution made to adsorption by the dispersion forces and by the other specific forces.

Table 1-3 - Specific Bonding Energies [113]

ADSORBATE	FREE ENERGY OF ADSORPTION (kJ mol^{-1}, 20°C)		
	TOTAL (Experiment)	DISPERSION (Equation)	SPECIFIC (Difference)
n-Hexane	24.36	24.36	0.0
Benzene	36.96	24.46	10.5
Diethyl Ether	41.16	21.42	19.74
Acetone	47.96	19.36	28.14
Methanol	49.14	13.02	36.12

Table 1-3, shows the contributions to the adsorption onto alumina, a polar sorbent material, made by dispersion forces and by specific forces, for a series of different polarity compounds.

1.3.2.1.2 Dipole-Dipole Forces

A dipole moment involves a permanent movement of electrons within the molecule so that a permanent partial charge separation or dipole moment is formed. Molecular interactions occur by the attraction of the aligned dipoles. The strength of these are dependent upon the strength of the dipole moments. The strength of the attraction is increased if the charge separation occurs over a larger intramolecular distance by resonance

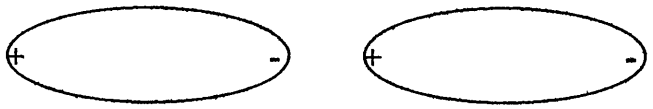
effects, especially through double bonds, aromatic structures, or conjugated systems where π–electrons are present.

The energy of interaction of two adjacent dipoles is expressed as:

$$E = \frac{-2\mu_1\mu_2}{4\pi r^3\varepsilon_0} \qquad \textbf{1.38}$$

where μ is the dipole moment, ε_0 is the measure of attraction and r is the intermolecular distance. From this equation it can be seen that the strength of the bond is related to the strength of the dipole. Molecules with larger dipoles, generally, form stronger bonds.

The equation holds fast if the arrangement of the dipoles is "head-to-tail". This configuration is shown in the diagram below .



Dipole-Dipole interactions have a longer range than dispersion forces. The force is related to $1/r^3$, the strength of which drops off less rapidly than the $1/r^6$ that is found with the dispersion forces. The Van der Waals radius of the molecules and the repulsive effects mentioned above limit the strength of the effect.

Another factor which affects the strength of dipole-dipole interactions is temperature. As temperature increases the strength of the interaction decreases. This is due to the fact that at higher temperatures all orientations of the dipole become possible.

1.3.2.1.3 Dipole-Induced Dipole, Induction or Debye

Debye forces exist when one of two adjacent molecules has a permanent electrical field associated with it. Under the influence of the permanent electrical field, the electrons of the adjacent molecule, whether polar or not, are polarised to give an induced dipole moment which interacts with the field. All molecules can undergo some sort of induction but certain types of molecule are more easily polarisable. These are molecules that contain loosely held electrons in some part of the molecule. Such molecules contain heteroatoms (O, N, S, and halogens), a double bond or a triple bond, a conjugate unsaturation system, or an aromatic π-electron system. The energy of this inductive interaction can be expressed as:

$$E = -\frac{1}{2}\frac{Z^2\alpha}{r^4} \qquad \textbf{1.39}$$

Where α refers to the inherent polarisability of the neutral molecule and Z is the field strength (arising from the other molecule) in the vicinity of the polarised molecule.

Likewise a dipole can induce another dipole in an uncharged, non-polar molecule. The energy of such an interaction is described by the equation:

$$E = \frac{-\mu^2\alpha}{r^6} \qquad \textbf{1.40}$$

Where μ is the moment of the inducing dipole.

The forces tend to be weak since the polarisability of most species is small. Also the effective distances of these forces is very short because the energies of interaction vary inversely with high powers of r.

Data presented by Snyder[113] show that inductive forces are unimportant in the adsorption of polar adsorbates onto non-polar sorbents. The data for n-Hexane in Table 1-3 also shows this to be so. However polar adsorbents can have quite a strong surface field and inductive interactions can be relatively important in some cases. It has been suggested that inductive forces make a major contribution to total adsorption energy in the cases of adsorbents such as alumina .

1.3.2.1.4 Hydrogen Bonding Forces

A definition of a hydrogen bond can be given as a bond between:

"...a functional group A—H and an atom or group of atoms B in the same or a different molecule when

(a) *there is evidence of bond formation (association or chelation)*

(b) *there is evidence that this new bond linking A—H and B specifically involves the hydrogen atom already bonded to A"* [114]

It is generally accepted that the term hydrogen bonding was first used by Latimer and Rodebush in 1920[114]. They surmised that "*...the hydrogen nucleus held between two octets constitutes a weak "bond"...*" These simple descriptions have been superseded by more complex interpretations. The hydrogen bond is still written using the simple notation of: **A—H · · · B**. Unlike the previously described types of intermolecular forces, there is no simple mathematical expression for the strength of the hydrogen bond.

The mechanism involved in hydrogen bonding can be explained simply by electrostatic interactions. It has been observed that the atoms of A and B, and B and H in the hydrogen bonding system **A—H · · · B** are closer together than would be expected from their Van der Waals radii. This suggests that the hydrogen atom is interacting with the electron cloud of atom B.[115]

In a typical hydrogen bonding system the hydrogen is attached linearly to two very electronegative atoms, e.g. O—H···O. Molecules that have groups such as —OH or —NH show strong attraction, or association, by donating their protons to a proton acceptor. Therefore under the Lowry-Brønsted definition a hydrogen bond is an example of a proton-donor—acceptor system, i.e. an acid-base system. Hydrogen bonding is strongest for acidic donors and basic acceptors when the three nuclei involved are aligned. Linus Pauling suggested that increasing the electronegativity of a donor atom increases the strength of the hydrogen bond formed. [116] This effect is shown in

Table 1-4. [114]

Table 1-4 - Hydrogen Bond Strengths

Compound	$\Delta H_{sublimation}$
Benzene	10.5
Phenol	16.1
Benzoic Acid	21.8
p-Hydroxybenzoic Acids	27.7

Hydrogen bonds form between two types of molecule called the donor and the acceptor. It is possible for certain molecules to fall into both categories. Table 1-5 shows a list of common organic donors. Table 1-6 shows organic acceptors.[117]

Table 1-5 - Organic Donors

Bond	Compound
O—H	R—O—H {Alcohols and phenols}
	Silanols $R_1R_2R_3SiOH$
	R—COOH {Carboxylic Acids}
N—H	$R—NH_2$ {Primary Amines}
	R_1R_2—NH {Secondary Amines}
S—H	R—SH {Thiols, Thiophenols}
C—H	Cl_3—C—H {Chloroform}
	R—C≡C—H {Acetylene's}
	N≡C—H {Hydrogen Cyanide}

Table 1-6 - Organic Acceptors

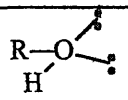
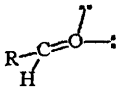
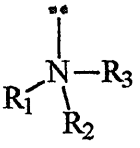
Bond	Compound
	Unshared Electron Pairs
	H—O—H (Water)
	R—O—H (Alcohols, phenols)
	R—CO—O—H (Carboxylic Acids)
	R—COR =O (Carboxylic Acids, Esters)
	R_1R_2C=O (Ketones, Aldehydes)
	$R—NH_2$ (Primary Amines)
	R_1R_2—NH (Secondary Amines)
	$R_1R_2R_3$—N (Tertiary Amines)

Table 1-6 (Continued)	
π-Electron Systems	
	Benzenes (C_6R_6)
R—C≡C—R	Acetylene's
R—C≡N	Nitriles, cyanides

Hydrogen bonding interactions decrease in strength with increasing temperature and steric hindrances. Hydrogen bonding, though, is one of the strongest selective interactions.

1.4 Analysis of Air Samples

1.4.1 Introduction

In section 1.3, the various ways of obtaining samples of air and the corresponding theoretical considerations were discussed. After the sampling and extraction procedures have been completed the next process is the analysis of the sample. There are several factors that need considering when choosing which method of analysis is to be used.

The initial consideration is what type of sample we have available and what results are required. With this in mind there are several questions that need to be asked:-

- Are there unknown analytes in the sample?
- Do we require qualitative or quantitative results or both?

We should also be asking questions like:

- What is the purpose of the final results?
- And is the sensitivity of the technique suitable for that purpose?

With the widespread availability of advanced techniques such as mass spectrometry, we need to ask if we are using techniques that are too complicated for our needs. Would a simpler detection system give similar (if not better) results?

Many compounds can be determined using both liquid and gas chromatography. We need to choose the correct one.

The final consideration in the choice of analytical technique is based on the equipment the laboratory has available. Also the budget for consumable items such as solvents and gases must be considered.

By asking questions such as these there is a tendency for a wide range of techniques to be used for the analysis of volatile organic compounds in air. The flow chart Figure 1-14 shows the various techniques that have been used.

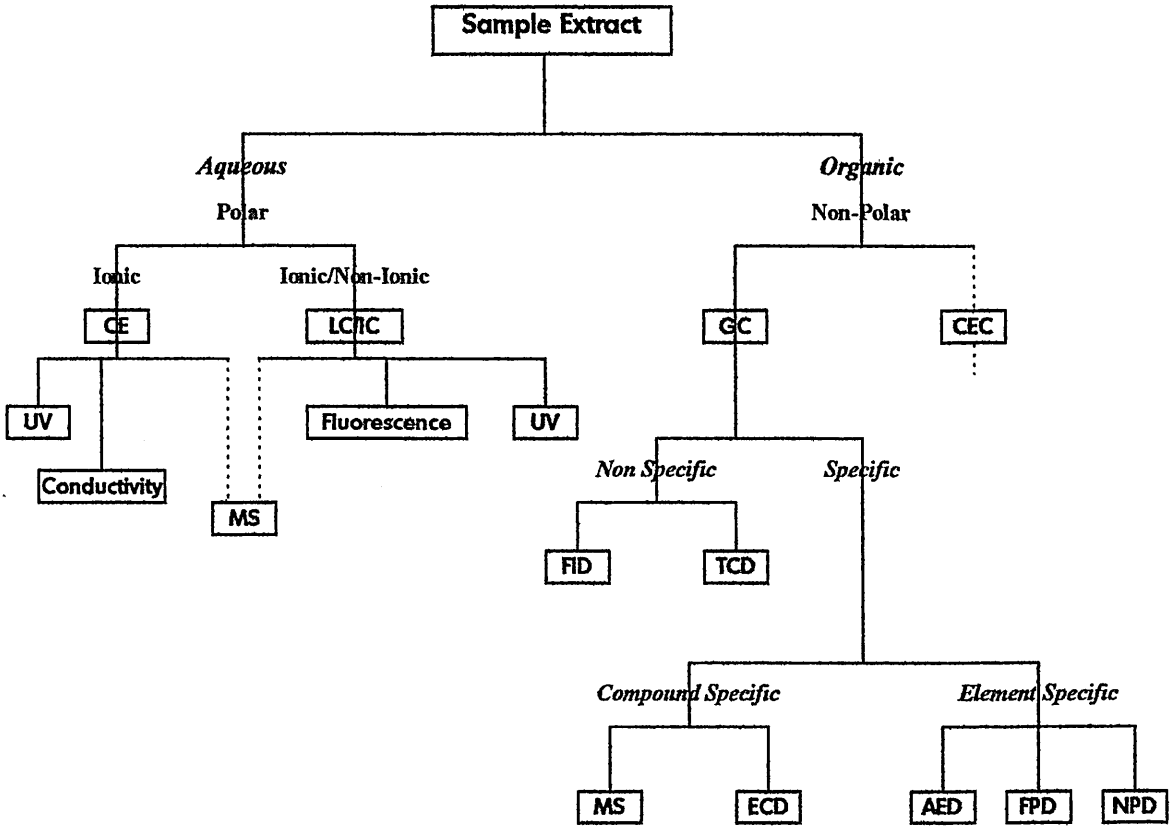


Figure 1-14 - Analytical Techniques Flow Chart

This section will give a brief discussion of the analytical techniques that are used for the analysis of air.

1.4.2 Aqueous Phase Samples

For the determination of polar and ionic compounds many workers use aqueous phase samples for the analysis. Aqueous samples allow the ready dissolution of alcohols, phenols and organic acids. Also some derivatisation reactions occur in the aqueous phase, such as 2,4-dinitrophenyl hydrazine-carbonyl reaction. There are two techniques that are

readily compatible with aqueous phase samples. These are liquid chromatography and capillary electrophoresis.

1.4.2.1 Liquid Chromatography

Liquid chromatography is a technique that is not only well understood but also widely used in analytical science. There are many different facets to liquid chromatography that can, and have been, used for the analysis of air. Techniques included under the term liquid chromatography include ion chromatography, gel permeation chromatography and both normal and reverse phase liquid chromatography.

The detection systems used for LC analysis are not as varied as for gas chromatography. They are generally spectroscopic detectors such as UV/Vis and fluorescence, as well as electrochemical and conductivity. There is a steady increase in the use of mass spectrometry as a detection system but not for routine analysis.

1.4.2.1.1 Organic Acids

The use of adsorption and partition liquid chromatography for the determination of organic acids is limited due to the use of the more sensitive technique of ion chromatography. However, LC methods have been used successfully for such determinations.

Grosjean[42] used LC with UV detection for the analysis of formic and acetic acids. He obtained results that gave levels of formic and acetic acids in the 3.4-5.1 and 2.8-5.55ppb(μg L^{-1}) range respectively.

Zhang *et al.*[108], used a IOA-1000 (Alltech Associates Inc.) organic acids analytical column with a 10mM sulphuric acid mobile phase for the determination of formic and acetic acids in indoor air. Other experimental conditions of note were a detection wavelength of 210nm and a column temperature of 60°C. Results obtained gave formic acid in the ranges of 0-19.2ppb(μg L^{-1}) and 0-3.00ppb(μg L^{-1}) for indoor and outdoor air, and acetic acid in the ranges of 3.6-53.9ppb(μg L^{-1}) and 0-15.2ppb(μg L^{-1}) for indoor and outdoor air respectively. Zhang *et al.*[26], used similar analytical conditions determining formic acid concentration in the range 8.9-46.0 μg/m^3.

Reiss *et al.*[118], also used liquid chromatography to determine the levels of organic acids in residential environments. They reported limits of detection for the determination of formic acid as 1.54ppb(μg L^{-1}) and 0.98ppb(μg L^{-1}) for acetic acid.

Carbonyls

Carbonyl compounds are determined by liquid chromatography as 2,4-dinitrophenylhydrazones. The hydrazones are orange coloured compounds that absorb in the UV region. The hydrazones are formed through an aqueous phase reaction with 2,4-dinitrophenylhydrazine. The reaction (Figure 1-15) that occurs is a simple one that is learned early in the student chemist's career, and is basically an acid catalysed nucleophilic addition of the hydrazine to the carbonyl group.

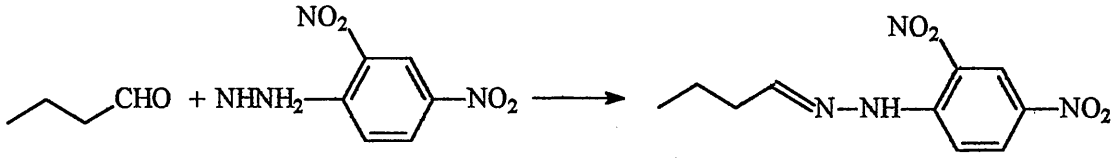


Figure 1-15 - Carbonyl/Hydrazone Derivatisation

There are many publications that use the LC-UV determination for the analysis of carbonyl compounds in air. Kuwata *et al.*[67], using an octadecyl silica packed column and either 70/30 or 62/38% acetonitrile/water, determined a series of C_2-C_6 aliphatic and aromatic carbonyl compounds. Sample detection limits were observed of 0.1ng for formaldehyde, 0.2ng for acetaldehyde, acrolein and propionaldehyde, and 0.5ng for C_4-C_6 aldehydes. Beasley *et al.*[119], also used a C_{18} column but used a 65/35 acetonitrile/water isocratic system and measured absorbance at 254, 336 and 340nm. They found that by measuring at higher wavelengths they managed to obtain a better background signal. Cofer and Edahl[65] used similar conditions but used methanol/water as the mobile phase. Although less polar than the acetonitrile/water system adequate results were obtained. Many workers, due to the simplicity of the system, have used Isocratic analysis. This allows for rapid sample turn around as the time between runs can be minimised, as there is no column equilibration time. The equipment needed for isocratic operation is simple and inexpensive. [29 32 50 120–126]

The use of a gradient system generally gives better chromatographic separation of sample peaks. Dye and Oehme[127] used a ternary gradient system that allowed the separation

of acrolein from other C_3 carbonyls. The system used is shown Figure 1-16 below. Although complicated it was possible to obtain baseline resolution of acrolein, acetone and propanal.

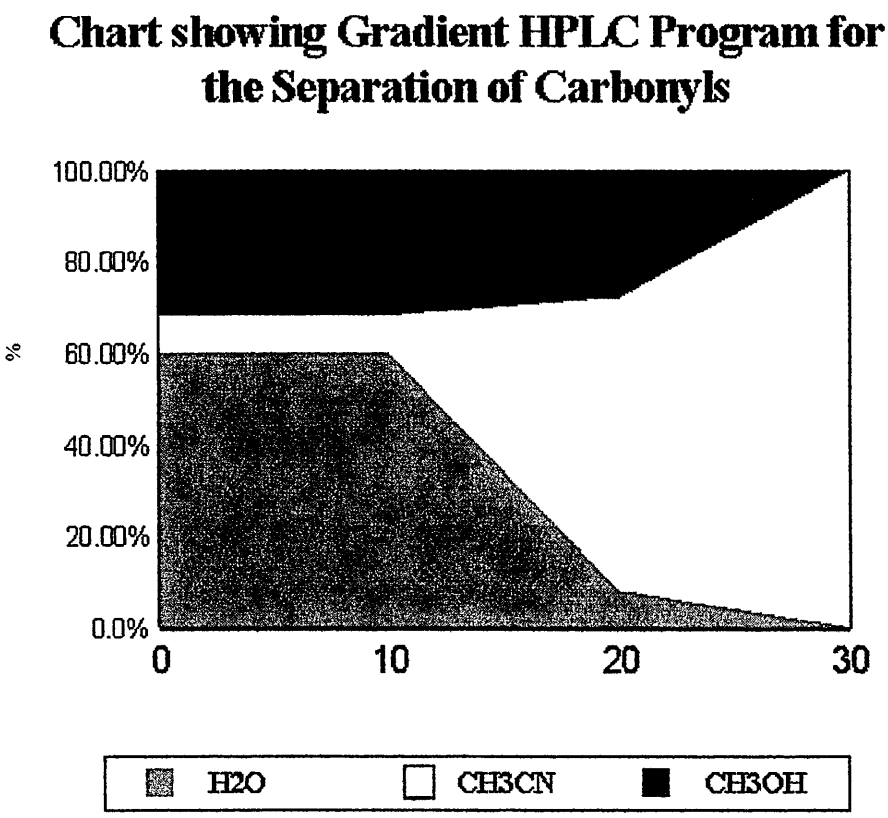


Figure 1-16 - Chart Showing Gradient HPLC Program

Using a detection wavelength of 360nm it was possible to determine 0.2 μg m^{-3}(ng L^{-1}) of acrolein in air.

Zhang *et al.*[20] [26], used a ternary gradient system of acetonitrile, water and tetrahydrofuran with measurement at 360nm. This system was also employed by Reiss *et al.*[118]. Brown et al.[58], used a binary gradient system of water and methanol with measurement at 345nm.

Other Organic Compounds

There are other airborne compounds that have been determined using liquid chromatography. Levin *et al.*[54], used LC for the determination of diethylamine in air, using a

C_{18} column and a mobile phase of 50%water in acetonitrile to determine the diethylamine derivative. Measurement was made at 254nm and a limit of detection of 0.5ng was obtained.

Lindahl *et al.*[55], used a 1:1 acetonitrile-water system with a C_{18} column for the determination of thiourea in air. Derivatives were determined at 254nm, with limits of detection of 0.5ng being found.

Polyaromatic hydrocarbons (PAH) can be determined using either LC or GC. Koo *et al.*[81], used a C_{18} column with a mobile phase of 80/20 acetonitrile/water. Detection was performed using a fluorescence detector. Excitation and emission wavelengths were varied for the different compounds being analysed. Limits of detection were in the 0.01-0.05ng range. This approach was also used by Gardner and Hewitt[128].

1.4.2.2 Ion Analysis

Certain volatile organic compounds that are found in air samples can be determined as ions. These are the organic acids, including mono-, di- and keto- acids. There are three techniques that have been used. These are ion exchange chromatography, ion exclusion chromatography and capillary electrophoresis. All these techniques have been successfully used for the analysis of organic acids in aqueous samples. This review however is limited to air samples.

Ion Exchange Chromatography

Ion exchange chromatography is a form of liquid chromatography that uses a chromatographic column with an ion exchange resin packing. There are two modes of IEC, anion exchange and cation exchange. The separation is achieved through equilibrium of the analyte ions between charged sites on the resin and the mobile phase. With most ion exchange chromatography after the separator column there is a suppressor column, which removes the effects of the eluent from the detector, increasing analyte signal strength.

Dawson and Farmer[22] used IC to determine nitric, formic and acetic acids in air samples taken in South-Western United States. Using a borate buffer they obtained limits of detection of 0.1ppb($\mu g\ L^{-1}$). Using either a bicarbonate or borate eluent Andreae *et al.*[41], determined formic and acetic acids over the Central Amazon region. They measured formate, acetate, pyruvate, and oxalate ions from rainwater, aerosols and from direct air samples. Arlander *et al.*[24], also used IEC for the determination of organic acids in remote

marine tropospheres. Using a sodium tetraborate eluent and a sulphuric acid regenerant for the suppressor column they determined formic and acetic acids. They observed levels of formic and acetic acids in the 0.07-1.72 and 0.07-1.92 ppbv($\mu g\ L^{-1}$) ranges respectively.

Ion Exclusion Chromatography

Ion exclusion chromatography is a technique that utilises the differences in the charge of ionic species between the solution and the resin particles and the sorption properties of the analytes, to effect a separation.

Grosjean *et al.*[44], used IEC for the determination of organic acids in various air samples. Using a polystyrene-divinylbenzene sulphonate column and a 5mM sulphuric acid eluent they obtained limits of detection of 14 ng for formate and 34ng for acetate. Detection was by UV at 210nm. Analysis time was reported as 2 minutes for formate and 4 minutes for acetate.

Hekmat and Smith[106], also used IEC for the determination organic acids in air using a commercial column and detection with conductivity detector. The eluent used was 1mM pentadecafluoroheptanoic acid in 15% isopropyl alcohol.

Capillary Electrophoresis

Capillary electrophoresis is a technique that has great potential for ion analysis. It employs a fused silica capillary as the support medium, instead of a gel or paper as is used in other electrophoretic techniques. It is possible to obtain high resolution, and rapid analysis times using the minimum amount of solvent and sample. Development work in CE has been mainly in the biological sciences with the separation of large molecules such as peptides and oligonucleotides. However its use for the separation of low molecular weight organic acids in air, has been reported.

Röder and Bächmann[47] used an electrolyte system based on *p*-aminobenzoate for the determination of organic anions from rain water. Electroosmotic flow modification was by tetradecyltrimethylammonium hydroxide. The system used operated at high pH. This has two effects. Primarily the acids are in the completely ionised form thus reducing any problems. Secondly this aids the ionisation of the silanol groups on the surface of the capillary. Using a separating voltage of -30kV it was possible to separate 27 anions in 30 minutes. They also report a detection limit of 30nmol L^{-1}. Tenberken *et al.*[129], used a similar

system for the analysis of compounds in single raindrops. They also reported the use of a phosphate/borate buffer for the analysis of derivatised carbonyls.

1.4.3 Organic Phase Samples

As organic solvent phases are more compatible with the most frequently used sampling phases, it therefore follows that the majority of analyses connected with the study of volatile organic compounds in air use organic solvents. Unlike aqueous phase samples, samples in the organic phase cannot be generalised as polar or non polar. The diversity of solvents does mean, however, that it is possible to obtain a high degree of compound selectivity in the samples. By careful choice of solvent, column and operating conditions it is possible therefore to determine most compounds that are found in the atmosphere. In reviewing the analytical methods that are used with the organic phase samples we find that the majority use some form of gas chromatography.

1.4.3.1 Gas Chromatography

Gas chromatography is possibly the most common analytical technique that is used in the laboratories of the world and as such is used for the majority of organic phase samples. Since its beginning in late 1952[130], GC, has developed into a highly sophisticated and diverse area of analytical science. Yet as the detectors and oven control systems become more technologically advanced the fundamentals of the technique have remained virtually unchanged.

In reviewing the use of GC in the analysis and study of organic compounds in air we find that many applications use the same type of column and that many of the column operating conditions are very similar. Of more importance are the types of detectors that are used and the selectivity given by those detectors. Detectors can be divided into two classes, specific and non-specific.

Non-specific detectors include the flame ionisation detector (FID) and the thermal conductivity detector (TCD). These detectors are simple in use, cheap, and widely used. They are considered to be universal detectors.

The TCD was one of the first detectors available for gas chromatography. It consists of a tungsten-rhenium filament that is set at a fixed temperature.[131] When the carrier gas is flowing over the filament the conductivity through the filament remains constant. When

column eluent containing compounds other than the carrier gas pass over the filament there is a change in the thermal conductivity of the gas stream, the filament temperature increases therefore the resistance increases, and a change in signal is monitored.

Thermal conductivity detectors have very poor sensitivity and as such are not used for trace analysis. However their universality makes them ideal for the analysis of macro constituents of the air such as O_2, N_2 and CO_2.[132]

The FID is possibly the commonest detector used with gas chromatography. The flame is produced by mixing the column eluate with H_2 and air. Inside the flame, carbon atoms produce CH• radicals, which then further produce CHO+ ions. The CHO+ ions carry a current to the cathodic detector situated above the flame (the anode being the flame tip jet). Changes in current are recorded as the signal. There are some exceptions, carbonyl and carboxyl carbons and inorganic certain compounds such as carbonyl and carboxyl carbons do not produce responses from the FID.

Since the advent of specific detectors, the use of the FID in current research is slowly decreasing. However there are some exceptions. Karpe *et al.*[75], used an FID in conjunction with mass spectrometry and a sniffer device for the determination of odorous volatile organic compounds in air. The apparent complexity of this apparatus does have advantages when examined more closely. The FID and sniffer device are connected to the same column thus allowing correlation between the two. The MS, due to its need to operate under vacuum, is connected to a different column, and is used for the identification of the VOC's. By comparing FID, MS and sniffer results it is possible to determine the effects of odorous compounds on various environments.

Grob et al.[110], used an FID/ECD combination for the determination of volatile organic compounds in air. Using a form of thermal desorption they obtained results with limits of detection of 1-3 $\mu g\ m^{-3}$ ($ng\ L^{-1}$) for benzene and toluene. Poy and Cobelli[132], used an FID in conjunction with a TCD for the determination of light hydrocarbons in air. Lewis *et al.*[74], used an FID for field measurements of isoprene, methacrolein, methyl vinyl ketone and other monoterpenes. Detection limits of 0.2ppb($\mu g\ L^{-1}$) were recorded as was a linear range between 0.2-100ppb($\mu g\ L^{-1}$). The FID is a useful general detector with relatively good sensitivity. The robustness and proven "track record" of this system make it ideal for general

use. However, as discussed, there is a limit to the information that can be obtained from an FID.

Specific detectors range from electron capture detectors (ECD) to atomic emission detectors (AED). The specific detectors give more information about the compound than do the non-specific detectors. These detectors range in complexity and are generally more expensive than non-specific detectors. Specific detectors are available in two classes, compound specific (ECD, MS) and element specific (NPD, AED).

The ECD is a detector that is specific for compounds that contain electrophilic groups, such as halogens. It is in this field that this detector has found most use. The ECD, however, is not a halogen specific detector. Ionisation of the carrier gas by the β-particles, emitted from a Ni^{63} source, releases electrons that generate a current within the detector. As electrophilic compounds pass through the detector with the column eluent the electron current drops as the analytes capture the electrons. This drop in current is recorded as the signal.[133]

Electron capturing groups are known as electrophores. Halogens are generally regarded as good electrophores but there are differences. Table 1-7 shows a comparison of electron affinities for a series of halobenzenes. The data is shown relative to chlorobenzene, which has an affinity of 1. [134]

Table 1-7 - ECD Halogen Electron Affinities

Compound	Affinity
Chlorobenzene	1
Bromobenzene	6
Iodobenzene	370
Hexachlorobenzene	1100

The data shows that there is some selectivity with a greater response than bromobenzene and chlorobenzene. The data also shows that compounds containing multiple electrophores give a non-linear response, e.g. hexachlorobenzene has an affinity that is three orders of magnitude greater than that for chlorobenzene, rather than six times as might be expected.

Other compounds or functional groups that can be considered electrophores are nitrates and quinones.

Lehmpuhl and Birks[135] used an ECD for the determination of derivatised carbonyl compounds. Using 2,4,6-trichlorophenylhydrazine as a derivatising agent they produced electrophilic hydrazones which gave a response when passing through the detector. Detection limits were typically of the order of 0.02-0.03ppbv($\mu g\ L^{-1}$), with the exception of formaldehyde, which gave a LOD of 0.1ppbv($\mu g\ L^{-1}$),

Mass spectrometry is a compound specific method of detection. Usually the column eluents is ionised by a beam of electrons, with the energy imparted by the electrons causing the ionisation and fragmentation of the compounds. Each compound or functional group gives fragment ions of characteristic mass and abundance. From the characteristic spectra given by these fragments compound identification is possible.

The use of mass spectrometers as detectors for gas chromatography is well established in all fields of analytical chemistry. Since the development and production of relatively cheap bench top mass selective detectors by companies such as Hewlett-Packard and Finnigan MAT many laboratories find both routine and research use for such equipment. Thus GC-MS is replacing the FID as the most commonly used detector for routine analysis.

GC-MS is frequently used for the analysis of air. Riedel *et al.*[72], used GC-MS for the determination of benzene and alkylated benzenes in air. Limits of detection reported were 1.6ng for benzene, 3.0ng for toluene, 0.2ng for ethylbenzene, 1.4ng for *m* + *p*-xylene and 0.4ng for *o*-xylenes. Black *et al.*[136], used GC-MS as the detection system for the analysis of chemical warfare compounds. Using the compound specific information obtain from the MS they were able to establish the presence of chemical agents on bomb fragments collected in Northern Iraq.

Most GC-MS systems are equipped with computer based spectral libraries that allow the rapid, though sometimes tentative, identification of species. Although reliance on library results as a sole means of identification can give misleading results, if used in conjunction with the masses of selected ions and retention time data from standards, satisfactory results can be obtained.

Such an approach was used by Ciccioli *et al.*[73], when studying atmospheric volatile organic compounds. Results showed the separation of some 137 peaks in 40 minutes. Using selected ion monitoring, (i.e. measuring just the characteristic ions as opposed to full spectra), retention indices and known standards they were able identify the majority of the

compounds. Heavner *et al.*[78], also used this approach to monitoring volatile organic compounds in indoor air. Using target ions they detected compounds that were specific to environmental tobacco smoke such as 3-ethenylpyridine, with limits of detection in the range 0.09 - 3.37ng per sample.

Unlike the other detectors described so far the nitrogen-phosphorus detector is element specific, meaning that more specific information about the compounds being analysed can be obtained, i.e. is there a nitrogen atom present? The NPD is similar in construction to that of the flame ionisation detector, with the addition of a bead or ring of an alkali metal salt, e.g. KCl, around the flame jet. The potassium is thermally ionised producing a constant current between the jet tip and the cathode, which is 100 times higher than the basic current in an FID. This in effect causes a plasma, which when compounds enter it, only those containing nitrogen or phosphorus elicit a responce. Variation in the conditions, i.e. H_2 flow changes the selectivity of the detector.[137]

The prime use of the NPD for air samples has been for the analysis of atmospheric compounds that contain either nitrogen or phosphorus atoms. Andersson *et al.*[138], determined N-methylmorpholine in workplace air using an NPD. They present results that show comparison for the FID detection. The NPD had a limit of detection of 0.05ng compared to 0.5ng for FID. Fulcher *et al.*[139], also used an NPD for the determination of atmospheric acrylonitrile. The use of an NPD for the determination of nitrogen containing derivatives is another use that has been reported in the literature. Stashenko *et al.*[140], used an NPD to determine derivatised saturated volatile aldehydes. The derivatising agent that was used was 2-hydrazinobenzothiazole, a compound containing three hetero-nitrogen atoms.

Element specific detection has been used for many years with techniques such as atomic absorption spectroscopy and inductively coupled plasma spectroscopy. These systems are not compatible with the low carrier gas flow rates used in gas chromatography. With the advent of the atomic emission detector, however, chromatographers now have the capability to gain extra information about the analytes that is not available from compound specific techniques such as mass spectrometry.

The atomic emission detector uses a microwave induced helium plasma (MIP), which, although having less energy than an ICP, has sufficient to atomise the column eluent,

and causes excitation of the fragments. The subsequent electronic rearrangements cause the emission of light energy, which is monitored.

Yamashita *et al.*[76], used AED in conjunction with GC-MS in the determination of volatile organic compounds in air. Using the Cl_{479nm} and the C_{496nm} emission lines, they could confirm results obtain from GC-MS. Similar work was performed by Clarkson and Cooke[141], for the identification of volatile components of tobacco aroma.

1.5 Air Quality

1.5.1 Introduction

Air and water are the two main ingredients for life. Without either, it would rapidly cease. In Western society, as we pay the utilities for our water, the quality is now taken for granted. We accept that if we drink contaminated water, that is water of poor quality, we can expect illness. So, using this logic, we must assume that if we inhale poor quality air we can expect some adverse effects, from mild discomfort as with certain odours to serious illness. Air is a commodity that does not come from a tap however, and as such its quality is not easily controllable and also is generally not known.

In the previous sections we have discussed the role that several organic compounds have in the atmosphere, and how they are affected by anthropogenic intervention. We have also examined the methods used to determine and monitor these and other compounds. This section will be examining the effects atmospheric compounds have on human health and how they affect air quality.

1.5.2 Environmental Factors of Air Quality

There are several environmental factors that need to be considered in relation to air quality. These include air types and the sources of indoor VOC.

1.5.2.1 Air Types

Air is a dynamic mixture, that is constantly in motion, either by mass transport through the wind or on a micro scale through vibration, convection and diffusion. Also the composition of air is dynamic, through the continuous addition and removal of compounds.

There are two *types* of air that are important when discussing air quality: indoor and outdoor.

The bulk of the atmosphere can be defined as outdoor air. Outdoor air is the most dynamic portion of the atmosphere. It is exposed to intense ultra-violet light, dramatic temperature changes, and the effects of the weather. There are many sources that emit into outdoor air, including anthropogenic, geogenic and biogenic. Contrary to media reports it is biogenic sources that add the greatest mass of compounds to the atmosphere annually.

Generally, Europeans and North Americans spend up to 90 percent of their time indoors, consequently, it is indoor air that we breath most.[142] The indoor environment is generally very controlled. Thus, effects of UV and weather are limited. Although there is an interchange between the outdoor and indoor environments, indoor air is very much affected by the indoor environment itself.

1.5.2.2 Sources of Indoor Volatile Organic Compounds

The volatile organic compounds that are found in air come from a variety of different sources, both biogenic and anthropogenic. Several of these have already been discussed in earlier sections. The major anthropogenic source of VOC in the outdoor environment is the motor car, whereas plant life is the major biogenic source. There is some overlap between compounds that are naturally released into the atmosphere and those that can be considered pollutants (Section 1.2.2.).

Indoor air, however, is different. The relatively closed system of the indoor environment is the major contributor to the air quality found there. The indoor environment is complex in that it differs from building to building and activity to activity.

1.5.2.2.1 Building Materials

The first major source of volatile organic compounds in indoor air to consider is the materials used in the construction and decoration of the building. These materials are generally permanent and are only removed on the renovation or destruction of the room or building. Table 1-8 shows the volatile organic compounds that have been found to be emitted from materials that are used in the building and furnishing of the indoor environment. These materials, therefore, emit into a closed environment. Due to the low UV conditions the major source of removal is through ventilation.

Table 1-8 - Sources of Volatile Organic Compounds from Building Materials

Source	VOC's Observed	Ref.s
Adhesive	C_9-C_{11} Alkanes, toluene, styrene	96,
Carpets	C_3-C_6 Alkyl aromatics, styrenes, 4-phenylcyclohexene, vinylcyclohexene, 2-ethylhexanol, siloxanes, amines	143, 144
Wood	C_5-C_6 Aldehydes, terpenes	96,
Particle board	Alkanes, aldehydes, butanol, formaldehyde, ketones	145
Sealant	Ketones, esters, glycols, polychlorinated biphenyls, siloxanes	146, 147
Paint	Alkanes, glycols, glycol esters, texanol	96,
Textiles	Acetone, ethyl acetate, methyl furan, thiophene, dimethyl disulphide	148
Wall Paper	Hexanal, terpenes	149

Due to their permanent nature, it must be assumed that emissions from building materials are constant. But emissions from human activity will be subject to temporal variations. [96] The concentrations of VOC could also vary due to reactions with compounds such as ozone.

1.5.2.2.2 **Human Activity**

The activities of humans in buildings are another source of volatile organic compounds. The type of VOC that is emitted by human activity is dependent on the function of that building. Domestic homes will have different VOC emissions than office buildings. Furthermore modern office buildings with air conditioning will have different VOC profiles to older buildings.

Table 1-9 - Sources of Volatile Organic Compounds from Human Activity

Source	VOC's Observed	Ref.s
Household products	A variety of different polar and non-polar VOC's including fragrances	[150], [151]
Human Emissions	A variety of different VOC's	150,151
	Ethanol, methanol, acetone, butyric acids, isoprene, toluene, phosphine	[152],
Room Freshener	Alkanes, limonene, fragrances	151, [153]
Correction fluid	Chlorinated hydrocarbons	150
Personal Care Products	Siloxanes, oxygenates particulates	[154]
Environmental Tobacco Smoke	Aliphatic hydrocarbons, aldehydes (+formaldehyde, acrolein), benzene, styrene, 3-vinylpyridine, 2- and 3-picolines	151, [155]
Shampoo	Ethylene glycol butyl ether	150

Table 1-9 shows the volatile organic compounds that are emitted from sources that are related to human activity. It is worth noting that environmental tobacco smoke (ETS) is the source of the widest range of both VOC's and particulate matter.

1.5.2.2.3 **Bioeffluents**

Bioeffluents are another source of volatile organic compounds in indoor air. Wang[152] classified the bioeffluents into four categories (Table 1-10), depending on function.

Table 1-10 - Table Showing Classes of Bioeffluent

Category	Source
Oral	Expired Air
Dermal	Skin, sweat
Urinary	Urine
Faecal	Faeces, flatus

Wang, using a college classroom as a closed system, found that dietary variations gave differences in levels of the bioeffluents studied. Also observed were higher concentrations of certain VOC's under conditions of stress. For this study examinations were used. Another finding of note, was that there was some sex differentiation in the levels of methanol observed. It was found that mostly male classes produced higher levels than female classes.

1.5.3 Health Factors

The purpose of determining air quality is to assess the effects of the environment on the human individual and to gain knowledge that may improve public health. Humans are one of the most adaptable animals known, living in environments from extreme cold to extreme heat. Yet, even with this adaptability, humans only have certain tolerances to external chemical compounds, both in water and air. Once these tolerance levels have been exceeded discomfort and illness usually occur. Such compounds enter the body through the respiratory system, the membranes of the eyes and the skin.

Although this work is not clinically based, in investigating the effects of atmospheric compounds on air quality it is interesting to discuss the toxicological, physiological and epidemiological effects of air quality.

1.5.3.1 Basic Physiology

The respiratory system (Figure 1-17) provides oxygen to the cells of the body and removes waste carbon dioxide from them. There are three parts to the respiratory system: the nasopharyngeal structure, the conducting division and the respiratory division. As air is passed through the nasopharyngeal structure it is warmed and moistened before passing into the conducting division. The conducting division, (trachea and bronchioles) are the tubes that carry air into the lungs. Mucus glands line the walls of the tubes and cilia, or hair cells, transport particulate matter slowly up the throat. The respiratory division begins with tubes that branch off the terminal bronchiole, called respiratory bronchioles, and end in small alveoli. It is in the alveoli that oxygen and carbon dioxide are passed between the air and the blood. Particles that reach the alveoli may also be absorbed into the bloodstream.[142]

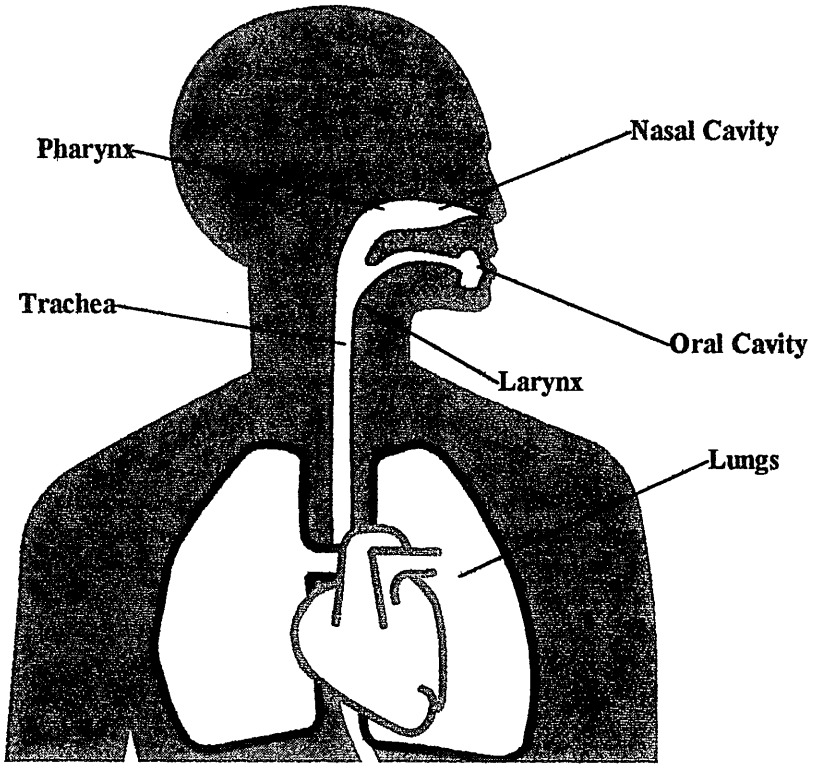


Figure 1-17 - A Diagram of the Respiratory System

As well as transporting oxygen into the body the respiratory system may also transport any other compound and particles that are present in the air. Compounds and particles entering the lungs may cause damage to the lung membranes or even be transported through to other parts of the body.

1.5.3.2 Respiratory Diseases

Poor air quality and air pollution are thought to aggravate several respiratory diseases. These diseases include bronchial asthma and chronic bronchitis.[156]

1.5.3.2.1 Chronic Bronchitis

Bronchitis is caused by either pathogenic infections or by respiratory irritants. Such irritants are associated with cigarette smoke, industrial, ambient and indoor air pollutants. Inflammation of the membranes that line the bronchioles is characteristic of bronchitis. This is a disease of the upper respiratory tract. When this inflammation persists for over three months it is termed as chronic. Characteristic symptoms of chronic bronchitis are a persistent

cough and excessive mucus production. Damage to the cilia and thickening of the membranes may also occur. Inflammation to the bronchial membranes restricts the airways and thus the person may have difficulty in breathing.

One of the main factors in chronic bronchitis is cigarette smoke. This causes difficulty in determining whether ambient air pollution has a major role in aggravating the condition. However studies suggest that ambient pollutants such as SO_2 and particulate matter may contribute to the initiation of the condition under conditions of chronic community air pollution.

1.5.3.2.2 **Pulmonary Emphysema**

Pulmonary emphysema is a disease of the gas exchanging tissues deep in the lung. It is characterised by the degeneration or destruction of the walls of the alveoli and the associated capillary blood vessels. This reduces the total lung surface area, leading to reduced aeration of the blood. Pulmonary hypertension is often associated with emphysema as well as increased pulmonary resistance. This leads to the patient suffering from shortness of breath, and difficulty in exhalation causing over inflation of the lungs.

There is little epidemiological evidence to suggest that ambient pollutants are involved in the initiation and development of emphysema. However animal studies have shown that chronic exposure to NO_x can initiate pre-emphysematous changes to the tissues of the lungs.

1.5.3.2.3 **Lung Cancer**

Cancer is a disease of unrestrained cell growth producing malignant tumours. These tumours have a higher growth rate than surrounding cells. Malignant tumour tissue compresses, invades and destroys normal tissue. Tumours can also spread to other parts of the body causing secondary growth elsewhere. Lung cancer cells have a higher tendency to spread, or metastasise. Lung cancer patients have a 92% mortality.

Lung cancer has a long latent period between exposure to a carcinogenic agent and the onset of the disease. This makes identification of specific agents difficult. This long period of latency can also give individuals a false sense of security to the dangers of the compounds to which they are exposed.

Lung cancers that originate in the bronchial membranes are the commonest. The malignancy spreads through the bronchial tree, to the rest of the lungs, and to other parts of the body, usually the brain.

A major proportion of the deaths through lung cancer is caused by chronic exposure to tobacco smoke. Other causes are exposure to asbestos, arsenic, radioactive gases and dusts. There is contradictory evidence as to whether ambient air pollutants are casual agents for lung cancer.

1.5.3.2.4 **Bronchial Asthma**

Asthma is the narrowing of the smaller air ways in the lungs caused by constriction of respiratory muscles, swelling of the airway walls, excessive mucus production and greatly increased airway resistance. An asthma attack, can occur suddenly and without any warning symptoms, causing the sufferer to experience extreme shortness of breath.

Asthma may have a number of causes, including allergenic reactions. However a wide range of pollutants that act as non-specific irritants may induce attacks.

1.5.3.3 Pollutants

A given mass of air may contain hundreds of different compounds.[73, 157] Of these only a relatively small number are thought to cause any adverse health affects at the levels experienced in ambient air. According to Koltai[158], there are three categories of pollution. These are the complexes of sulphur dioxide, photochemical complexes of ozone and nitrogen dioxide, and a mixed assortment of toxic agents and heavy metals. Although this generalisation of pollutants tends to ignore specific compounds it is a good starting point for a review of the effects of certain compounds on the human body. These compounds are regulated in the United States by two standards, the National Ambient Air Quality Standards (including CO, O_3, HC and NO_x) and National Emission Standards for Hazardous Air Pollutants (benzene, lead).[156]

1.5.3.3.1 **Sulphur Dioxide**

Sulphur dioxide is a very soluble gas that is removed from inhaled air by moisture in the nasopharyngeal structure. Only about 1% of inhaled SO_2 is thought to reach lung tissue. The principal effects of SO_2 exposure are therefore on the upper respiratory tracts. These

include increased nasal flow resistance and reduced rate of mucus flow. SO_2 effects start at relatively low concentrations (0.25 to 0.5ppm(mg L^{-1})), and so could cause broncho-constriction in strenuously exercising asthmatics.

The health effects associated with SO_2, may really be attributed to the highly irritating effects of sulphate aerosols which are produced from SO_2.

1.5.3.3.2 **Carbon Monoxide**

Carbon monoxide acts on the haemoglobin in the blood by binding to the sites normally occupied by oxygen. Haemoglobin has a greater affinity for CO (to form a carboxyhaemoglobin complex) than it does for O_2. This impairs the transport system that moves O_2 around the body. Carbon monoxide is highly toxic in concentrations exceeding 1000ppm(mg L^{-1}). These levels are not encountered in ambient air, however, even ambient levels can have some effects on the level of saturation of the haemoglobin. The physiological effects of increasing levels of carboxyhaemoglobin (COHb) saturation are shown in Table 1-11.

Table 1-11 - Effects of Carboxyhaemoglobin Saturation

Blood COHb Level	Effects
0-1%	None
2.5%	Impairment of time interval discrimination in non smokers
2.8%	Onset of *angina pectoris* pain shortened in exercising patients; duration of pain lengthened.
3.0%	Changes in relative brightness thresholds
4.5%	Increased reaction time to visual stimuli
10%	Changes in performance in driving simulation
10-20%	Headache, fatigue, dizziness, loss of co-ordination

Arteriosclerosis, and other central nervous system disorders, are associated with exposure to increased levels of carbon monoxide Carbon monoxide is a major by-product of tobacco smoking, and might account for many of the physiological symptoms associated with smoking. Cigarette smokers expect COHb saturation levels of 3-8%. These levels are more significant than the ambient levels experienced by non-smokers.

It is known that the level of COHb production in the blood is directly related to the CO dose, for example, exposure for one hour to 35ppm(mg L^{-1}) carbon monoxide, or 9ppm(mg L^{-1}) carbon monoxide for 8 hours, will result in 1.3% COHb saturation. Figure 1-18 shows the carbon monoxide levels for the ambient air in Sheffield City Centre.[159] It shows that for a period of 36 hours there were elevated levels of carbon monoxide in the city centre. Although these levels are low compared to those observed around tobacco smoking, pollution events may have some effect on the carboxyhaemoglobin saturation.

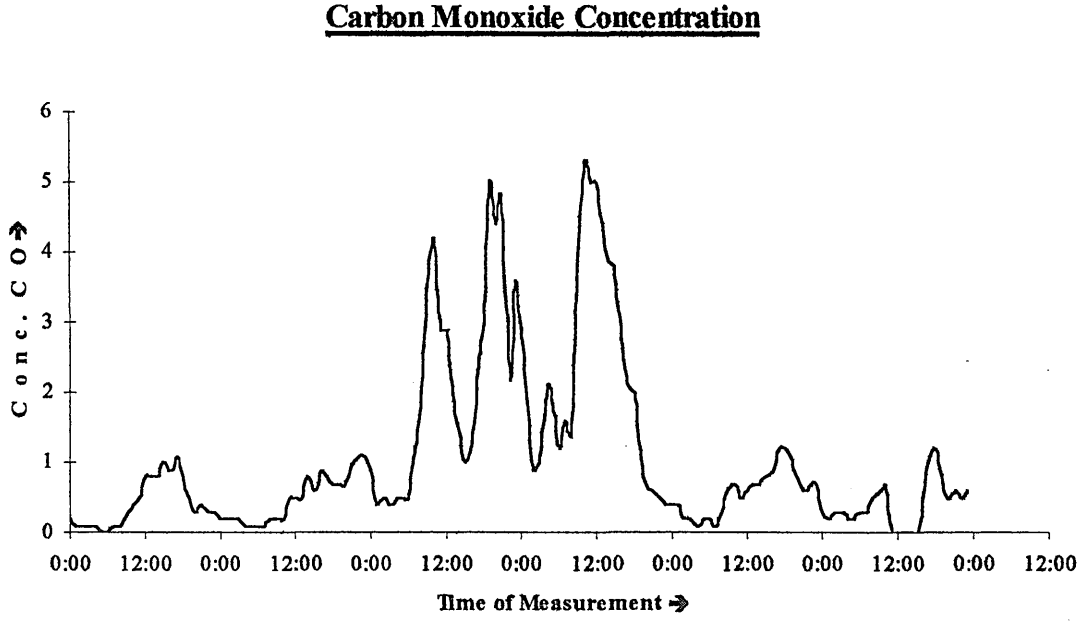


Figure 1-18 - Diagram Showing Daily Carbon Monoxide Variations

1.5.3.3.3 **Ozone**

Ozone causes significant physiological and pathological changes in humans in the ranges that are observed in polluted ambient air. The NAAQS for ozone is 0.12ppm(mg L^{-1}) (235 μg m^{-3}(ng L^{-1})) averaged over 1 hour. At exposures in the range of 0.1-0.4ppm(mg L^{-1}) (196-784μg m^{-3}(ng L^{-1})) for 1-2 hours significant changes in lung function have been

observed. These include increase respiratory rates and pulmonary resistance and decreased tidal volume. After the exposure is discontinued the lung function returns to normal. Even at the NAAQS symptomatic responses are observed in adults including dryness of throat, chest tightness and pain on deep inhalation.

Although ozone does not facilitate asthmatic attacks it is thought to make the lungs responsive to other inhaled substances which in turn could trigger some response. Results of studies have shown that some lungs adapt to prolonged exposure of ozone with the effective response by the lungs decreasing. The adaptation is thought to persist for up to a week after the cessation of the exposure to others. However, although the lung appears to adapt, damage to lung tissue still occurs!

1.5.3.3.4 **Nitrogen Oxides**

Nitric oxide and nitrogen dioxide are the two compounds that comprise NO_x. Nitric oxide is thought to have no adverse health effects, but is easily oxidised to NO_2. Nitrogen dioxide is a gas that, due to its reduced solubility, penetrates deep into the lungs where tissue damage is thought to occur.

Toxicological studies have suggest that NO_2 may be a causal or an aggravating agent in respiratory infections. There is evidence to suggest that NO_2 damages the respiratory defence mechanisms thus allowing the invasion by bacteria and subsequent proliferation of the lungs by bacteria.

1.5.3.3.5 **Hydrocarbons**

As already discussed in section 1.1, non-methane hydrocarbons play a major role in the production of ozone in the atmosphere through photochemical degradation. Therefore air quality standards and controls are enforced. However there are several hydrocarbon chemicals that are controlled. These include formaldehyde, acrolein and peroxyacyl nitrate (irritant) and benzo(*a*)pyrene (carcinogen). There is a threshold range of 0.1-1.0ppm(mg L^{-1}) for HCHO-induced eye irritation.

1.5.3.3.6 **Benzene**

The major sources of atmospheric benzene are emissions from motor vehicles and evaporation of petrol during storage, handling and distribution. Benzene is also released into

the atmosphere from plant and animal matters, as well as from the burning of wood and organic material, such as tobacco. Tobacco smoke contains 204 mg m^{-3} (μg L^{-1}) of benzene.[160] This is considered to be high.

Approximately 50% of inhaled benzene is absorbed by the body. This constitutes an average daily intake of 160μg per day based on an average ambient benzene concentration of 16 μg m^{-3}(ng L^{-1}).

Benzene is carcinogenic to humans, with leukaemia being the form of cancer contracted. A study of approximately 600 benzene exposed workers found a relative risk of 3.75:1 at exposure levels of 1-30ppm(mg L^{-1}).[161]

Dependant on traffic volume benzene levels of 3-30μg m^{-3} (ng L^{-1}) have been observed in residential areas (a daily intake of 30-300μg). This daily intake is increased somewhat when tobacco smoking is considered. A person smoking 20 cigarettes per day has an approximate benzene intake of 600μg.

1.5.3.3.7 **Toluene**

Toluene is the most abundant non-methane hydrocarbon in the troposphere. As discussed in section 1.1 it photochemically degrades to a wide range of compounds. The principal sources of toluene emissions are from petrol, both use and marketing, as well as paints, thinners and tobacco smoke. Toluene, therefore, is an anthropogenic compound, the sources and concentrations levels of which vary between areas. Table 1-12 shows the observed concentration ranges for toluene in various environments.

Table 1-12 - Estimated Toluene Exposure Levels

Type of Exposure	Observed Concentration Range[162]
Urban Areas	0.1-204 μg m^{-3}(ng L^{-1})
Rural and Remote Areas	trace to 3.8 μg m^{-3}(ng L^{-1})
Areas near Manufacturing and User Sites	0.1-20 mg m^{-3}(μg L^{-1})
Indoor (non-industrial)	17-700 μg m^{-3}(ng L^{-1})
Cigarette Smokers	0.1 mg per cigarette

Toluene is considered to be narcotic in nature affecting the central nervous system. Unlike benzene, however, toluene appears to have no mutagenic or carcinogenic effects. Toxicological studies have shown that toluene concentrations of greater than 375 mg m^{-3} ($\mu g\ L^{-1}$) show CNS alterations that cause fatigue, confusion and lack of co-ordination. Additionally, studies have shown that acute low level exposure of 1 mg m^{-3} ($\mu g\ L^{-1}$) will have an effect on electroencephalogram activity in the subjects. Toluene has an odour detection threshold of 1 mg m^{-3}($\mu g\ L^{-1}$). [163]

1.5.3.3.8 **Formaldehyde**

Formaldehyde is one of the simplest organic compounds that is found in the atmosphere. As already discussed in section 1.1, formaldehyde plays a pivotal role in the chemistry of the atmosphere and the carbon cycle. There is a natural background level in the low $\mu g\ m^{-3}$(ng L^{-1}), with an average annual background in the 0.005-0.01mg m^{-3} ($\mu g\ L^{-1}$) range. Indoor air concentrations, especially in buildings where chipboard and other prefabricated materials are used are in the 0.1-5.0mg m^{-3} ($\mu g\ L^{-1}$) range.

Other sources of formaldehyde include tobacco smoke, with 60-130mg m^{-3} ($\mu g\ L^{-1}$) being determined in mainstream cigarette smoke. Environmental tobacco smoke constitutes 10-25% of total indoor air exposure. Table 1-13 show the contributions of various daily atmospheres to the total daily exposure to formaldehyde. It can be seen that indoor air and smoking are important factors in the levels of exposure.

Table 1-13 - Contributions to Formaldehyde Exposure

Source	mg/day[164]
Air	
Ambient Air (10% of time)	0.02
Indoor Air	
Home (65% of time)	
- conventional	0.5-2.0
- prefabricated (chipboard)	1.0-10.0
Workplace (25% of time)	
- without occupational exposure	0.2-0.8
- with 1mg m^{-3} ($\mu g\ L^{-1}$) occupational exposure	5.0
- with environmental tobacco smoke	0.1-1.0
Smoking (20 cigarettes/day)	1.0

The symptoms of short-term exposure to formaldehyde include eye, nose and throat irritations, as well as exposure dependent discomfort, lachrymation, sneezing and nausea. Symptoms are often more severe at the start of the exposure episode diminishing after a period of time ranging from minutes to hours. Eye irritation is experienced between the concentration ranges of 0.01-1.2 mg m^{-3}, ($\mu g\ L^{-1}$) with throat irritation between 0.1 and 1.9 mg m^{-3}($\mu g\ L^{-1}$).

Studies suggest that formaldehyde is a potential factor in inducing respiratory tract infections in certain groups, especially children.

Formaldehyde is also thought to be carcinogenic in animals, but, as yet, there are insufficient data for humans available.[165]

1.5.4 Air Quality Issues

Environmental tobacco smoke and sick building syndrome, along with the motor car, are associated in the media with poor air quality. Although related, the understanding of both will give a fuller picture of air quality issues.

1.5.4.1 Sick Building Syndrome

Sick building syndrome (SBS) is a phenomenon associated with new or recently refurbished buildings, where the occupants suffer illness. The symptoms of the illness generally follow a similar pattern of headaches, dizziness, unusual fatigue, eye, nose and throat irritations and shortness of breath. The occurrence of the symptoms is shown in Figure 1-19. It can be seen that the symptoms reported are generally mild, with only 15% of cases experiencing nausea.[156]

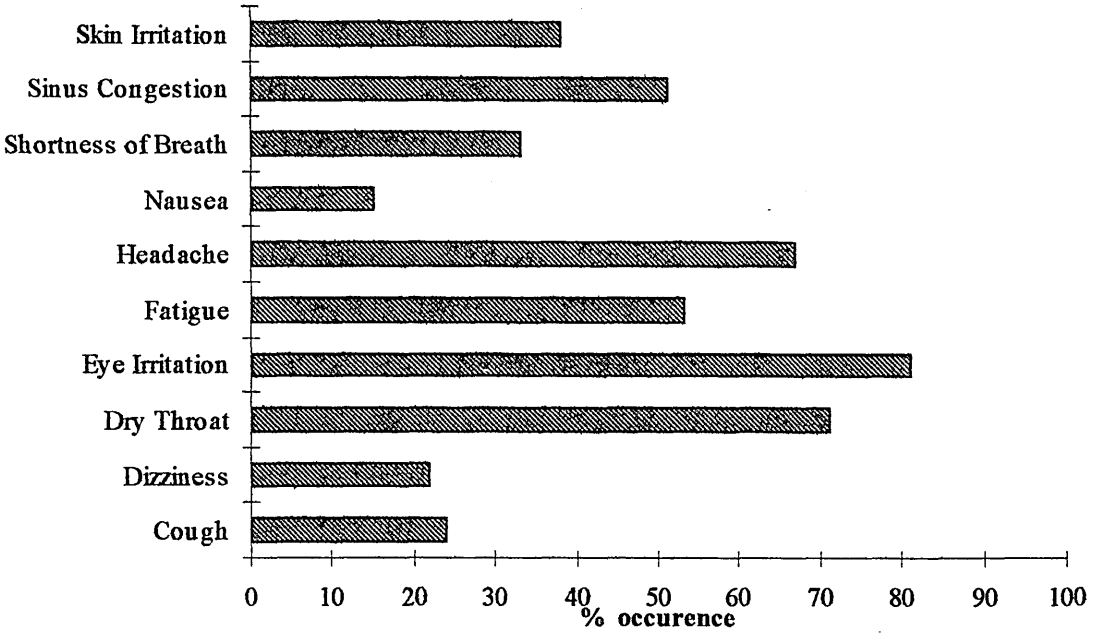


Figure 1-19 - Diagram Showing Percentage Occurrence of Symptoms of SBS

In outbreaks of sick building syndrome, it has been reported that up to 40% of the population in the building has been affected. The causes of SBS are thought to be poor ventilation, as well as other factors such as furnishings and and building materials.[156] Other sources may include office electrical equipment, especially laser printers and photocopiers that produce ozone.

In a study of sick and normal housing, Kostiainen[166], showed that although levels of VOC in certain sick building were higher than those found in normal buildings, many sick buildings showed concentrations that were similar to their normal counterpart. The conclusion was that, although VOC may play a major role in SBS, there must be other factors that contribute to the symptoms.

Recent studies have shown that the occurrence of sick building syndrome is highest in buildings with artificial air conditioning. In a study in Swedish hospitals, Nordström *et al.*[167], studied the effects on perceived air quality of humidifying the air. By humidifying the air to 40-45% the perception of dry air and malodours was reduced, as was the symptoms of SBS.

1.5.4.2 Environmental Tobacco Smoke

Environmental tobacco smoke is the term used to describe any smoke that is present in the indoor environment. The presence of ETS in an atmosphere is easily detected by the strong, pungent odour that the smoke produces. The effects of ETS on air quality are as much a political issue as they are a scientific one.

ETS is a mixture of mainstream and sidestream smoke from the cigarette. It has been shown that differences in the rate of combustion produce very different smoke compositions.[168] There are more than 4000 individual compounds present in tobacco smoke, as well as the obvious particulate matter.

There is wide debate into how ETS should be defined and measured. Needless to say in the United Kingdom there has been little headway made towards producing suitable legislation.

The direct effects of tobacco smoke on the health of the smoker are widely documented both in the media and in the scientific literature. It is the effects of ETS that are not so widely studied.

It should be noted that the role that ETS plays in indoor air quality is only important where people smoke. The effects on air quality of smoking soon diminish as the distance from the source increases.

Chapter 2

Experimental

2.1 Capillary Electrophoresis

2.1.1 Determination of Organic Acids by CZE

2.1.1.1 Equipment

All electropherograms were generated using a Crystal CE 310 with a ATI Unicam 4225 UV/Vis detector (ATI Unicam, Cambridge, UK) measuring at 185nm. Fused silica capillaries (Composite Metal Services, Hallow, Worcs., UK) of 75μm (I.D.), 375μm (O.D.) of total length 70cm were used. The detection window was 10cm from the end of the column. The signal was recorded on a Spectra-Physics 4290 integrator (Spectra-Physics, UK). The sample was introduced onto the column using both hydrostatic and electrostatic injection techniques, the details of which are given later.

2.1.1.2 Chemicals

Lactate and pyruvate (Aldrich, Gillingham, Dorset, UK), malonate, maleate, succinate, butytrate, acetate, formate (BDH, Poole, Dorset, UK) were obtained as the sodium salt. 3-Hydroxybutyric acid (Lancaster, Lancaster, UK) was obtained in liquid form.

CIA-Pak™ OFM Anion-BT (Waters-Millipore, Milford, MA, USA), an osmotic flow modifier, and sodium tetraborate (BDH, Poole, Dorset, UK) were used for the buffer.

All solution were prepared using Milli-Q water.

2.1.1.3 Procedures

The fused silica capillary column was initially conditioned by rinsing through with 0.1M NaOH for 30 minutes followed by Milli-Q water for 10 minutes, before being flushed through with buffer solution for 20 minutes.

Before each run the column was rinsed with 0.1M NaOH for 20 seconds then with Milli-Q water for 30 seconds, then finally with buffer for 2 minutes. The buffer was prepared to the composition 50mM Borax, 0.4mM Ca^{2+}, and 1.0mL OFM per 50mL of buffer solution. The *p*H was then adjusted to *p*H 10 using 0.1M NaOH.

The applied voltage was -15kV which gave a range of operating currents between -25 and -70μA.

2.2 Liquid Chromatography

2.2.1 Determination of Carbonyls as DNPH Derivatives by HPLC

2.2.1.1 Equipment

A gradient HPLC system was used for the analysis of carbonyls. The pumps were two Waters 501 HPLC pumps controlled by a Waters Gradient Controller with a flow rate of 1mL min^{-1}. The column used was a Millipore Nova-Pak C-18 (3.9mm x 150mm). Detection was by UV measuring at 365nm. The signal was recorded on a Hewlett-Packard HP3996A integrator. A 20 μL injection loop was used.

2.2.1.2 Chemicals

Mobile phase A was 40% Acetonitrile to 60% Water whereas mobile phase B was 100% Acetonitrile. Acetonitrile purchased from BDH (BDH, Poole, Dorset, UK). 2,4-Dinitrophenylhydrazine (Aldrich, Gillingham, Dorset, UK) was prepared as described in the literature. Carbonyls were obtained from Aldrich, Gillingham, Dorset, UK [67]

2.2.1.3 Procedure

Sampling was performed using two different solid phase techniques. Primarily DNPH-coated quartz filters were exposed to air at flow rates of greater than 7L min^{-1}. The hydrazones were extracted into acetonitrile, before being reduced to dryness and then reconstituted in 1mL of mobile phase A. The second technique was using DNPH coated C-18 solid phase extraction cartridges. The methods were similar to those described in the literature. [50]

2.2.2 The Determination of Phenols by HPLC

2.2.2.1 Equipment

An isocratic HPLC system was used for the analysis of phenols. The pump was a Waters 501 HPLC pump with a flow rate of 1mL min^{-1}. The column used was a

Millipore Nova-Pak C-18 (3.9mm x 150mm). Detection was by electrochemical detector with a voltage of +1.8V. The signal was recorded on a Hewlett-Packard HP3996A integrator. Injection was by pre-concentration onto a 3cm x 0.5mm pre-column packed with ODS-5, through a 2mL-injection loop. Analytes were passed from the loop onto the pre-column using a small reciprocating pump. The analytes were eluted from the pre-column with mobile phase.

2.2.2.2 Chemicals

The mobile phase was 40% methanol to 60% 0.5M acetate buffer, prepared from sodium acetate. Methanol and sodium acetate were purchased from BDH. Phenol standards were purchased in the prepared form from Aldrich, Gillingham, Dorset, UK.

2.2.2.3 Procedure

Large volumes of aqueous sample were injected onto the pre-column using a small reciprocating pump. "Injection" onto the column was through reverse elution with the mobile phase directly onto the analytical column.

2.3 General Gas Chromatographic Methods

2.3.1 General AED Analysis

1μL of sample was injected using a splitless injection into the GC. The sample was then chromatographed with a 5% Phenyl column (RTX-5 Thames Chromatography, UK) (25m x 0.25mm). Using a He carrier gas with a flow rate of 1mL min_1. Starting from 35°C the oven temperature was ramped at 15°C min^{-1} to 280°C with a final hold of 2 minutes. Detection was by HP5921A MIP-AED determining carbon, nitrogen, oxygen and sulphur at 193nm, 174nm, 777nm and 181nm respectively.

2.3.2 General GC-MS Analysis

1μL of sample was injected using a splitless injection into the GC. The sample was chromatographed on a RTX-5 (Thames Chromatography, UK) (25m x 0.25mm) column in a Hewlett-Packard 5890 series II gas chromatograph, using He carrier gas at 1mL min^{-1}. The general temperature program used was 35°C for 6 minutes ramping to 280°C at 15°C min^{-1} with a final hold time of 2 minutes. Detection was by a Hewlett-

Packard HP5971A mass selective detector, over a mass range of 50-550m/z. Mass chromatograms were recorded and peaks were initially identified using the ChemStation library search routines.

2.3.3 General FID Analysis

1μL of sample was injected using a splitless injection into the GC. The sample was then chromatographed with a 5% Phenyl column (25m x 0.25mm), using a He carrier gas with a flow rate of 1mL min^{-1}. Starting from 35°C the oven temperature was ramped at 15°C min^{-1} to 280° with a final hold of 2 minutes. Detection was by flame ionisation detector, the signal was recorded on a Hewlett-Packard HP3996A integrator

2.4 Specific Gas Chromatographic Methods

2.4.1 Automated Thermal Desorption-Gas Chromatography

Using a Perkin-Elmer ATD-50 (Perkin-Elmer, UK), exposed Tenax tubes were desorbed for 10 minutes at 250°C onto a cold trap at -130°C before being rapidly injected 300°C for 2minutes into a Hewlett-Packard 5890 GC via a heated deactivated fused silica transfer line. The analytical separation was performed on a 5% Phenyl column (30m x 0.32mm ; d_f = 0.25μm) using a temperature programme. Starting from 35°C the oven temperature was ramped at 15°C min^{-1} to 210°C then at 25°C min^{-1} to 280°C. Detection was by a Trio-1 mass spectrometer using a mass range of 40-600m/z.

2.4.2 Manual Thermal Desorption-Gas Chromatography

Air sampled onto 0.1mg Carbotrap C in a 8.1cm x 0.5cm glass was thermally desorbed in an Optic Programmable Temperature Injector 400 (Ai, Cambridge, UK) at 330°C for 2 minutes, with a thermal ramp rate of 16°C s^{-1}. During the desorption period the carrier gas flow rate was reduced to 0mL min^{-1}, to reduce band broadening. The sample was chromatographed on a RTX-5 (Thames Chromatography, UK) (60m x 0.25mm) column in a Hewlett-Packard 5890 series II gas chromatograph, using He carrier gas at 1mL min^{-1}. The general temperature program used was 35°C for 6 minutes ramping to 280°C at 7.5°C min^{-1} with a final hold time of 2 minutes. Detection was by a Hewlett-Packard HP5971A mass selective detector, over a mass

range of 50-550m/z. Mass chromatograms were recorded and peaks were initially identified using the ChemStation library search routines.

The thermal desorption tubes were initially conditioned by holding at 330°C for 12 hours with a helium gas flow. By holding the thermal desorption tube at 330°C for the duration of the analysis it was possible for the tube to be "cleaned" of any organic components, allowing further sampling to occur on the same tube.

2.4.3 Direct Headspace Analysis

Using a gas tight syringe 1ml of the head-space was taken from through the septum from the vial or gas bag. This was injected at a steady rate into a Hewlett-Packard 5890 II GC with a 5% Phenyl column (25m x 0.32mm ; d_f = 0.52μm). Starting from 35°C the oven temperature was ramped at 15°C min^{-1} to 210°C then at 25°C min^{-1} to 280°C. Detection was by HP5921A MIP-AED determining carbon, nitrogen, oxygen and sulphur at 193nm, 174nm, 777nm and 181nm respectively.

2.5 Air Sampling Methods

2.5.1 Organic Acids - Impinger

Air was bubbled through an impinger (Supelco, Dorset, UK) filled with 10mL of distilled water, at a rate of 1L min^{-1}. Samples were then taken directly for analysis by CZE.

2.5.2 Carbonyls - Impinger

Air was bubbled through an impinger (Supelco, Dorset, UK) filled with 10mL of a concentrated solution of 2,4-dinitrophenyl hydrazine, at a rate of 1L min^{-1}. The solution was then extracted in triplicate with dichloromethane. The DCM was allowed to evaporate, and the hydrazones were redissolved in methanol. Samples were then analysed by HPLC.

2.5.3 Quartz Filters

Quartz filters (Whatman) were washed in distilled water, after which they were soaked in concentrated 2,4-dinitrophenyl hydrazine solution. After drying in a desiccator the filters were placed in cartridges. Samples were taken by passing air

through the filter at a rate of 1L min^{-1}. The filters were then extracted in methanol. Analysis was by HPLC.

2.5.4 Solid Phase Extraction Cartridges

The solid-phase extraction cartridges (J.T.Baker, Deventer, Holland) were conditioned using consecutive washes of 10mL of n-pentane (Aldrich, Dorset, UK), dichloromethane and methanol (J.T.Baker, Deventer, Holland) prior to use. The air was sampled at a rates of between 2 - 10 L min^{-1}, for 1 - 6 hours, using high volume sampling pumps (J.D.Technical Services, Old Ynysybwl, Mid. Glam., Wales).

The samples were extracted by using positive pressure to force through the cartridge 1mL of each of the extracting solvents, n-pentane, dichloromethane and methanol directly into autosampler vials.

Chapter 3

Multi-Method Approach

3.1 Introduction

The chemical composition of air can be broken down into a range of different compound classes. The chart shown Figure 3-1, shows a breakdown of the types of volatile organic compounds found in air with special attention paid to the oxygenated compounds.

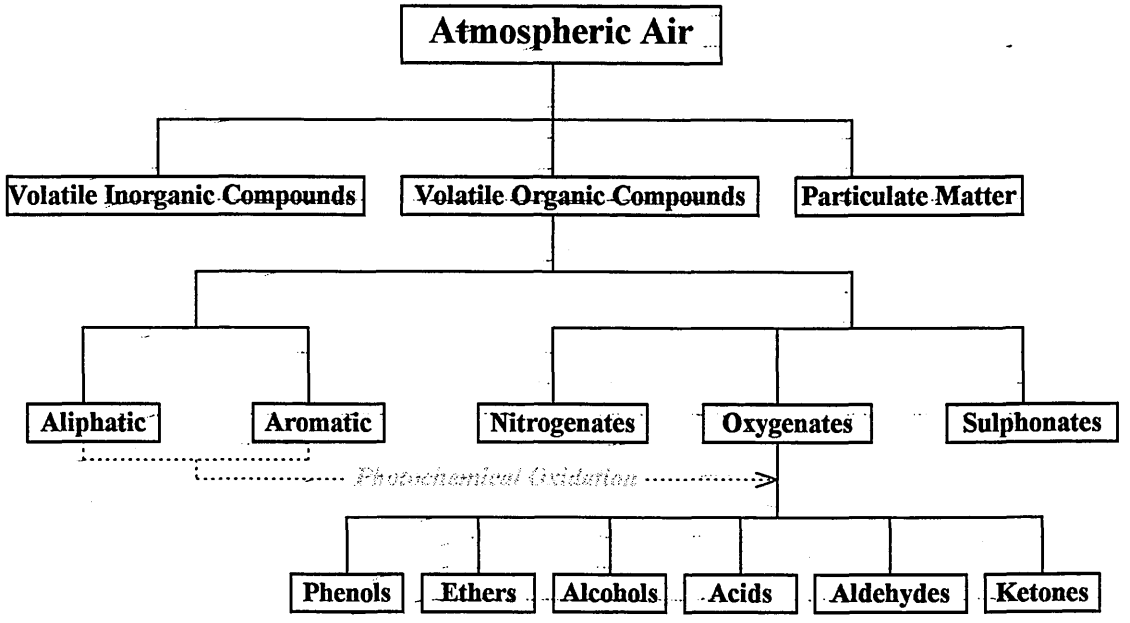


Figure 3-1 - Chart Showing the Chemical Composition of Air by Compound Class

The diagram also shows the link between non-polar compounds and polar oxygenated compounds, through the photochemical oxidation mechanisms discussed in Chapter 1.

From the diagram it can be seen that there are six major classes of oxygenated compound that may be found in the atmosphere. For the purposes of determining air quality it was decided, however, to study organic acids, phenols, and the carbonyl compounds, because of their potential impact on human health. In order to achieve this a multi-method approach was adopted, utilising capillary electrophoresis, liquid chromatography with electrochemical detection, liquid chromatography with UV detection and gas chromatography, with MS and AED.

This chapter will, therefore, be a discussion of the various methods developed for the determination of these key components in order to achieve the desired 'Multi method'.

3.2 Capillary Electrophoretic Methods

Capillary electrophoresis was the method used for the determination of organic acids in various sample matrices. Using the flow chart shown in Figure 3-2, a sampling and analysis protocol was developed.

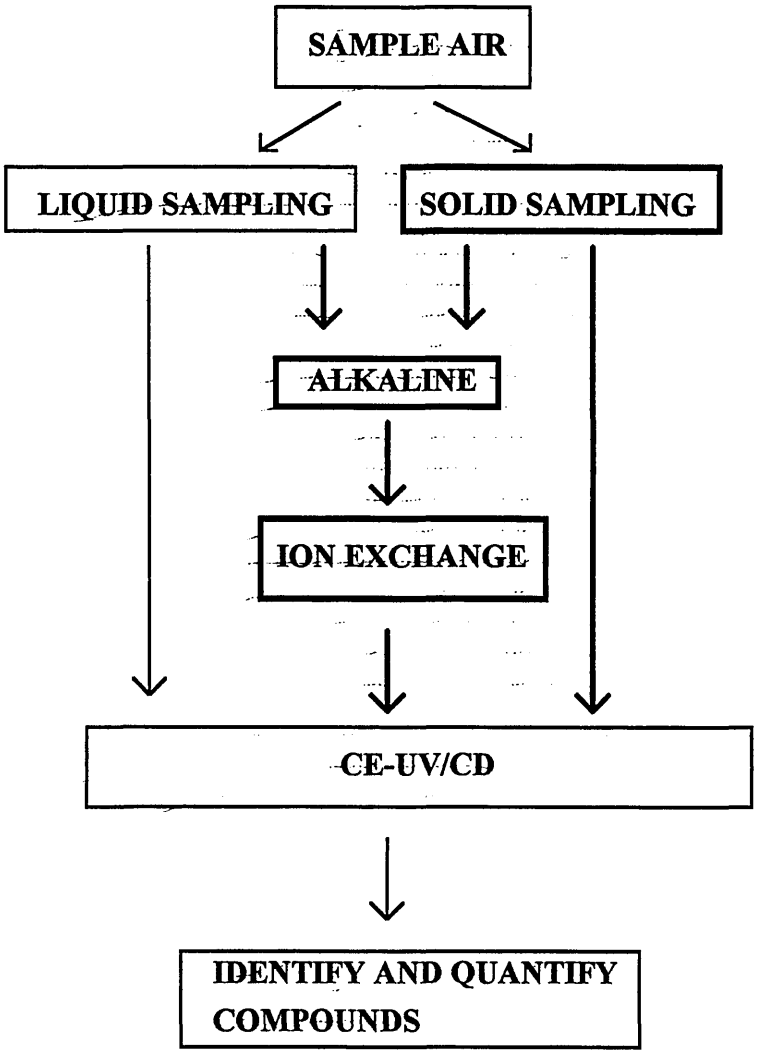


Figure 3-2 - Chart Showing the Methods for the Determination of Organic Acids in Air

3.2.1 Background

The technique of capillary zone electrophoresis uses the electrophoretic mobilities of the analyte ions and the electroosmotic flow of the buffer ions to affect a separation.

Using ultra violet detection there are two modes, direct and indirect. Direct UV detection is where the absorption of the chromophore on the analyte is used giving a positive signal response. Whereas using indirect UV detection the buffer solution is UV absorbing and the analyte causes "clear spots" in the detection window giving a negative signal response. These two techniques are both used for the analysis of organic acids.

3.2.1.1 Buffer Considerations

The mobilities of the ions in solution are affected by the pH of the electrolyte solution. This is predicted in the equation:

$$\mu = \mu_{A^-} \frac{\frac{K_a}{[H^+]}}{1 + \frac{K_a}{[H^+]}}$$

Equation 3-1

where μ is mobility at a given *p*H, μ_{A^-} is the mobility of the anionic form of the acid, and K_a is the dissociation constant of the acid. Using this equation it is possible to predict the elution order of the acid anions at various pH values.

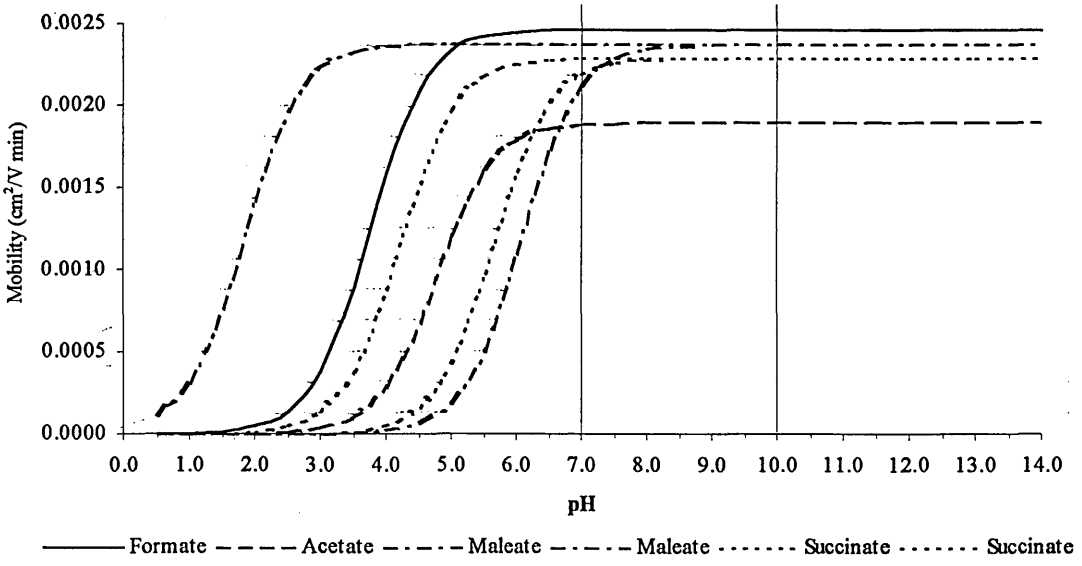


Figure 3-3 - Chart Showing the Effects of pH on Ion Mobility

The chart in Figure 3-3 shows ion mobilities as a function of *p*H for four different organic acids. Formic and acetic acids are mono basic acids and therefore have single plots.

Maleic and succinic acids however are dibasic acids and as such the dissociation constants are different for the two protons. This is shown by two separate plot lines.

It can be seen that at *p*H 7.0, although the formate and acetate ions are at the maximum ion mobility, maleate and succinate are not. This is due to the second proton not being fully ionised. However at *p*H values greater than 9.0 it can be seen that the organic acids are fully ionised and will have the maximum electrophoretic mobility. Therefore, the use of a high *p*H buffer was one of the prerequisites of the system being developed.

Another reason for using high *p*H buffers was the ionisation of the capillary wall. The silanol groups that comprise the inner surface of the capillary are readily de-protonated by the buffer. (Figure 3-4)

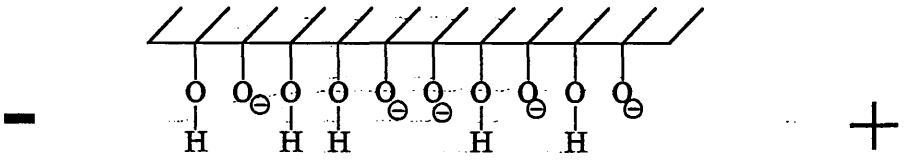


Figure 3-4 - Diagram Showing the Surface of Capillary Wall

This ionisation occurs over a pH range of 2 - 5. It is therefore common practice to ionise the capillary surface by rinsing with hydroxide solutions even when the running buffer is at a low pH's. The general feeling is that the protonation processes that will occur at low pH's cannot be reproducible due to external environmental factors, such as temperature and air pressure, and irregularities in the surface of the silica. This led to the difficulties in reproducibility that capillary electrophoresis is renowned for. The charged surfaces of the capillary cause an electric double layer to be formed that leads to a phenomenon known as electroosmosis, which is used in the separation mechanism. Electroosmosis is the bulk flow of the solution caused by the movement of the ions in the double layer towards their attracting electrode, i.e. the cathode for cations. (Equation 3.1)

$$E = \frac{-2\mu_1\mu_2}{4\pi r^3 \varepsilon_0} \qquad (3.1)$$

For the determination of anions, however, the bulk flow towards the cathode would only allow the detection of analytes that have:

$$\mu_{ep} > \mu_{eo} \qquad (3.2)$$

Where μ_{ep} is electrophoretic mobility and μ_{eo} is electroosmotic mobility. This means that without any modification of the electroosmotic flow only anions such as formate will be detected.

The addition of flow modifiers to the buffer solution allows the analyst to control the rate and direction of the electroosmotic flow. Compounds that are commonly used as flow modifiers for the determination of anions are non-ionic and cationic surfactants. TTAB, or tetradecyltrimethylammonium bromide, was used as an electroosmotic flow modifier. It is also the active component of the Waters-Millipore OFM-Anion-BT solution.

The ionic "head" of the surfactant is attracted to the anionic silanol group on the surface of the capillary. (Figure 3-5) This attraction reduces the formation of the ionic double layer, therefore, reducing the electroosmotic flow toward the cathode.

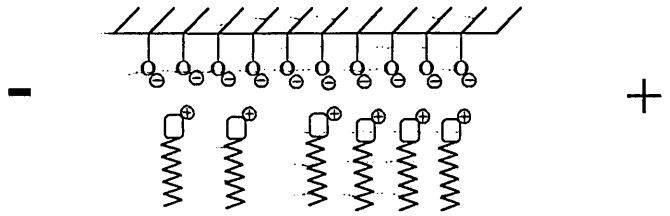


Figure 3-5 - Diagram of Cationic Surfactant Flow Modifier at the Capillary Wall

As the concentration of the flow modifier in the buffer increases the concentration of silanol sites on the surface of the capillary reduces to a point where no ionic double layer will form. A continuing increase in the concentration of the flow modifier will cause the formation of hemimicelles on the surface of the capillary, giving an effective net positive charge to the wall. (Figure 3-6) A double layer consisting primarily of anions from the buffer, OH^-, will then form. Under an applied voltage there will be a bulk flow of the electrolyte solution towards the cathode, i.e. in the desired direction for the analysis of anions.

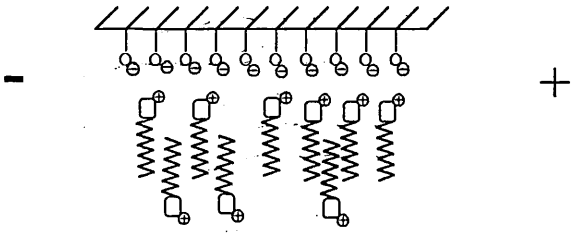


Figure 3-6 - Diagram Showing the Formation of Hemimicelles in the Capillary

The electrophoretic mobility of the ions of the analyte and the buffer should be matched to achieve the optimum sensitivity, resolution and speed. A chart showing how the mobilities of selected anions and electrolytes compare is shown in Figure 3-7.[169]

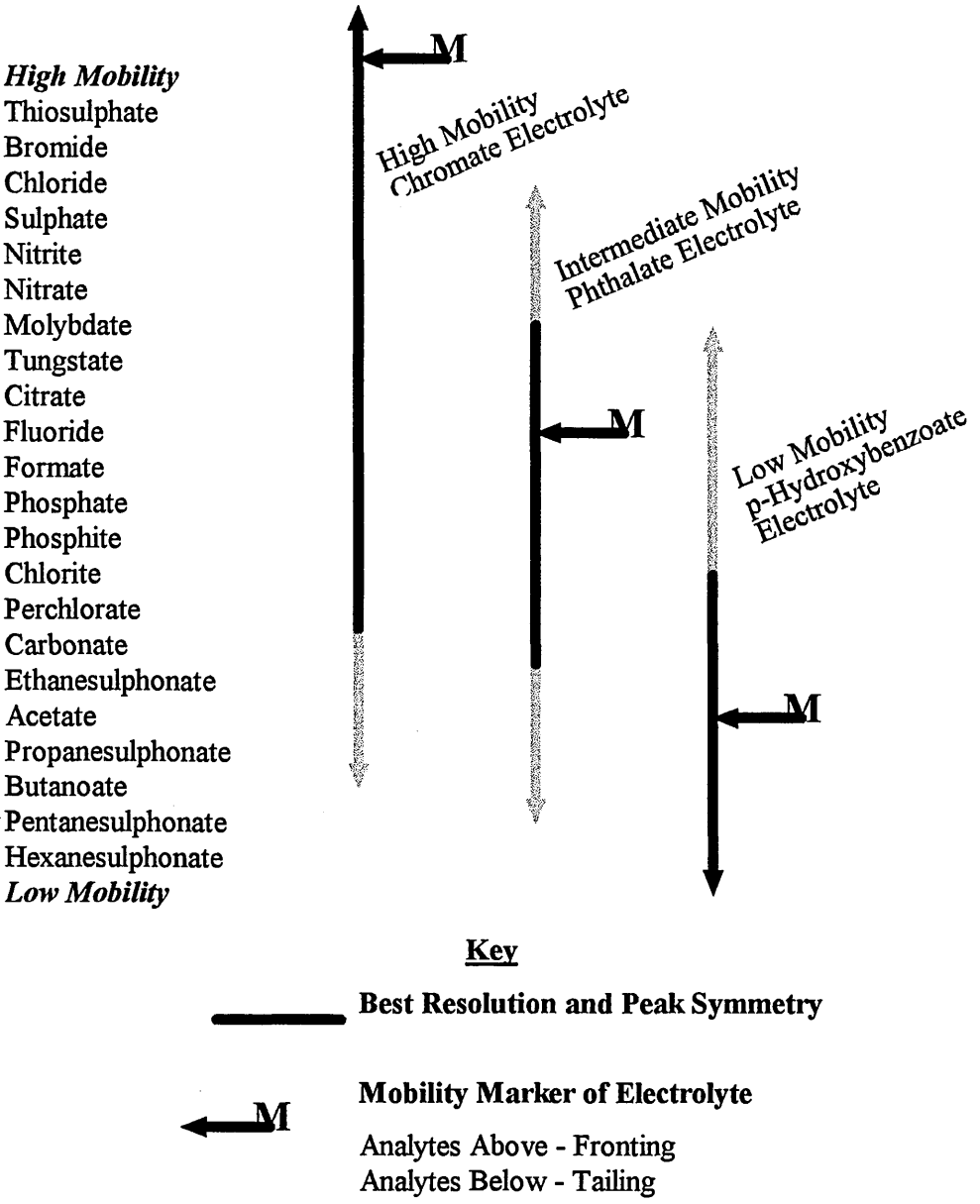


Figure 3-7 - Diagram Showing the Electrophoretic Mobilities of Different Ions

3.2.1.2 Injection Methods

In capillary electrophoresis there are three main methods of injecting the sample onto the column. However, with the Crystal 300, only barometric injection and electrokinetic injection modes were available. The hydrostatic method, although more user controllable was not possible due to instrument design.

Barometric injection is a non-selective method of placing a plug of the sample mixture at the end of the capillary. By pressurising the sample vial for a set period of time a controlled amount of liquid is forced into the capillary, displacing the buffer through the column. A maximum pressure of 50mBar is used for the injection, however, this low pressure is difficult to calibrate and therefore difficult to control, resulting in a wide variation in the volume of sample loaded onto the column.

Electrokinetic injection is a selective technique, in that only charged analytes are loaded onto the column. By applying a voltage for a set time period in the sample vial, sample ions migrate into the capillary. There is further selectivity, with the ions which have high electrophoretic mobilities migrating at a greater rate onto the column than the slower ions. This form of size and charge exclusion selectivity may be useful with "dirty" samples. However, the drawback with electrokinetic injection is that the sample composition is changing with each subsequent injection from the sample vial, making statistical studies difficult.

3.2.2 Phthalate Buffer Development

The initial work for the determination of organic acids by capillary electrophoresis was performed using a phthalate buffer system. This was the initial choice for an electrolyte because of the similar mobilities of the phthalate and the organic acids. (Figure 3-7) Based on the work of Lalljie *et al.*[170], a buffer solution was prepared, the details of which are shown in Table 3-1.

Table 3-1 - Experimental Conditions Using the Phthalate Buffer

Buffer	
Phthalate	10 mM
TTAB	5 mM
adjusted to *p*H 7.0 using 0.1M NaOH	
Conditions	
Applied Voltage	-15 kV
Injection	Pressure 15s @ 20mBar
Detection	254nm Indirect

An indirect UV detection system was initially used so that the analysis of a wide range of organic acids could be achieved, regardless of chromophore.

3.2.2.1 Results

For a 20mM solution of acetate, initial results showed both an increase in migration time and peak area. (Table 3-2) The primary explanation for this phenomenon was that the column was not yet conditioned.

Table 3-2 - Initial Results for Acetate Ion using Phthalate Buffer

Run #	RT	Area
1	6.710	1885941
2	6.769	1714565
3	7.164	2099450
4	7.362	3357032
5	7.386	4626189
6	7.345	4860602

The purpose of column conditioning is to achieve an equilibrium between the buffer and the capillary wall, i.e. that the proton exchange between silanol and $OH^-_{(aq)}$ is constant. Column conditioning is achieved by rinsing the capillary with 0.1M NaOH. By adding a conditioning step into the run program it was possible to have a continuous and on-going cycle of conditioning. These results therefore showed the importance of conditioning the capillary before and also during use. Subsequent results showed an improvement, with little linear drift in migration times.

For multiple compound standards good peak shape and separation were obtained. However, peak area reproducibility was very poor, especially for low analyte concentrations. The reproducibility of the migration times was also poor.

Peak area ratios of a 20mM sample containing formate, acetate, butanoate and an unknown contaminant, against formate, are shown for six consecutive runs in Table 3-3.

Table 3-3 - Peak Area Ratios

Run #	Formate	Acetate	Butanoate	Unknown
1	1.0	0.3	0.2	0.3
2	1.0	0.4	0.2	0.3
3	1.0	1.2	1.0	1.1
4	1.0	0.7	1.1	1.1
5	1.0	0.3	0.4	0.4
6	1.01	0.7	0.6	0.5

However, the results show that this is not the case. The %RSD for acetate, butanoate and the unknown are 55%, 65% and 64% respectively.

It was also observed that the %RSD increased as the sample concentration decreased. This is shown in

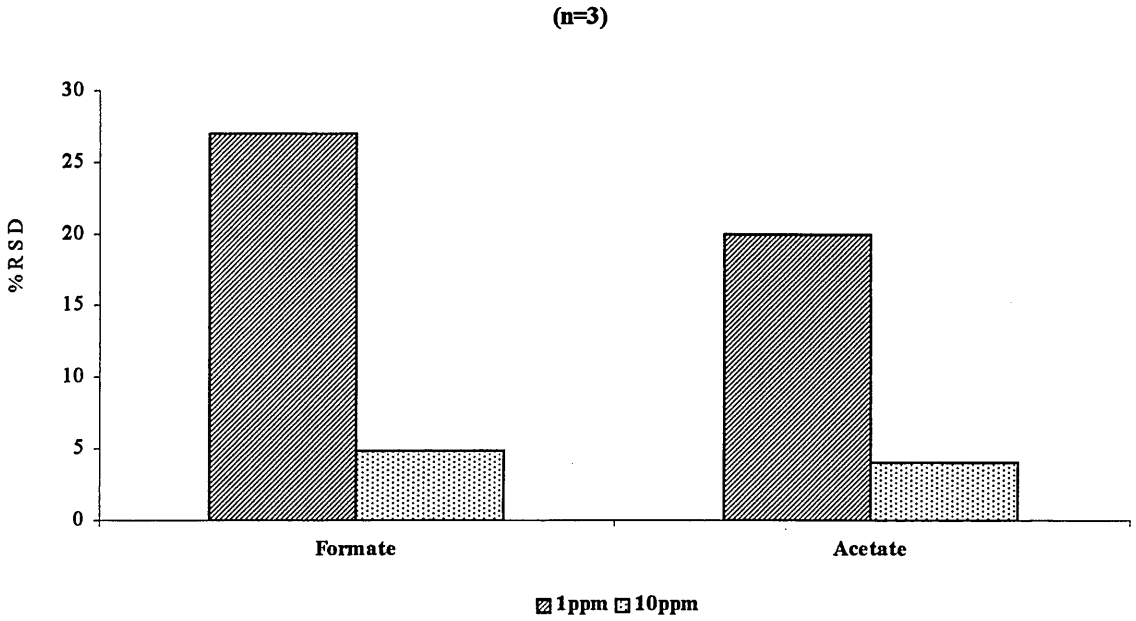


Figure 3-8.

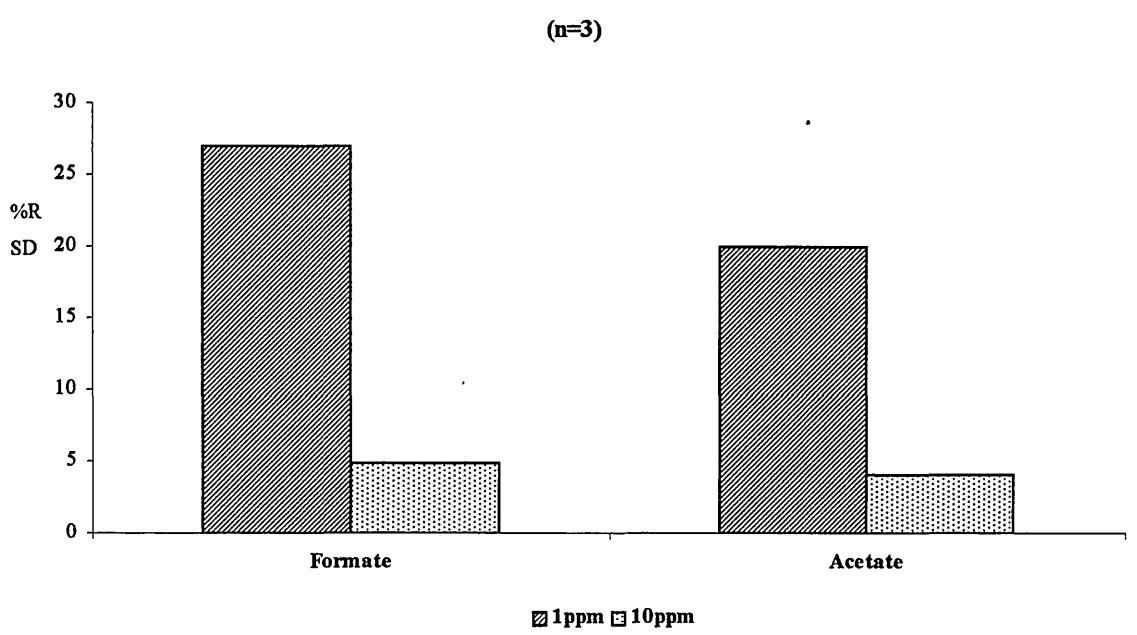


Figure 3-8 - Graph Showing Reproducibility of Phthalate Buffer System

Irreproducibility of the peak area could be due to two factors. Primarily, it may be caused by slight differences in injection volume. However, if this was the case one would expect the run-to-run ratios for peak area to be similar.

The second possible reason is that the column and buffer conditions are generally not suitable for the given application. At *p*H 7.0 the buffer is operating just above the *p*Ka for the de-protonation of the second carboxylate group of the phthalate and the de-protonation of the silanol groups of the capillary, and as mentioned earlier it is thought that this might cause reproducibility problems.

Problems with migration time are due solely to the buffer and column, however, the %RSD were not as great as for the peak areas, with values of 11% for acetate, butanoate and the unknown.

Preparation of the buffer solution is critical in obtaining reproducible results. By measuring the ion current over a range of voltages it is possible to show the similarity between buffer solutions.

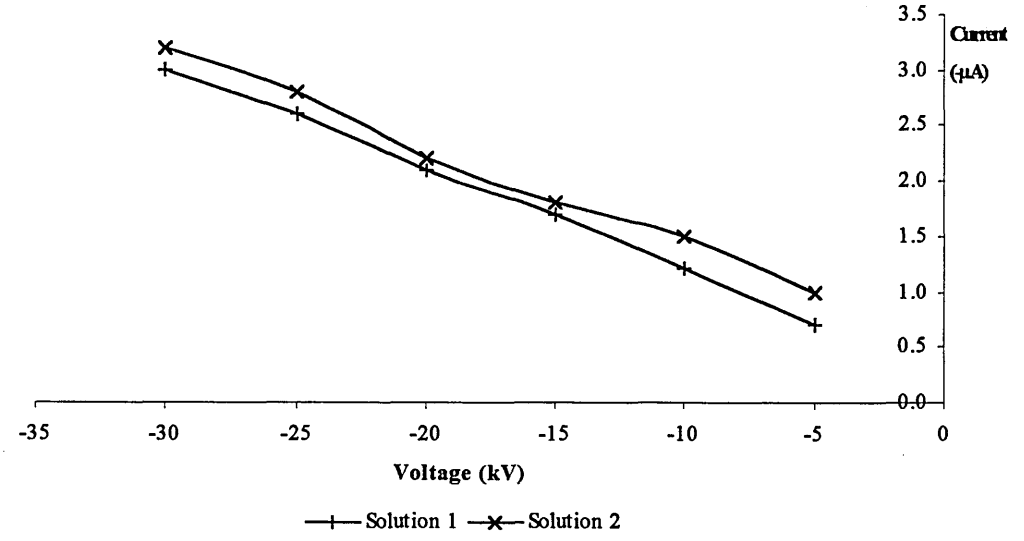


Figure 3-9 - Graph Showing a Comparison of Buffer Currents

Figure 3-9 shows the electrolyte currents obtained from two batches of buffer solution. Although they are similar in appearance there are still differences.

3.2.2.2 Conclusion

Although irreproducibility of the migration times was not excessive, this coupled with the variation in peak area values, indicates that this technique has some major drawbacks. The reproducibility of any technique is of primary importance in presenting valid results.

Also noted was the noise level of the baseline obtained using indirect UV detection. Although *p*H has been suggested as a major factor in causing poor results, it should be mentioned that this might also lead to poor reproducibility.

From these results it was concluded that this technique is not suitable for the trace analysis of organic acids.

3.2.3 Borax Buffer Development

Work reported by Shirao *et al.*[171], on the separation of organic acids in urine, used a sodium tetraborate (borax) buffer. Direct UV detection was required as Borax is effectively UV transparent. Shirao *et al.*, used a detection wavelength of λ_{185nm}, however UV spectra of borax and organic acids showed that wavelengths up to λ_{210nm} could be successfully employed.

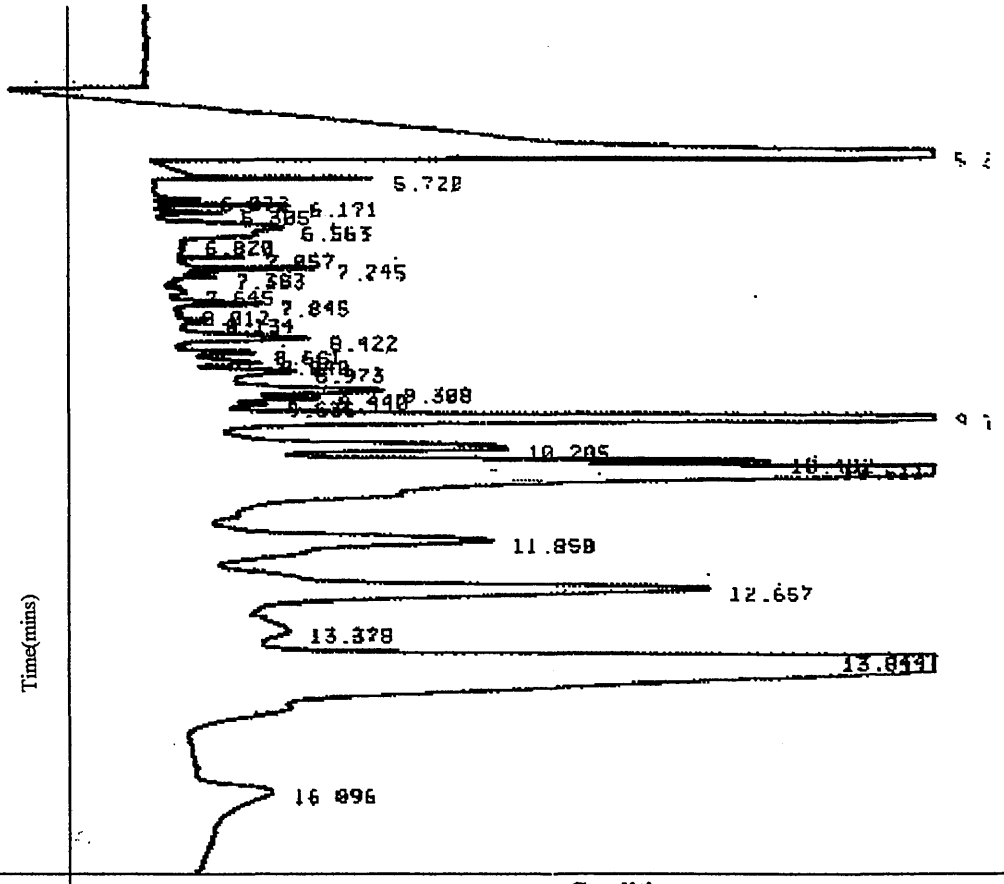
Table 3-4 - Experimental Conditions Using the Borax Buffer

Buffer	
Borax	50 mM
OFM	2mL per 50mL of buffer
adjusted to *p*H 10.0 using 0.1M NaOH	

Conditions	
Applied Current	70μA
Injection	Pressure:
	5s@20mBar (Water)
	15s @ 20mBar
Detection	196nm Indirect

3.2.3.1 1.1.3.1 Results

Initial runs showed that the buffer system was able to separate upwards of twenty peaks in a sample of urine with, in most cases, baseline resolution.



Buffer		Conditions	
Borax	50 mM	Applied Current	70μA
OFM	2mL per 50mL of buffer adjusted to *p*H 10.0 using 0.1M NaOH	Injection	Pressure: 5s@20mBar (Water) 15s @ 20mBar
		Detection	196nm Indirect

Figure 3-10 - Borax Buffer Electropherogram of Organic Acids in Urine

With this in mind it was possible to optimise the system variables, such as *p*H and voltage, to offer maximum efficiency.

The problems of peak area reproducibility observed using the phthalate buffer were thought to be instrumental, and as such a qualitative approach was employed in the initial stages of the development of this method.

3.2.3.1.1 pH

The natural *p*H of the borax solution is approximately *p*H 9.0. However by altering the hydroxide concentration it is possible to alter the buffering *p*H. This affects the ion mobility, as already discussed, which in turn affects the separation efficiency of the system.

Also affected by *p*H is the current within the system. Figure 3-11 shows the plot of current versus voltage for four electrolyte solutions with different *p*H values. It can be seen that the solution of *p*H 10.0 allows the maximum current with the lowest applied voltage.

There are other considerations of this buffer system. At *p*H 10.0, the capillary wall and the acid ions in the analyte will be almost fully ionised. (See Figure 3-3)

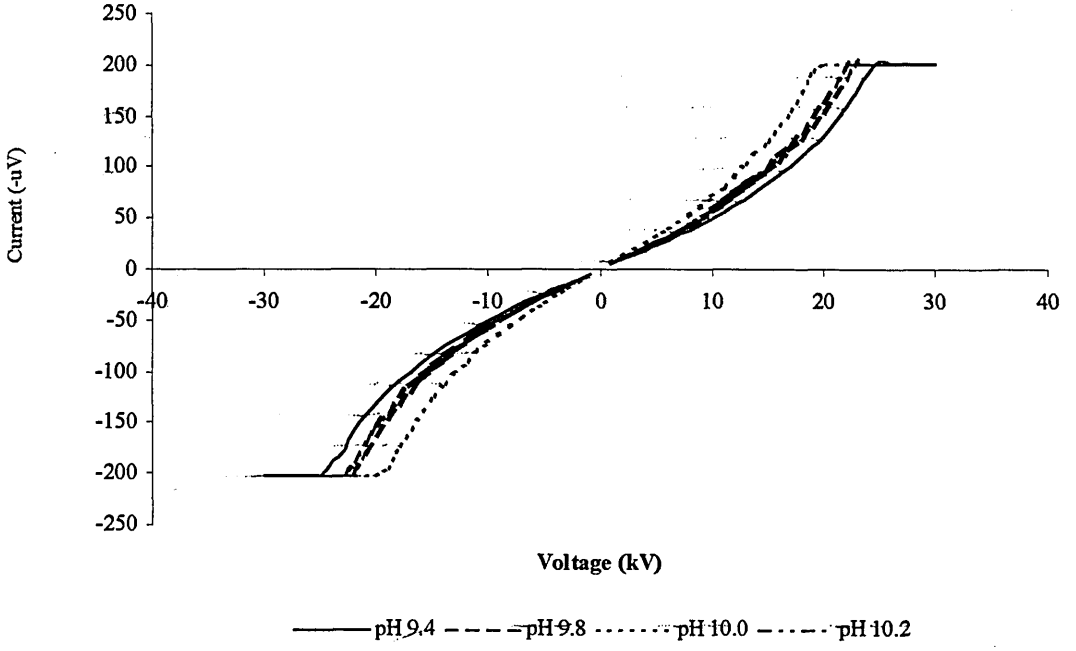


Figure 3-11 - Chart Showing the Effects of pH on Current

The theoretical separation that was predicted by Equation 3.1 showed that formate would be eluted before maleate. The data obtained supports this, and is shown in Figure 3-12 below. The mobilities of the three ions studied are shown for different *p*H values. It can be seen that at *p*H 10.0 the mobilities of all three ions are at a maximum.

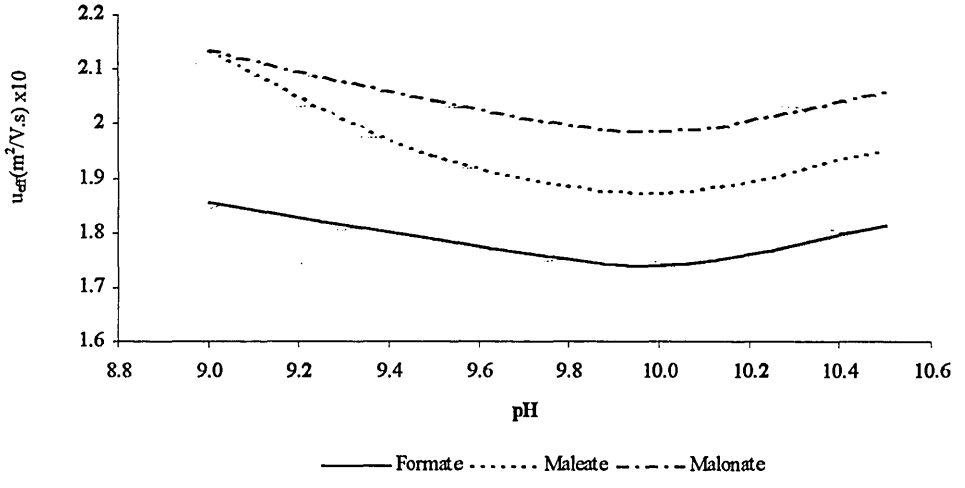


Figure 3-12 - Chart Showing the Effects of pH on Separation

It can be seen that the dibasic maleate ion and the malonate ion have similar mobilities at *p*H 9.0. As the *p*H increases, however, a separation between the two occurs. It is around *p*H 9.0 that the maleate ion becomes fully ionised.

3.2.3.1.2 Voltage

The applied voltage in capillary electrophoresis is analogous to the mobile phase flow rates in chromatography. As with chromatography, the optimum separation is a function of flow rate or applied voltage.

Figure 3-11, as mentioned, shows the plots for current versus voltage for the varying buffer solutions. It can be seen that there is both a linear and non-linear section to the lines. It is generally thought, that the voltage, at which the current changes from linear to curved, i.e. the point of inflection, is the optimum for separation.

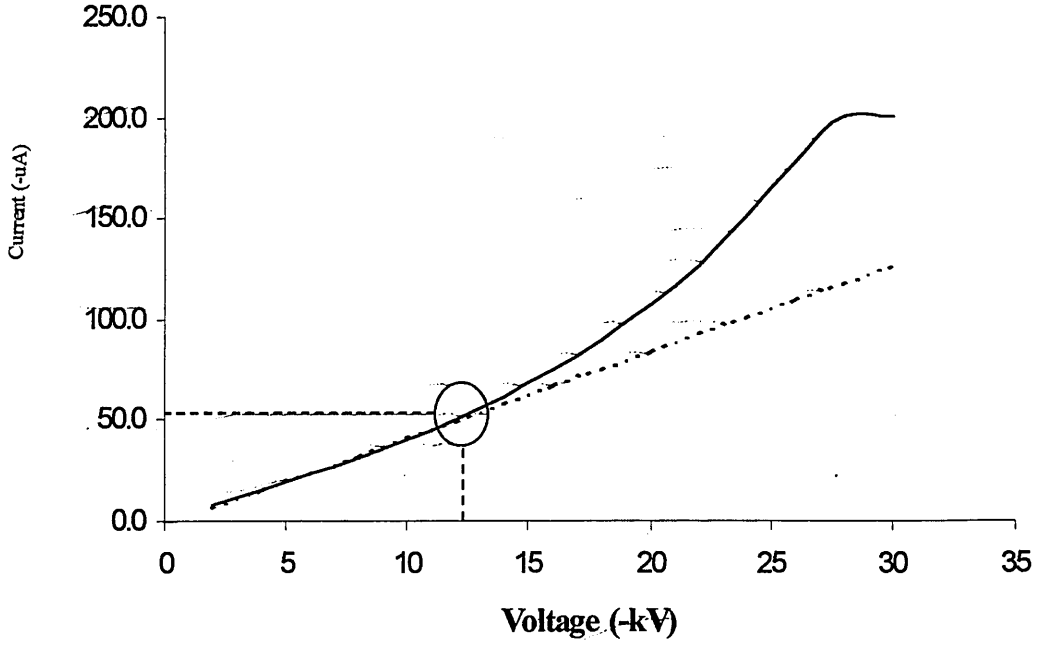


Figure 3-13 - Chart Showing Optimum the Separation Voltage and Current

It can be seen from Figure 3-13, that the point of inflection is at around -12kV and -50 to -70μA. It was therefore decided to use a constant separation of -70μA for the analyses. This instrumental feature limited the maximum current available by varying the

applied voltage accordingly, thus limiting Joule heating which can occur when high currents are used.

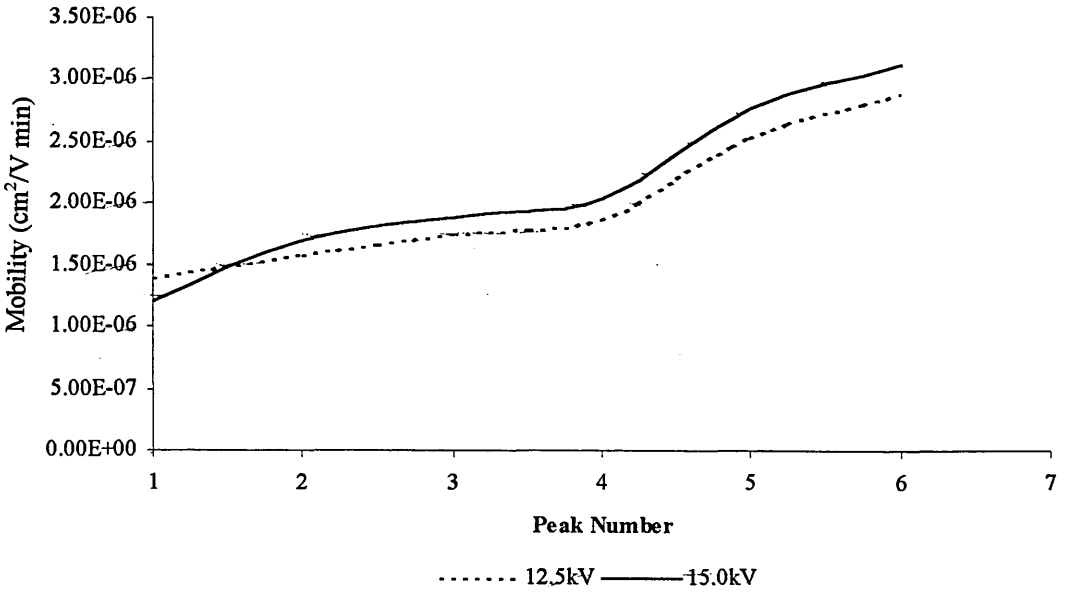


Figure 3-14 - Chart Showing the Effects of Voltage on Mobility

Although the optimum voltage was obtained through observation of the current, the effects on mobility of two separate applied voltages were studied. The mobilities of six peaks in a sample were plotted for -12.5kV and -15.0kV (Figure 3-14) It can be seen that the higher the applied voltage the greater the mobility. It does not follow, however, that increasing the voltage will improve the separations.

3.2.3.1.3 Migration Times

With the phthalate buffer there were problems with the reproducibility of the migration times. By measuring the migration times of the acetate ion, when using the Borax buffer, it was noted that migration times also varied dramatically between runs with this buffer. Of particular note was that samples of known higher concentrations were migrating slower than weaker samples.

A technique known as isotachophoretic stacking was used in the sample injection stage of the run to help in the enrichment of the sample. This involves the introduction of a small plug of water into the capillary before the sample. A concentration gradient forms on the application of the voltage, allowing the ions of the analyte to form into discreet bands or stacks, at the same time the electrolyte ions are increasing in concentration within the water

plug. During this process the current is low due to the water plug, however, once the concentration of ions between the plug and buffer equilibrates the current rapidly increases.

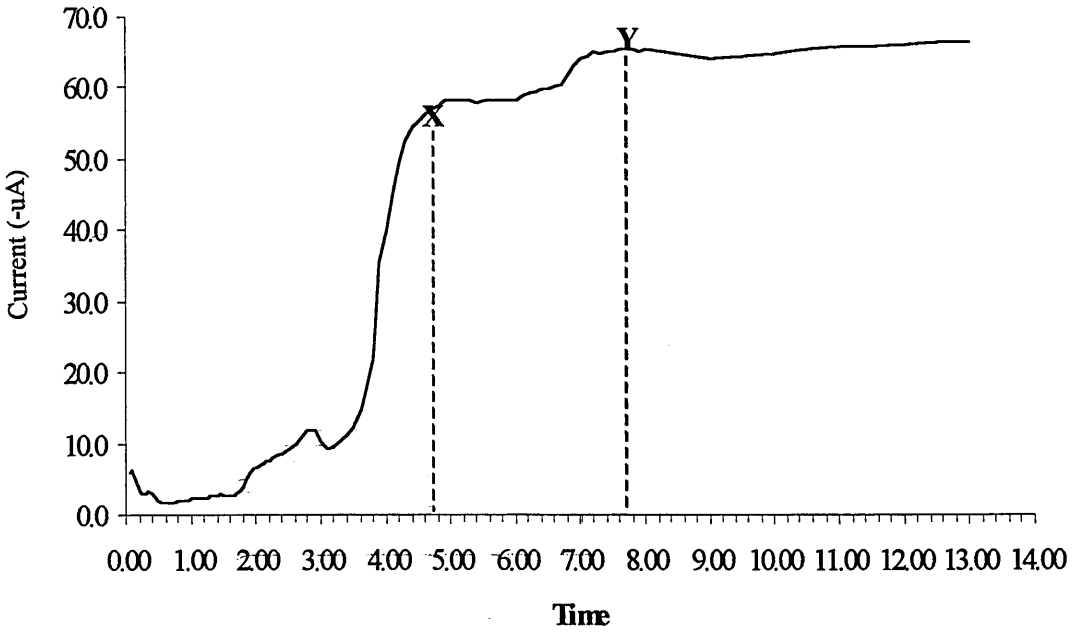


Figure 3-15 - Chart showing Current versus Time During an Electrophoretic Run

Figure 3-15, shows a plot of current against time over a run for an applied voltage of -16.5kV. It can be seen that the current takes approximately 4.6 minutes to increase to point X and another 3 minutes to reach a maximum, at point Y.

Point Y is the capillary electrophoresis equivalent of the solvent front. It is thought that the variations in migration time are caused by the irreproducibility of the time taken for the maximum current to be obtained, that is from $t = 0$ to point Y (or t_m). So by using the standard capacity ratio equation it can be shown that although migration times might vary T' is constant.

Figure 3-16, shows the migration times of t_m, t_r (acetate peak) and T' over 41 consecutive runs over a period of 1 week, using a range of concentrations, from trace to 600ppm(mg L^{-1}). Although there are slight variations in migration time and T', overall, there is only %RSD of 3.4%.

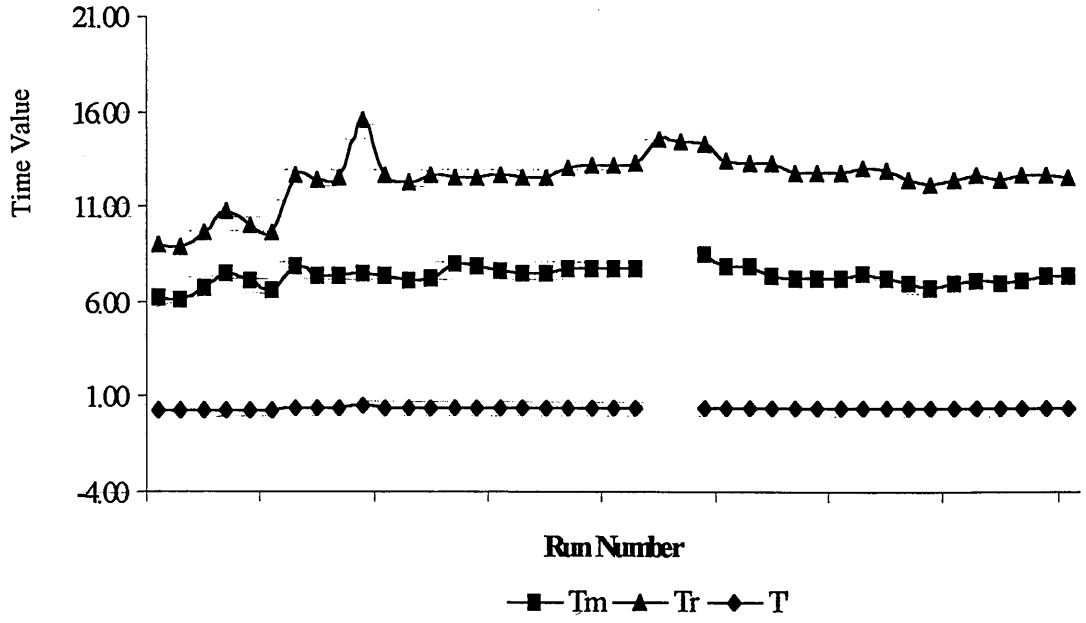


Figure 3-16 - Chart Showing "Capacity" Ratio for Consecutive Electrophoretic Runs

This reproducibility was considered good enough to suggest that this method was suitable for a qualitative investigation of organic acids in aqueous solutions.

3.2.3.1.4 **Electroosmotic Flow Modifier**

A proprietary electroosmotic flow modifier was used for this method in an attempt to limit the irreproducibility of the system. The Waters-Millipore OFM Anion-BT is a prepared solution of TTAB, at approximately 1mmol concentration. By varying the concentration of OFM used it is possible to affect the mobility of the ions. As the concentration increases the rate of electroosmotic flow decreases and the effects diminish. Further increase in concentration will show a stop of the EOF altogether, before a change of direction of migration toward the detector.

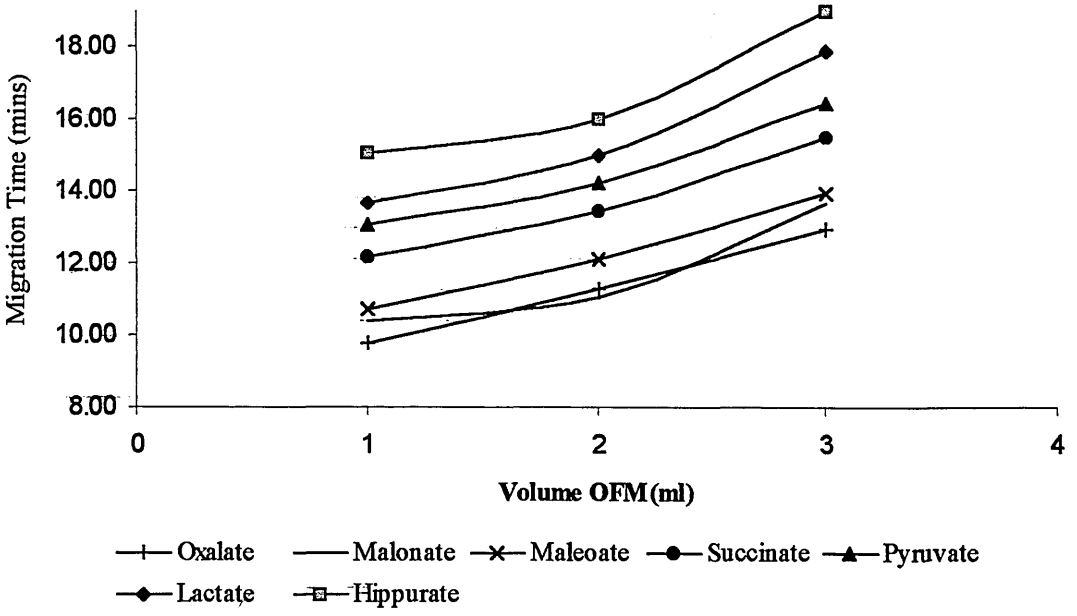


Figure 3-17 - Chart Showing the Effects of OFM on Separation

Figure 3-17 shows the effects of different concentrations of OFM in the buffer. The units of X-axis are given as mL of OFM per 50mL of buffer. Due to the lack of actual data regarding concentration of the OFM, it was thought that by using an easily understandable unit it would be possible to obtain better reproducibility.

The data obtained showed a steady increase in migration time. This corresponds to a decrease in electrophoretic mobility. Although this does not fit with our understanding of electroosmosis, we are assuming that the addition of surfactant to the solution is changing the viscosity and therefore decreasing the mobility of the ions.

3.2.3.1.5 Calibration

A simple linear calibration graph was constructed between 0 and 78.3 ppm(mg L^{-1}) for an acetic acid standard, for two separate runs. This linearity was reproducible, although actual areas were different due to differing laboratory environmental conditions. It was assumed, however, that the peak areas for both standard and sample would vary similarly.

These two different calibrations although both linear show the need for the constant checking of calibrations.

3.2.3.1.6 **Peak Area Reproducibility**

Using a highly spiked sample, three consecutive runs were performed. The peak areas measured gave a relative standard deviation of 2.8%. When samples of lower concentration were used this value was raised to 7-18% on the initial investigations. These changes in RSD can be seen in Table 3-5.

Table 3-5 - Peak Area Reproducibility

Concentration mg L^{-1}	RSD%
658	2.76
78.3	2.3
19.57	14.8

Although not linear, these results suggest that at low concentrations of organic acids, such as the levels expected in air, the error caused by irreproducibility will be greater than that at higher concentrations. This is not necessarily a fault of the electrophoresis technique but rather a factor of detector sensitivity.

3.2.3.2 Conclusions

From the data obtained it was possible to optimise the borax buffer based technique. It was decided that the direct UV detection method would reduce many of the problems associated with indirect UV such as noisy baselines.

By limiting the current it was possible to obtain a constant flow of ions within the capillary thus removing another possible source of reproducibility problems. Other optimisations such as *p*H and concentration of the osmotic flow modifier gave the best possible separation and reproducibilities.

Having developed a working method it was decided to use this method for two applications: the analysis of organic acids in air and the analysis of organic acids in urine.

3.2.4 Applications

3.2.4.1 Air Analysis

The simplest sampling technique that could be employed was the bubbling of air through a volume of water. Curious results were initially observed when Milli-Q water was used. This led to an investigation of the trace contaminants present in the different types of water that were available.

The results showed that glass distilled water had the lowest levels of formic and acetic acids. The other waters that were investigated were tap water, AnalR water (Aldrich), AnalR water (BDH) and Milli-Q. It was noted that waters stored in polyethylene containers and wash bottles were readily contaminated with organics. The source of the contamination in the Milli-Q water was thought to be the ion exchange resins that are used in the system. (Chromatograms in Appendix A)

Using glass stored, glass distilled water a simple sampling regime was set-up. Initially, air was sampled from within the laboratory to test the reliability of the technique. Air was pumped through an impinger into the water at a rate of 2L min^{-1}. An aliquot of this water was then analysed using the previously described technique.

3.2.4.1.1 Sample Results

Samples were taken from both indoor and outdoor urban sites, over the weekend of 8^{th} -10^{th} September 1995. The results are shown in ng m^{-3}, in Table 3-6, below. With such a limited amount of data available it is impossible to draw any environmental conclusions but it can be seen that initial results are similar to those obtained by other workers using other methods.

Table 3-6 - Acetic Acid in Air Samples

Sample	Date	Volume	Conc. ng m^{-3}	%RSD (n)
Laboratory				
	25/08/95	200L	0.00188	18% (3)
	31/08/95	90L	0.00113	16.8% (3)
	31/08/95	300L	0.00345	6.6% (3)
(Spiked)	25/08/95	2L	3.198	2.76% (3)
Urban Outdoor Air				
	03/09/95	456L	0.00007	3.6% (2)
	03/09/95	600L	0.00084	33.4% (3)
	03/09/95	360L	0.00034	13.1% (3)

There were two problems with this technique. The quantitation of the capillary electrophoresis data which has already been discussed and the actual sampling technique, improvement to which will be discussed in later chapters.

3.2.4.2 Neo-Natal Urine

3.2.4.2.1 Background

The identification of many disorders caused by inborn deficiencies of the metabolism of lipids, carbohydrates and protein has become possible since the profiling of organic acids in physiological fluids became a regular function of hospital laboratories. In the past two decades over twenty-four new diseases of the metabolism have been discovered through the screening of physiological fluids.[172] Other medical conditions have also benefited from such profiling techniques. Research is continuing into the use of profiling in aiding victims and potential stroke victims by profiling the long chain fatty acids and cholesterol in plasma.[173 174] Published reports also suggest that it will be possible to identify the type of bacterial and viral infections by the profile they leave from their metabolisms.[175 176]

In most laboratories the profiling of the organic acids is performed using gas chromatography-mass spectrometry (GC-MS). This involves preparation procedures in which the analytes are extracted from the sample into a solvent then derivatised before

analysis.[177,178] It was clear therefore that a simple, less time consuming method would be beneficial for the screening of urine samples.

3.2.4.2.2 **Samples**

The samples of neo-natal urine were obtained from Sheffield Children's Hospital, the details of which are shown in the table below. (Table 3-7) The values in the dilution column refer to the dilution at which the samples were analysed.

Table 3-7 - Neo-natal Urine Samples

Sample	Dilution	Age of Child	Sex	Condition
20	1:7	2yr	—	Profound Metabolic Acidosis + β-Ketothiolase Deficiency
16	1:7	2yr	—	Hypotonia, hepatosplenmegaly Developing Mevalonic Aciduria
18	1:7	3yr	—	Seizured during febrile illness, dev delay, Valpruate metabolites
21	1:7	2yr	—	Afebrile Fits
25	1:7	8yr	Male	Adoption Screen - NORMAL
26	1:7	8mth	Female	Seizures
27	1:7	3yr	Female	Failure to Thrive

Analysis was performed on unfiltered urine, with a dilution being the only sample preparation step employed.

3.2.4.2.3 **Results**

As the technique was being used for qualitative analysis only, it was the differences in the patterns in the electropherograms that were of importance. The electropherograms obtained are shown in the appendix B.

Comparing the electropherogram for sample 16 with that for sample 18 it is possible to see certain differences. In sample 16 the dominant acids are hippuric (t = 26.61), lactic (t = 21.00) and two unknowns at t = 16.93 and 19.93. In this sample the hippurate: lactate

area ratio is approximately 1, whereas in a normal sample the hippurate would be the dominant compound.

In sample 18, the hippurate: lactate area, is less than 1, indicating some abnormalities. Also present are pyruvate (t = 17.30) and 3-hydroxybutrate (t ≈ 23.00) and several other unidentified compounds between t = 17.00 and 26.00. The peak at t = 19.96 is, however, absent.

It was noted that there was some variability in the migration times of the EOF marker during a series of runs, although this did not affect the overall mobilities of the acids. The possible cause of these variations was thought to be proteins in the urine binding to the surface of the capillary. By using a longer buffer and NaOH rinse these were reduced.

3.2.5 Conclusions

The aims of developing a capillary electrophoretic method for the analysis of organic acids in aqueous based samples were completed successfully. However, several points were raised during the process that possibly have some bearing on the usefulness of the technique for the measurement of trace organic acids in air.

The primary problem was the poor reproducibility of the peak areas obtained. For trace analysis it should be noted that a %RSD of say 15% is the difference between the compound being present in the sample or not. Although these problems were instrumental as opposed to electrophoretic the validity of using capillary zone electrophoresis (CZE) for trace air analysis is brought into question.

A second problem that was observed was that of the sampling technique. Although the simplicity of bubbling air through a known quantity of water is appealing it became apparent that this was not only impractical for field sampling but also not reproducible. To obtain valid results for air samples, further investigation into air sampling techniques is needed.

The use of the qualitative profiles during the analysis of the urine samples is a promising technique. Each urine sample had a unique profile or fingerprint, and by comparing this against known norms it was possible to screen the samples allowing those that warranted further investigation to be quickly identified. T0his technique could therefore be used for other aspects of analytical work, such as air sampling. The ability to obtain

"fingerprints" would allow the analysts to be able to focus their investigation, thereby saving time and money.

3.2.6 Determination of Carbonyls

3.2.6.1 Introduction

Carbonyl compounds are ubiquitous in both the urban and indoor environments, however, similarities in mass spectra between carbonyls and aliphatic alkanes require a confirmatory identification technique. Therefore the determination of carbonyl compounds via their 2,4-dinitrophenyl hydrazones by HPLC was used. Although this procedure is widely used and well developed it was hoped to be able to build this method into the overall protocol for the determination of volatile compounds in air. The basis of the method being followed is shown in Figure 3-18 below.

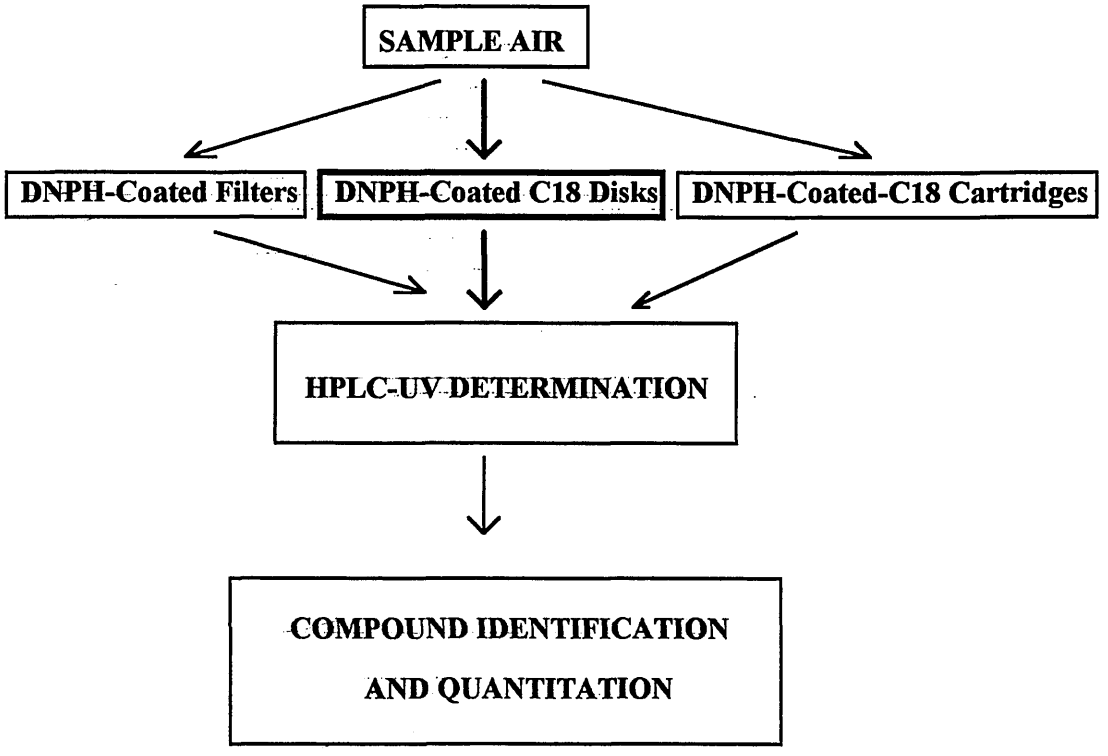
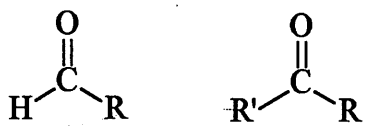


Figure 3-18 - Chart Showing the Methods of Determination of Carbonyl Compounds in Air

3.2.6.2 Carbonyl Chemistry

Compounds that contain the carbonyl group are broken down into two main categories, aldehydes and ketones. Aldehydes are characterised by one hydrogen and one alkyl group being attached to the carbonyl groups, whereas ketones have the carbonyl attached to two alkyl groups. (Figure 3-19)



Aldehyde **Ketone**

Figure 3-19 - Structures of Carbonyl Groups

In the carbonyl group, oxygen is more electronegative than carbon and as such attracts the bonding electrons more strongly. Therefore the bond is polarised in the direction C^{+}—O^{-}. The resonance structures for this effect are shown below.

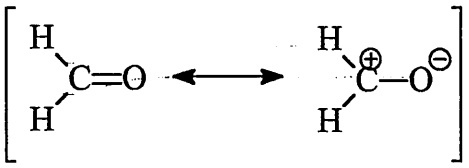


Figure 3-20- Resonance Structure of the Carbonyl Group

However a better descriptive picture is shown in Figure 3-21. This shows partial charges on both the carbon and oxygen, along with partial double bond/single bond character of the carbon-oxygen bond.

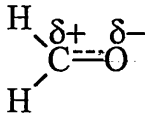


Figure 3-21 - Diagram Showing the Modified Carbonyl Structure

The bond polarity of carbonyl compounds plays an important role in the reactions and chemistry of the group.

3.2.6.3 Physical Properties

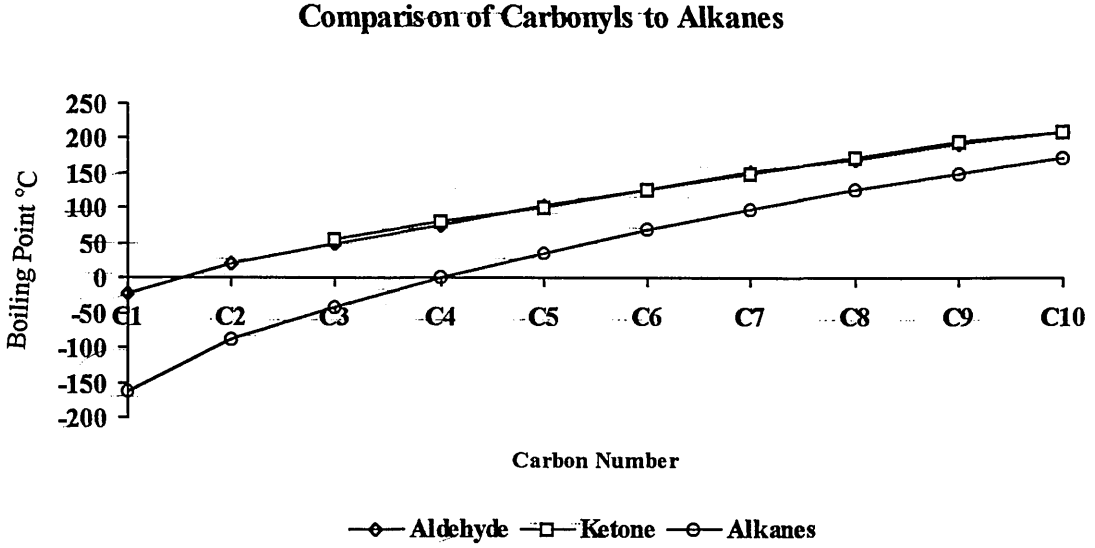


Figure 3-22 - Comparison of Boiling Points of Carbonyls with Alkanes

One of the major effects of the polarity of the carbon-oxygen bond is observed when studying the difference in boiling points of carbonyls and their analogous alkanes. The chart in Figure 3-22 shows this clearly. The dipoles that are formed attract, thus causing an increase in the boiling point of the compound as a whole.

3.2.6.4 Reactions of Carbonyl Compounds

There are several key reactions that need to be discussed in order to obtain a full picture of the chemistry of carbonyl compounds and how that can be used for their analysis.

3.2.6.4.1 Keto-Enol Equilibrium

In solution aldehydes and ketones exist in equilibrium between two isomeric forms, the keto form and the enol. (Figure 3-23) Although the equilibrium is generally in favour of the keto it is found that the importance of the enols cannot be overlooked.

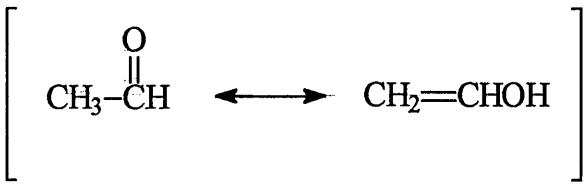


Figure 3-23 - Diagram Showing Keto-Enol Equilibria

Under basic conditions deprotonisation of the enol structure can occur, leaving the enolate ion that is in actuality a resonance hybrid rather than a localised carbanion. The structure of the hybrid is shown below.(Figure 3-24)

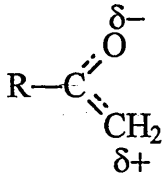


Figure 3-24 - Diagram Showing the Enolate Ion

Under neutral conditions this reaction is much slower due to water being a much weaker base than OH^-.

Under acidic conditions, however, the rate of enolisation is directly proportional to the concentration of the acid. Below pH 7, weakly basic carbonyl groups are protonated, and as such the protons are more easily lost from the carbon.(Figure 3-25)

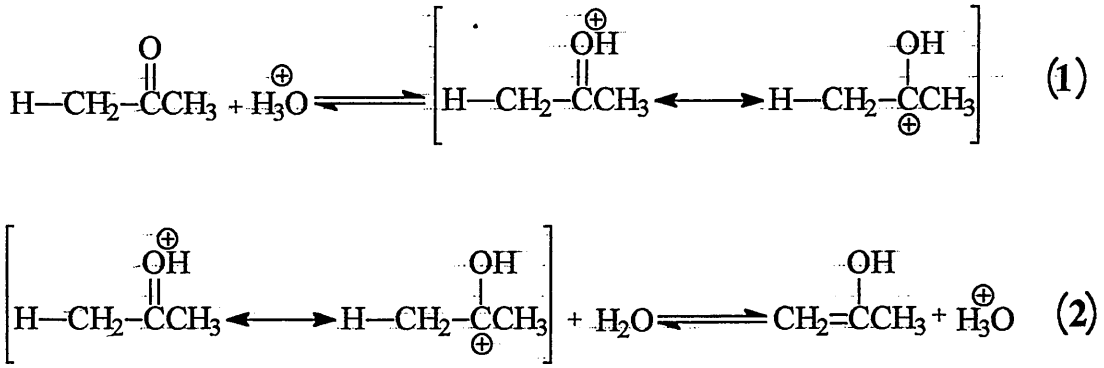


Figure 3-25 - Diagram Showing the Mechanism for Acid Catalysed Enolisation

In summary aldehydes and ketones in aqueous solution are in equilibrium between their keto and enol forms. This interconversion is either acid or base catalysed, however at any given moment the majority are in the keto form.

3.2.6.4.2 Addition of Nitrogen Nucleophiles

One of the fundamental reactions of carbonyls is the addition of nitrogen containing nucleophiles. The basic reaction originates from the reaction between a carbonyl group and ammonia. (Figure 3-26)

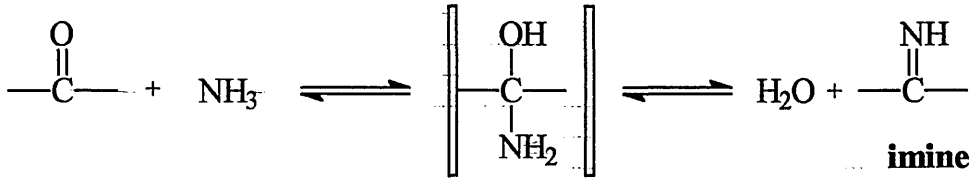


Figure 3-26 - Diagram Showing the Mechanism for the Formation of an Imine

The rapid hydrolysis of ammonia-carbonyl imines back to their constituent components means that they have limited importance. Substituted imines, however, produce much more stable compounds. Although compounds prepared from primary aliphatic amines still undergo hydrolysis. Stable compounds can be prepared if an aromatic group is present either on the carbon or the nitrogen. (Figure 3-27)

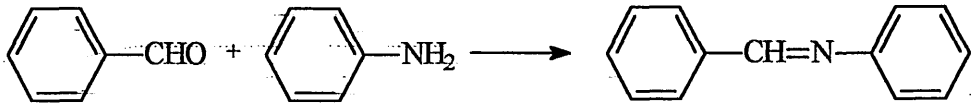


Figure 3-27 - Diagram Showing the Formation of Aromatic Imines

Carbonyl compounds also react with other ammonia derivatives to give stable compounds. Common reactants are hydroxylamine(Figure 3-28 A), hydrazine(Figure 3-28 B) and phenyl hydrazine(Figure 3-28 C).

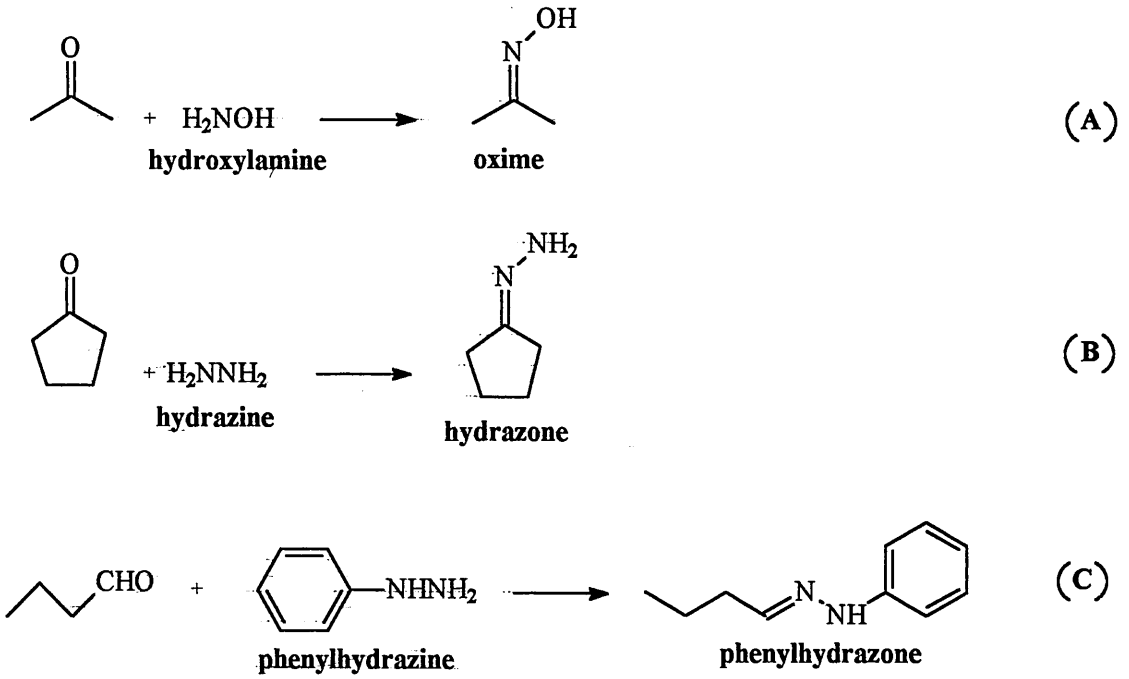


Figure 3-28 - Diagram Showing Other Nitrogen Containing Compounds

These reactions are generally acid catalysed, and follow the following five-step reaction mechanism. (Figure 3-29)

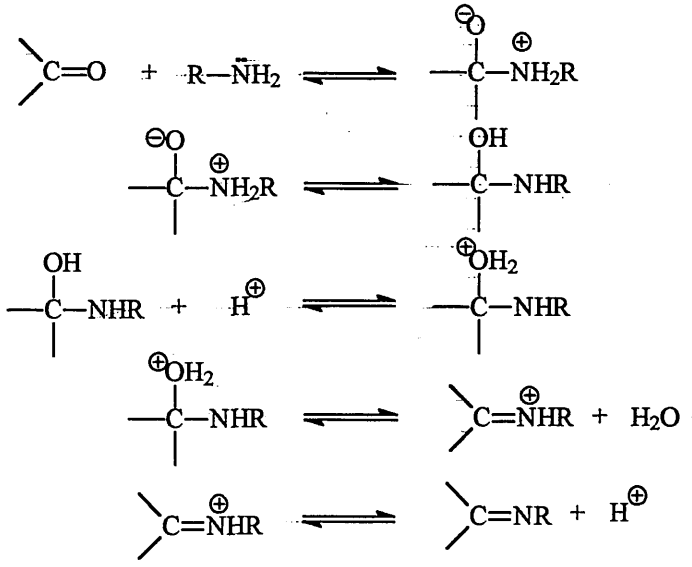


Figure 3-29 - Mechanism for Reaction of Substituted Ammonia with Carbonyls

It is the reaction with 2,4-dinitrophenyl hydrazine to produce a phenylhydrazone that is of interest when using HPLC for the investigation of carbonyl compounds. The 2,4-DNP

reaction is the standard test for the presence of carbonyl, with the vivid orange phenylhydrazone as the product.

The reaction of carbonyls to produce oximes will be discussed in a later chapter.

3.2.6.5 Method Development

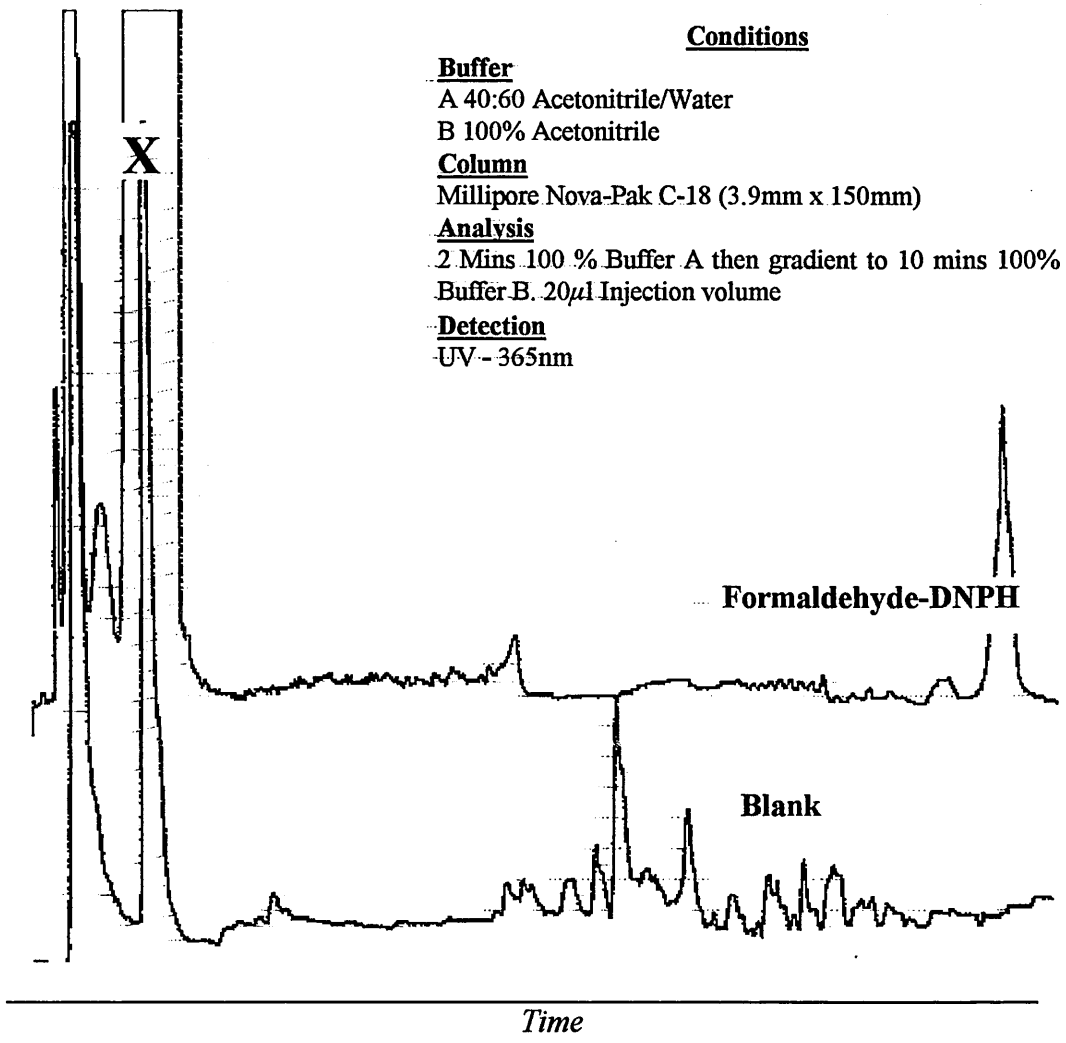


Figure 3-30 - Chromatograms showing DNPH Derivatives of 10ppm Formaldehyde and Solvent Blank

Figure 3-30, shows a chromatograms of formaldehyde alongside that of a reagent blank. The 2,4-dinitrophenyl-hydrazine peak is marked X in the diagram. In the blank there are several peaks that are caused by a combination of solvent pulsing and by artefacts found within the

blank solution. It should also be noted at this stage the poor quality of the baseline, which is caused by the equipment being used.

The analysis of carbonyls through use of 2,4-Dinitrophenylhydrazone derivatives, as already indicated, is a common method, combining simple organic chemistry with instrumental analytical techniques.

As can be seen in

Figure 3-31, the separation of the carbonyls is satisfactory. Several of the peaks appear as doublets, which is thought to be caused by the cis-trans isomers of the phenylhydrazones.

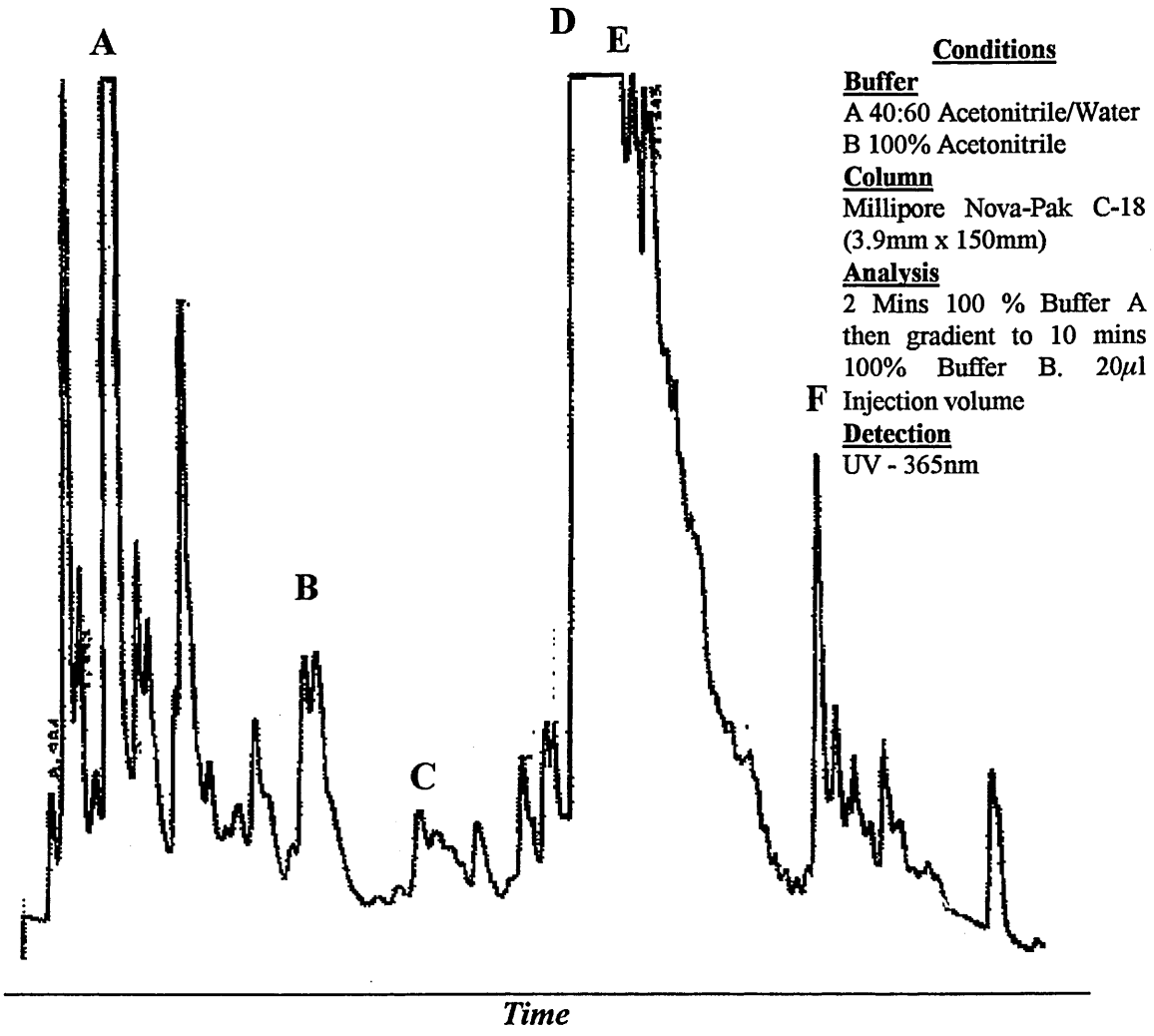


Figure 3-31 - Chromatogram showing DNPH Derivative of a Spiked Carbonyl Extract

A - Formaldehyde **B** - Ethanal **C**- Acetone **D** - Benzaldehyde **E** - Hexanal **F** - Decanal

3.2.6.5.1 Sampling

As always it is the sampling procedure that needs careful attention. In consideration of the two techniques used for this preliminary work, the benefits and weaknesses of both techniques need discussing.

The only apparent benefit of the quartz filter sampling method is that it allows the use of a high flow rate and hence a large sample volume. Initial results have shown however, in comparison with the other technique, the sampling efficiency is very low.

The reverse of these observations is applicable for the DNPH coated C_{18} SPE cartridges. Although only low sampling volumes can be used, the cartridges seem to be able to trap more sample than their quartz filter counter part.

Although the quartz filter technique gave poorer results, for initial investigations into sampling procedures, they were more cost effective. Prepared by pipetting 1ml of acidified DNPH solution onto a clean filter under vacuum, and then leaving to dry in a sealed desiccator, the filters had a pale yellow appearance. Three different sample types were taken; indoor lab air, outdoor air and tobacco smoke. The filters were place in filter cassettes and air was "sucked" through, this avoiding contamination being blown onto the filters from the pump.

For tobacco smoke, a chromatogram obtained from tobacco smoke, Figure 3-32, shows a tentative identification of formaldehyde, acetaldehyde, acetone, propanal, and benzaldehyde.

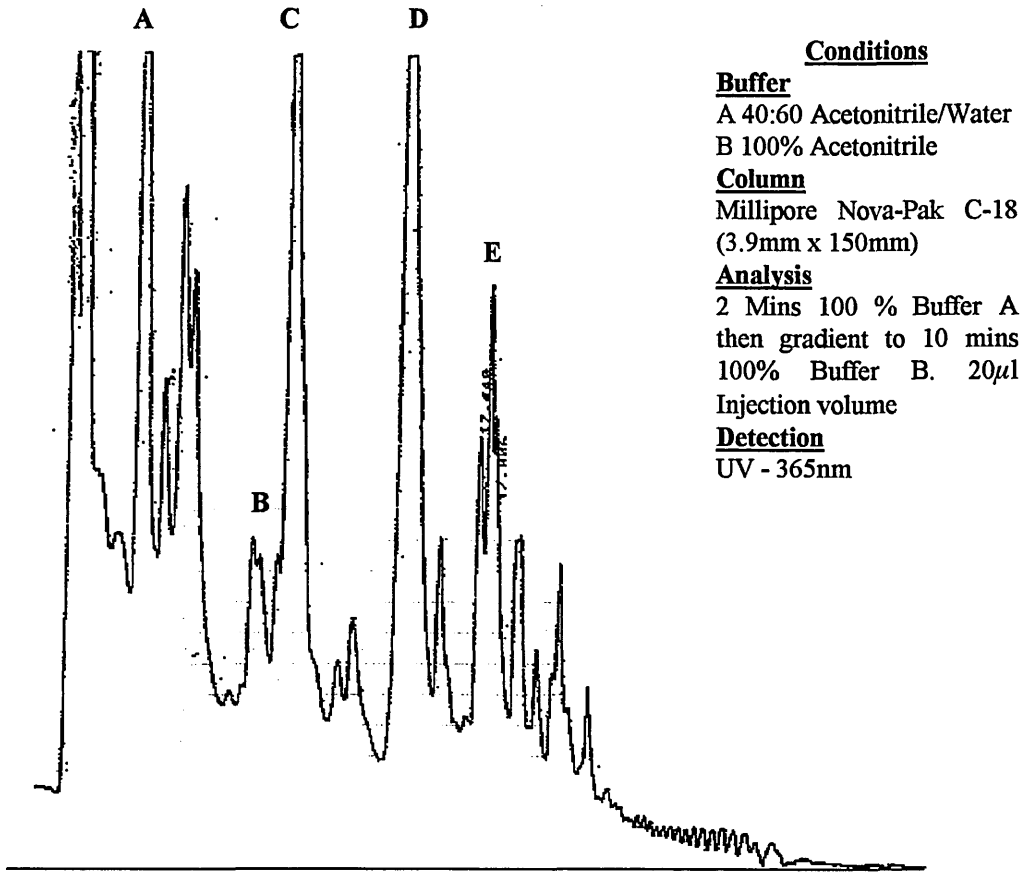


Figure 3-32 - Chromatogram showing DNPH Derivatised Carbonyls in Tobacco Smoke

A - Formaldehyde **B** - Acetaldehyde **C** - Propanal **D** - Acetone **E** - Benzaldehyde

It can be seen that the quantity of carbonyl compounds found in the tobacco smoke is significantly higher than those found in a normal air sample. This was to be expected from the literature.

3.2.6.6 Conclusions

The major problem encountered with this technique was not with the chromatographic separation but with the reliability of the instrumentation. Even on the chromatogram above the effects of pump pulsing can be observed. This was especially noticeable when solvent from the two separate pumps was being mixed. More advanced and

expensive equipment could have resolved these problems but because of limited budgets we had to make the best of the equipment that was available.

The second problem, as already mentioned, was that of sampling. Using the two sampling procedures that were frequently used in the literature, gave results that one would expect to be better. This could be due to the protocol that was used for our experiments, or our equipment, or maybe it was that the techniques were less reliable than the literature suggested.

It was decided, therefore, that with the instrumentation available for this project and the current sampling techniques available, the HPLC analysis of carbonyls was not an option that could be reliably used for the trace analysis of VOC's in air.

3.2.7 Determination of Phenols

3.2.7.1 Introduction

Phenols are present in the atmosphere in trace amounts as by-products from the atmospheric oxidation of aromatic compounds and also as direct emissions from vehicle exhausts and natural sources.

A high performance liquid chromatographic technique was to be developed to be used with an electrochemical detector, with mainly aqueous phase samples. Although other techniques for the determination of phenols are available, it was initially thought that the sensitivity and selectivity of the electrochemical detector would be beneficial for the trace determinations that were envisaged.

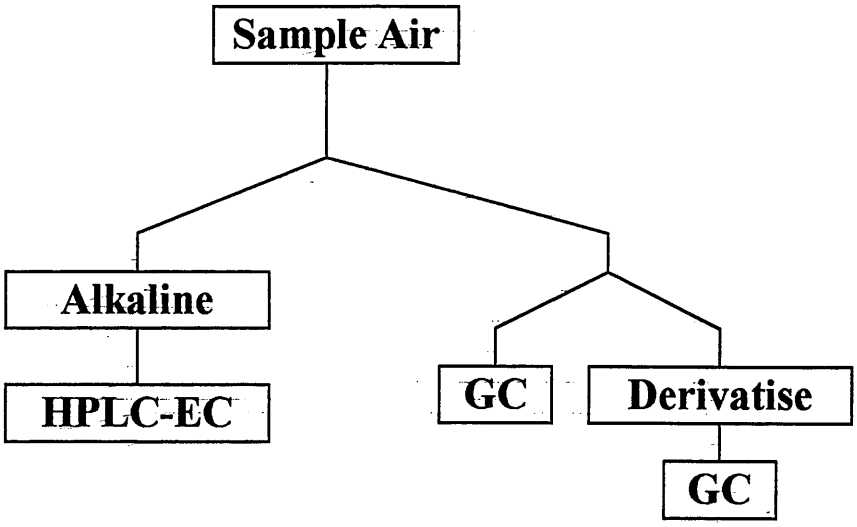


Figure 3-33 - Chart Showing the Method of Determination of Phenols

3.2.7.2 Background

To measure the small quantity of phenols that will be present in air, an on-line pre-concentration or trace enrichment step was introduced to a standard HPLC system. This involves passing the aqueous sample through a short non-polar pre-column, which is in the place of a traditional sample loop. Using a pump the sample is "injected" onto the pre-column, where the phenols are trapped and pre-concentrated. By turning the valve the mobile phase buffer passes through the pre-column where the sample is taken into the mobile phase and passes onto the analytical column where it is separated in the usual way. This apparatus is shown in Figure 3-1.

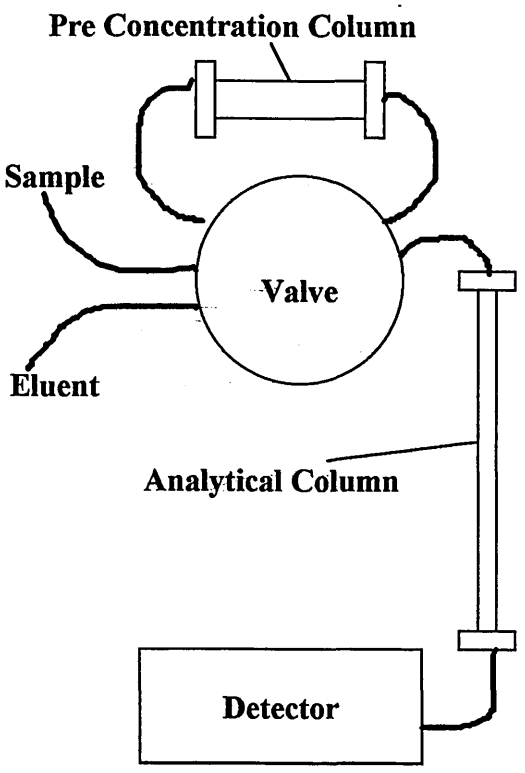


Figure 3-34 - Diagram Showing the Pre-concentration Apparatus

The pre-column was packed with ODS-5 column packing material, giving it an overall non-polar surface. With the analytes being in a methanol/water solution it was decided that the phenols would be in their acidic form and therefore non-ionic. The pre-concentration step was relying on the Van der Waals and dipole-induced-dipole intermolecular bonding mechanisms.

The separation of phenols using HPLC-EC was developed from a high speed analysis method.[1] Webster *et al.*, used a short column and low polarity solvent to elute all the phenols in one large peak. Using the electrochemical detector, therefore, this provided an extremely sensitive method for the measurement of total phenols.

3.2.8 Results

Initial work, carried out in order to optimise the separation technique, was performed without the pre-concentration apparatus. It was observed that by increasing the polarity of the buffer, i.e. increasing the methanol concentration, it was possible to achieve a satisfactory separation of 100ppm($mg\ L^{-1}$) phenol solutions.

Baseline separation was achieved for the majority of the peaks in the phenol standard. With this working method as a starting point, it was now possible to transpose the straight separation technique onto the pre-concentration apparatus.

Using a 10ppm(mg L^{-1}) solution of the phenol standard mix, diluted in water, the experiments were repeated. However, the results obtained were radically different from those obtained without the pre-concentration step. A large unresolved peak was observed at the beginning of the chromatogram. It was thought that this peak was caused by water being trapped on the pre-column as well as the phenols.

The major problem of the electrochemical detector was its sensitivity to changes in the background buffer composition. These changes were expressed as peaks or changes in baseline on the readout. This limited the HPLC techniques that could be used to isocratic elution. The problems experienced with the water peak could have been resolved if it had been possible to use a gradient elution. However, to keep a constant concentration of acetate ions would have required equipment that was not available to us.

It was therefore decided that the determination of phenols using HPLC-EC was not feasible as part of the overall study of VOC's in air.

3.3 Gas Chromatographic Determinations

3.3.1 Introduction

Although the research project was not primarily concerned with the "usual" volatile organic compounds, it became clear through the literature review that many of them were pre-cursors to the volatile oxygenated-organic compounds. It was therefore decided that if the difficulties in measuring VOOC could not be readily overcome, by measuring these compounds we could arrive at a similar conclusion in terms of air quality measurement.

Many of the compounds that are of interest to the scientist who is investigating the effect on air quality of volatile organic compounds have low boiling points. This physical characteristic creates an added difficulty for the analyst because many of the compounds of interest tend to be eluted along side in solvent peak, during chromatographic separation. To get around this problem, two solvent-free chromatographic techniques were investigated.

3.3.2 Cryogenic Focusing

3.3.2.1 Introduction

The first solvent-free technique that was investigated was that of cryogenic focusing using direct headspace sampling. The basic procedure that was adopted for the analysis of atmospheric air was initially developed for the determination of aroma components of processed tobacco.

For the determination of the tobacco headspace, large volumes (1 - 10mL) of air were taken from above the tobacco and then injected directly into the GC. By injecting at a steady rate it was possible to overcome the problems associated with the expansion of the gas in the injector. The compounds that were being analysed had boiling points of around 150°C, and thus the initial oven temperature was sufficient to enable suitable band focusing for these compounds.

However, for the volatile organic compounds that are found in air that have much lower boiling points, it was necessary to use temperatures of less than 20°C to achieve suitable band focusing and separation. As the ambient temperature of the laboratory was never less than 25°C it was difficult to obtain a temperature that was suitable for this work. Therefore the initial work concentrated on trying to use "dry-ice" to cool the oven to lower than the ambient temperature of the room. Due to the high background temperature this proved to be an expensive (in terms of CO_2) and fruitless exercise and was abandoned in favour of using column focusing.

3.3.2.2 Method Development

As with solvent based injection, the optimisation of the initial injection step to allow the focusing of the analytes at start of the column is of primary importance. By cryogenically cooling a small section of the column to lower than the boiling point of all the analytes it was possible to effectively stop all components of the sample, including oxygen and nitrogen, at a single point on the column. Only the carrier gas, helium, had a sufficiently low boiling point not to "freeze" onto the column.

After a given period of time, which was long enough to allow the volume of sample injected to pass onto the column from the injector, the column was removed from cryogenic

coolant. Once removed, the column quickly regained the temperature of the oven, thus releasing the compounds back into the carrier gas, where they would then be carried toward the detector. The apparatus used for the experiments is shown in the diagram below. (Figure 3-35)

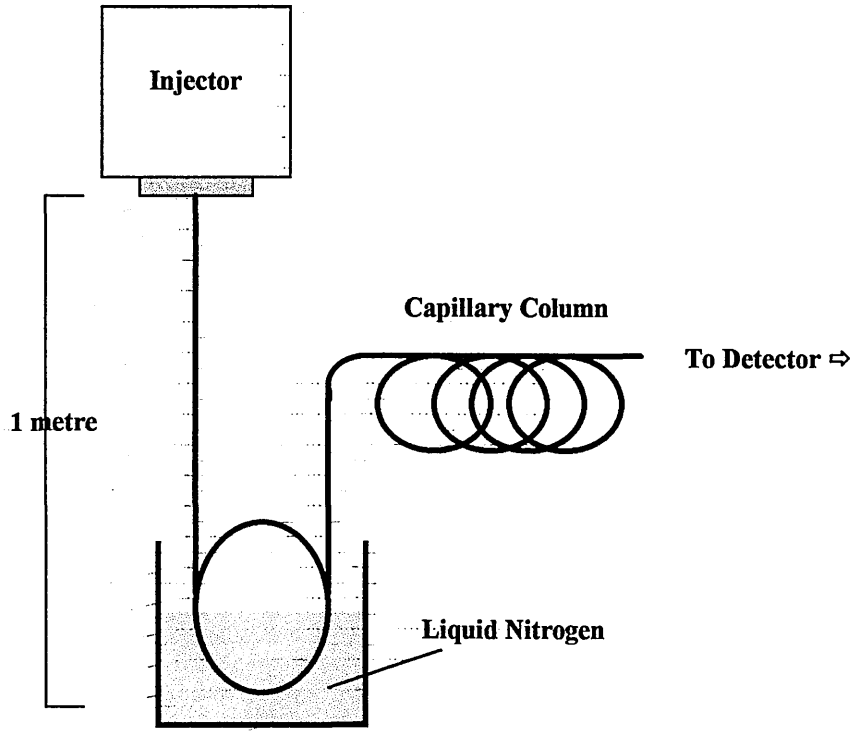


Figure 3-35 - Diagram Showing the Cryogenic-Focusing ApparatusResults

3.3.2.2.1 GC-MS

As the instrument being used was a GC-MS, the initial experiment that was performed was to determine the elution time of the air peak.

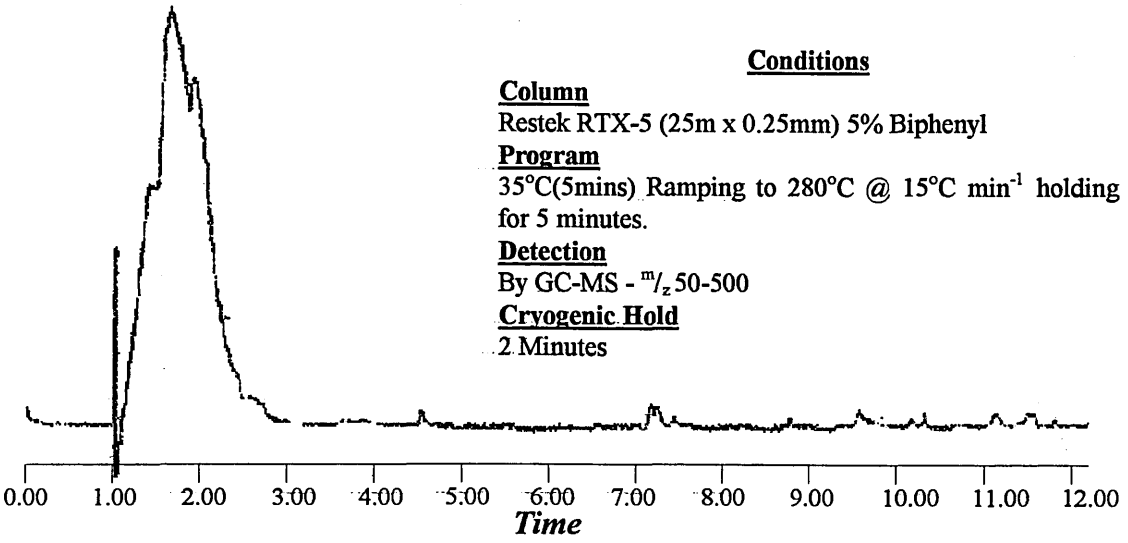


Figure 3-36 - Chromatogram showing Air Peak for Cryogenic Focusing Experiment

Figure 3-36, shows the chromatogram of the air peak. The main reason for this experiment was to prevent damage to the mass spectrometer filament. This can be caused when large volumes of gas or solvent are passed over it whilst in operation. Subsequent runs used the solvent vent program that turned on the filament after 3 minutes. Another benefit of using such a program was that it was possible to use larger samples volume without losing any sensitivity.

Further results indicated that it was possible to determine carbon dioxide, acetone and dichloromethane from a 1mL sample of air. The latter two compounds being used as solvents in the laboratory.

3.3.3 GC-AED

To help confirm the elemental identity of the compounds being detected the same experiments were performed using an atomic emission detector. By measuring the various emission lines it was possible to accurately determine the identity of certain compounds, especially dichloromethane, water, and carbon dioxide all of which have unique "hetero"-atoms.

3.3.3.1.1 Laboratory Air

The chromatograms shown below are from a 1 mL sample of laboratory air. The first chromatogram for C_{193nm} and Cl_{479nm}, (Figure 3-37) shows 13 peaks in a 2 minute time frame

on the C_{193nm} emission line. Using data from the GC-MS and elemental emission data it was possible to positively identify several peaks.

The definite chlorine mass spectra for dichloromethane was confirmed with the presence of a peak in the Cl_{479nm} line. Due to ventilation in the laboratory, the actual concentration in the air would be limited to just several ppm. (mg L^{-1})

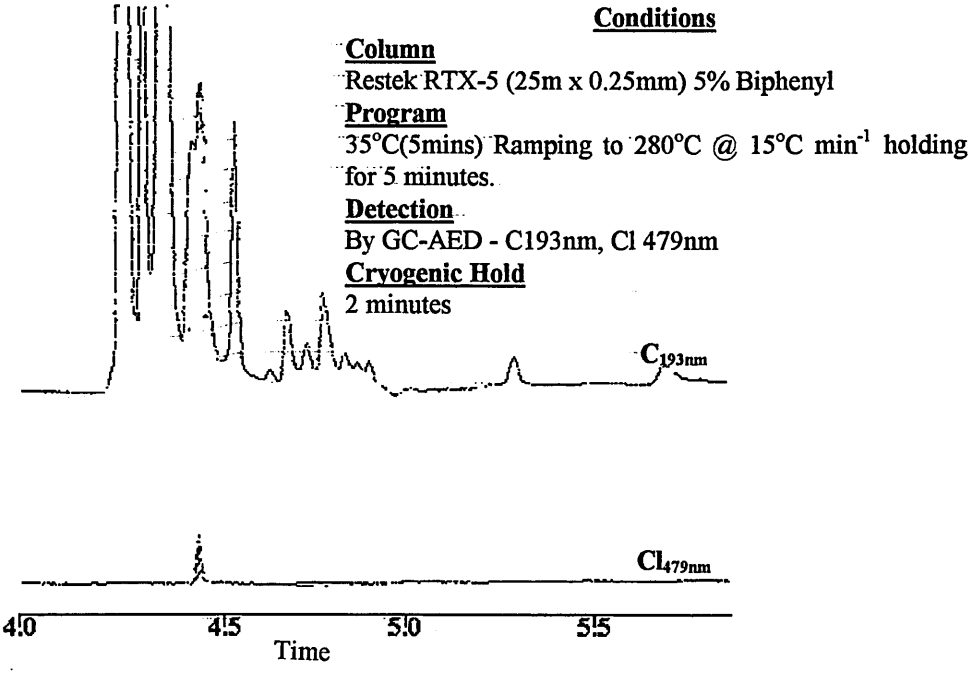


Figure 3-37 AED Chromatograms from Cryogenically Sample Air

Using the H_{486nm} emission line to confirm the presence of hydrocarbons a large unresolved peak was discovered which was not found in either the C_{193nm} or C_{496nm} lines. However by also examining the O_{777nm} line it was possible to establish that this peak was due to atmospheric water. It was also possible to confirm the identity of the carbon dioxide peak, through a lack of response on the H_{486nm} line.

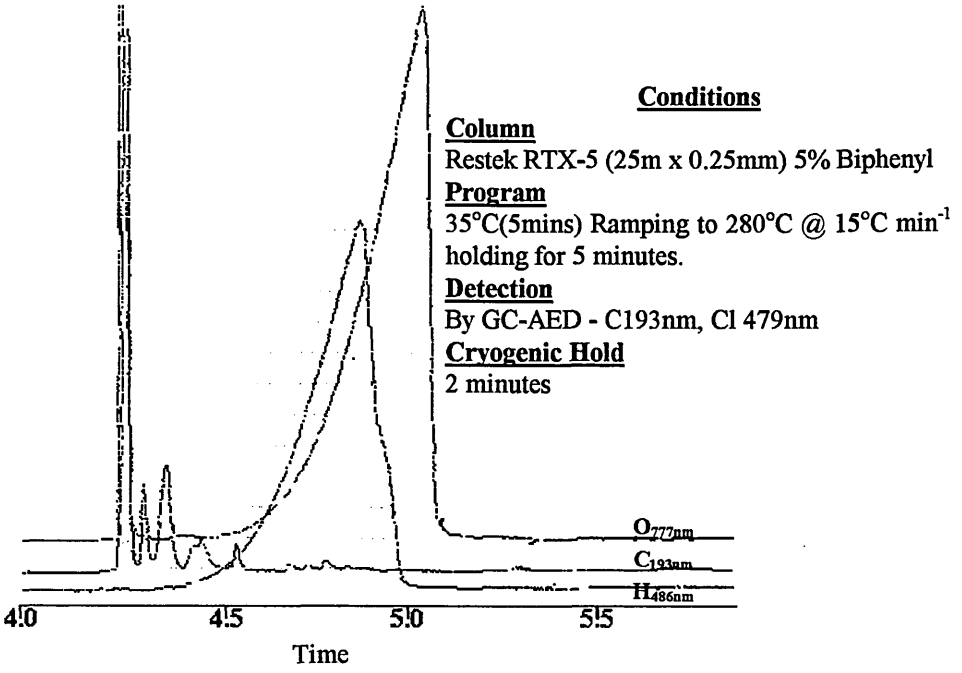


Figure 3-38 - Emission Chromatograms for a Cryogenically Trapped Air Sample

Therefore by using a combination of two detection techniques it was possible to identify several of the peaks in the air sample. The use of the N_{174nm} emission line however could not be used to reliably confirm the presence of nitrogen containing compounds. A response is obtained on this line at a place where it is already confirmed that CO_2 was being eluted. This does not rule out co-elution of compounds, but the more feasible explanation is that the effects of molecular emission lines cause this response from the strong carbon signal.

3.3.3.1.2 Apparatus Performance

The apparatus used for the experiments was crude in that the analytical column was physically moved into and out of the cryogenic coolant. The dramatic and rapid temperature changes soon led to damage occurring both to the column structure and to the stationary phase.

3.3.3.2 Conclusions

The results that were obtained from the cryogenic focusing method were satisfactory, to the point that the method worked and the results were seemingly reproducible. However, it was noted that the results were only showing small low molecular weight compounds, such as acetone and dichloromethane. This suggested two things: that

the concentrations of higher compounds in the air were less than expected or that we were losing compounds before the analysis.

The latter suggestion is based on the fact that large quantities of atmospheric water were found. This would have formed a ring of ice around the column, not through any physical interactions with the stationary phase, but although in-situ freezing. With this frozen layer covering the column many of the compounds would have simply passed through the cryogenic trap and to the detector before it was in operation. The layer of ice would also act as insulation from the cryogenic coolant and thus reduce the cooling effect on the hot gases coming from the injector.

With these conclusions it was decided that this technique was not suitable for the general purposes of this project. Also the damage that occurred to the column with use tends to preclude this technique from being useful for the routine analysis of compounds in gaseous samples.

However, for short-term projects the results obtained, such as concentrations of macro pollutants such as CO_2, acetone and dichloromethane, far outweigh the column damage. Also by using the atomic emission detector it was possible to examine the trace amount of water that were found in the indoor environment.

By using an inert pre-column it was possible to reduce the damage to the stationary phase. However, this technique was unsuitable for use with certain mass spectrometers because of flow restrictions that are caused by the inefficiency of the vacuum pumps.

3.3.4 Programmable Injector Thermal Desorption

3.3.4.1 Introduction

Thermal desorption, as already discussed, is a solvent-free sample introduction technique that places the analytes directly into the carrier gas stream. Using thermally stable sorbent materials such as Tenax, packed into either steel or glass tubes, thermal desorption can often provide a very versatile technique. The benefits of such methods are that the sample preparation step is limited to placing the sorbent carrier in the instrument. However, traditional thermal desorption techniques are very equipment intensive requiring special instrumentation.

Using a programmable temperature injector (PTI) as thermal desorbers, it is possible to obtain results that are on a par with standard thermal desorption equipment. A PTI can be considered as a piece of specialist equipment, but in terms of versatility, one can be used for more than just thermal desorption.

3.3.4.2 Method Development

The key to obtaining successful and useable results is getting the entire sample from the sorbent and into the gas phase with the minimum amount of band broadening. There are several ways that this can be achieved.

In solvent chromatography this is achieved by having the start of the column at a temperature significantly lower than that of the boiling points of the analytes so that the compounds may be formed into discreet bands at the top of the column. This in essence is similar to the cryogenic focusing, discussed in the previous section. With gaseous samples however this can prove difficult to achieve without specialist cooling apparatus.

Another way of reducing the band broadening is to limit the actual physical length of the sample band. In solvent chromatography injecting small volumes rapidly does this. In thermal desorption this can cause some difficulties. The volume of sample released is proportional to the amount trapped on the sorbent, and this cannot be reliably predicted. Also the rates of desorption of the analytes from the sorbent material vary between analytes. So getting a discreet and rapid sample from sorbent to gas phase is difficult and unpredictable. In dedicated thermal desorption apparatus the analytes are desorbed from the sorbent to be re-adsorbed on a cold trap. This rapidly heats from -130°C to 280°C in about 3 seconds giving a fairly discreet sample band. However, with the PTI, the rate of desorption was limited to 16°C s^{-1}, without a cold trap. It was found, however, that by stopping the carrier gas flow for 1 minute whilst the PTI was reaching maximum desorption temperature, it was possible to contain all the volatillised analytes within the injector. Once the carrier gas flow was re-established, the length of the sample was at the minimum obtainable, thereby giving the best achievable efficiency.

3.3.4.3 Results

Air samples were obtained from within the GC laboratory, which had been newly refurbished with melamine coated chipboard work surfaces, as found in many domestic

kitchens. The samples were taken at 1L min^{-1}, giving a total sample volume of around 15L. The samples were then desorbed and analysed using the protocol described in Chapter 2.

Using GC-MS with NBS-library post run analysis, chromatograms were obtained that showed a wide range of volatile organic compounds.

The chromatogram below Figure 3-39 is typical of those obtained using this method. It should be noted that all chromatograms showed the large unresolved peak at the beginning of the acquisition, onto which peaks were often superimposed.

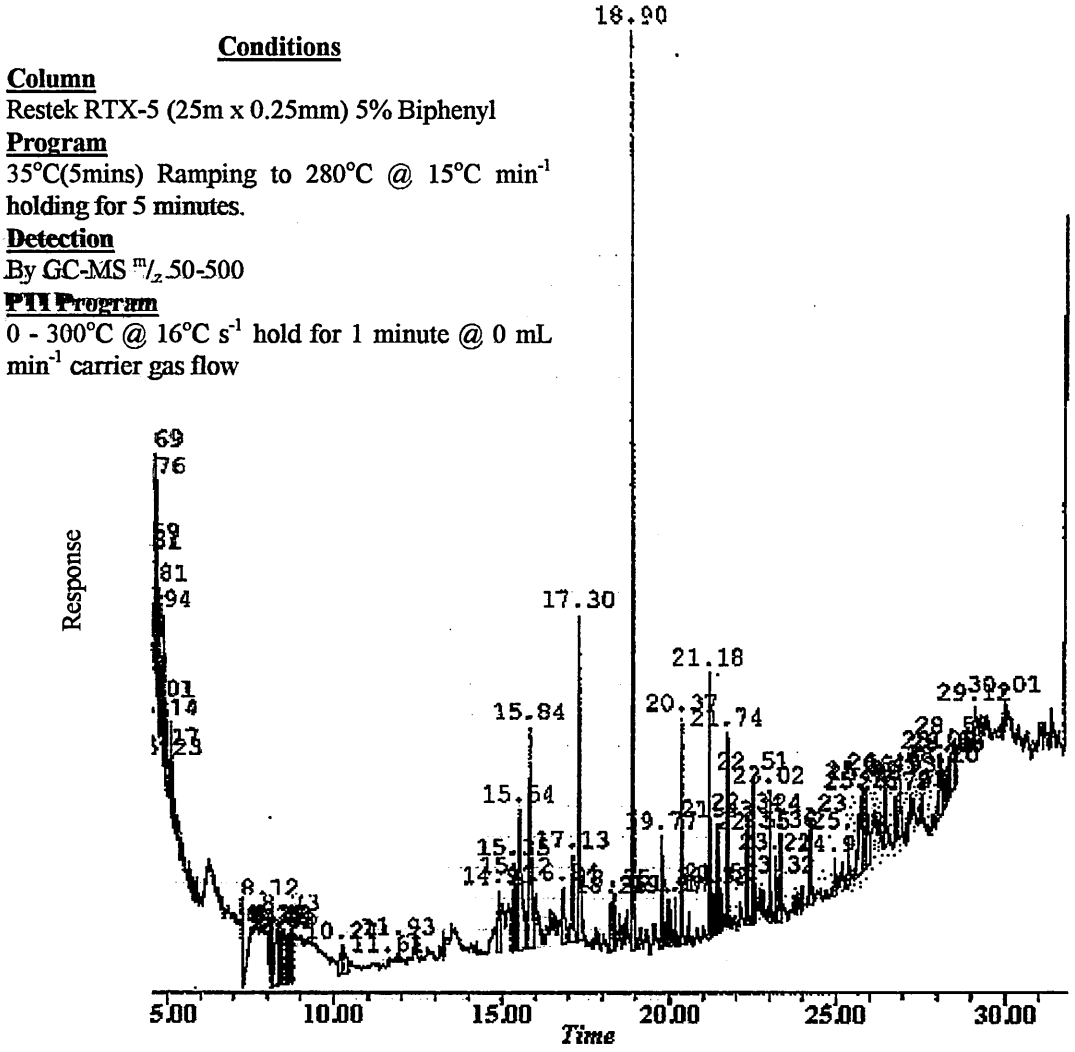


Figure 3-39 - Chromatogram of Indoor Air Sample obtained using PTI Injection

All the peaks after t_r=15min shows excellent peak shape and resolution. The poor shape of the earlier peaks suggests that the cold focusing at the top of the column is not working as efficiently as would be desired.

Using the NBS-library, tentative identifications of the peaks were made. These results are shown in Table 3-8.

Table 3-8 - PTI Thermal Desorption Compounds

Time	Compound
6.99	Hexane
11.95	Toluene
15.84	Nonane
17.30	Decane
18.90	1,4-Dichlorobenzene
19.54	Nonanal
21.18	Dodecane
21.74	Decanal
33.60	Plasticisers

Using the Carbotrap sorbent material the results from the samples showed a wide range of aliphatic carbonyl compounds, as well as aliphatic alkanes and small alkyl aromatic compounds.

3.3.4.4 Apparatus

Although the results being obtained appeared to be satisfactory and showed potential for further method development, it was the physical operation of the technique that showed the greatest weakness.

The sorbent materials were packed into the glass liners of the injector. Unlike ordinary injectors the PTI being used had an opening that allowed easy manual access. However, the act of opening and closing the injector on a regular basis proved damaging to the glass liners. This caused a potential safety hazard with pieces of broken glass regularly falling into the injector, which subsequently needed removing.

Another weakness of the technique was the cycle time. Under normal GC conditions the injector is kept at a continuously high temperature. But with this technique it was necessary to cool the injector back to a temperature at which the injector could be touched

by hand to change the sample. This took a period of time that was significantly higher than that of the cooling of the GC oven.

3.3.4.5 Conclusion

It was therefore concluded that although this technique had many valid points, such as limited sample preparation, it was not suitable for the routine analysis of VOC's in air. Time factors, as well as safety hazards, suggested that the development of this technique was not yet complete and therefore due to the time constraints of the project was not viable for use.

3.4 1.1 Conclusions

The idea of using several different analytical techniques, each for a different class of compound seemed, initially, to be viable. It was upon the examination of the required sampling techniques that it became clear that there would be major difficulties in trying to determine any meaningful data about the composition of the air and its relationship to air quality.

Although it was not possible to adopt this multi-method approach much of the work was used as a preliminary for the work described in the next section. This is especially so for the results from the PTI thermal desorption work.

The potential discovery of long chain carbonyls in indoor air was important in that it was predicted by the theoretical work discussed in Chapter 1. However, it is the ability to confirm these results, which is of greatest interest to the analytical scientist. Using one-shot, solvent-free techniques limits the investigative work that can be performed on any one sample. Therefore it was necessary to develop a more thorough and useable protocol for the determination of organic compounds is urban and indoor air.

Chapter 4

Single Method Approach

4.1 Sampling

4.1.1 Introduction

The multi-method analytical approach, although able to provide quite detailed information regarding the air sample, required high levels of maintenance, was too time consuming and required a multiple sampling protocol. Therefore it was decided that for monitoring the levels of volatile organic compound in air over an extended period of time this approach was unsuitable.

To overcome these problems it was decided to use only one sampling technique and one basic analytical technique. Initial objections to this proposal were that the compounds that would be determined would be limited to just one class, either polar or non-polar, Also it was considered that detection and confirmation of the compound would be limited by the instrumentation used.

Although these objections were valid, we were aiming to show that, by fully utilising the physical and chemical properties of the solvent, sampling media, and the analyte, it is possible to obtain samples that contain a wide range of compound classes.

4.1.1.1 Sampling Techniques

In the previous chapter it was discussed that one of the major limitations to all of the analytical techniques used was the problem associated with actually obtaining the analytical samples. One major aspect of this research project, therefore, was the examination and development of a technique that would not only allow the sampling of a wide range of volatile organic compounds but also give the maximum possible sampling efficiency.

Traditional air sampling techniques used for the analysis of volatile organic compounds in air generally use small sample volumes. This is because of a phenomenon known as breakthrough.

4.1.1.2 Breakthrough Volume

The breakthrough volume is generally described as the volume of air that can be passed through a sampling medium before a given analyte is observed at the exit side of the medium. Each analyte compound has a different set of physical and chemical characteristics, which means that each compound will have a different breakthrough volume.

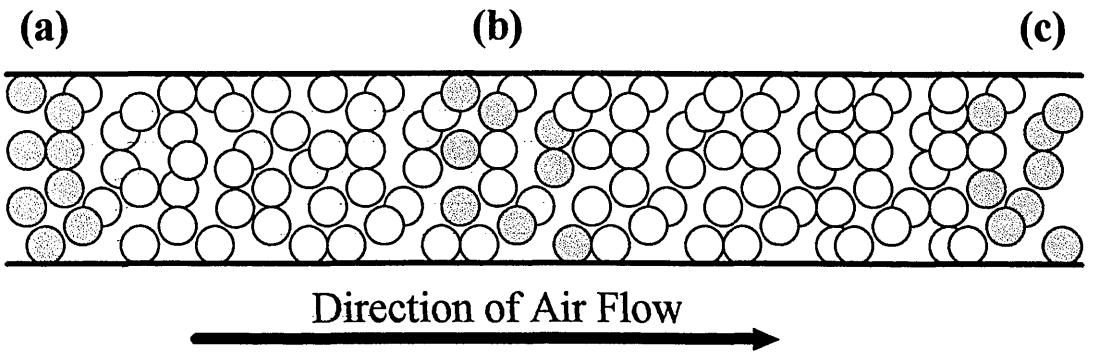


Figure 4-1 - Diagram Showing the Mechanism of Sample Breakthrough

In examining why breakthrough occurs it is necessary to look at the sampling process more closely. When an analyte is introduced onto a sampling medium (Figure 4-1a) it is held there only by relatively weak physical bonds. These bonding mechanisms were described in chapter 1. (1.3.2). As air is passed through the sampling medium equilibrium between the solid and gaseous phases is established in much the same way as in gas chromatography. The analyte will, therefore, chromatograph through the column (Figure 4-1b). However, unlike GC where a discrete and finite amount of sample is introduced into the system, in air sampling new analyte is continuously being introduced to the sampling medium. After a period of time the analyte reaches the end of the sampling medium and is released back to the atmosphere (Figure 4-1c). The volume of air that is required to move a sample from one end of the sampling medium to the other is known as the breakthrough volume.

Chapter 1.3 described many of the problems associated with air sampling, especially the fact that a given volume of air has so few molecules in it. Small sampling volumes will only trap relatively small amounts of analyte. This is not necessarily ideal when designing a protocol that will be used for the determination of trace analytes in air.

Given this and other considerations raised earlier it was felt that certain criteria should met by the sampling technique before it could be reliably used for the analysis of trace VOC's in air. These were: -

1. Allow large sample volumes
2. Allow high sample flow rates
3. Allow the trapping of a wide range of compounds
4. Use the minimum amount of solvents in desorption processes.
5. Be quick and easy to use.
6. Able to be used with many analytical techniques.

In this context, the first sampling medium that we examined was a styrene-divinyl benzene co-polymer that was supported in a 3mL syringe body. These are marketed by various companies as solid-phase extraction cartridges for liquid chromatographic use. The solid-phase extraction cartridge has found a rapidly expanding following within the analytical community for the preparation and pre-concentration of samples. Only the imagination and the ingenuity of the analytical scientist limit the possible uses of this technique within the field.

The extraction processes occur by maximising the differences in physical and chemical properties between the analyte, the sorbent material and the solvent. It was surmised, therefore, that if these processes could work for liquid samples they should, in theory, also work for gaseous samples.

4.1.2 Styrene-Divinyl Benzene

Styrene-Divinyl Benzene (SDB) was the first SPE material that was examined for use in air sampling. The reason was that they were readily available within the laboratory.

Styrene-divinyl benzene co-polymer is marketed under different trade names, but for air sampling it is generally sold as XAD. However, styrene-divinyl benzene based SPE cartridges go under the trade names of SDB-1 and ENV+ depending on which company the product originates from.

It is possible to take advantage of both the polar and non-polar characteristics of styrene-divinyl benzene when it is used as the sorbent material. (Figure 4-2)

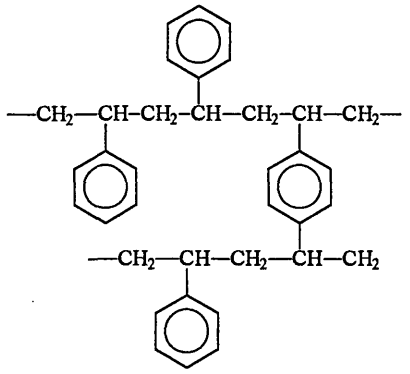


Figure 4-2 - Diagram Showing the Structure of Styrene Divinyl Benzene

In styrene-divinyl benzene (SDB) there are many general characteristics that will be referred to again when discussing other materials. These are features that we feel help to describe some of the results that were obtained.

4.1.2.1.1 "van der Waals" Backbone

The SDB material has an aliphatic or "van der Waals" backbone. -CH_2 and -CH2 units that form the backbone to which the phenyl moieties are bonded dominate this area of the material. Analytes attracted to this part of the material will be trapped, mainly, through dispersion or van der Waals forces. These compounds will be essentially non-polar compounds or compounds with an extended "van der Waals" area, such as n-aliphatic hydrocarbons. This is not to say that strongly polar compounds do not exhibit attractions toward these areas, however the bonds formed are not van der Waals but rather dipole-induce dipole.

4.1.2.1.2 Phenyl Moieties

Due to the nature of the styrene and divinyl benzene monomers, there are two types of phenyl groups present in the polymer. Firstly there are mono-substituted phenyl groups that originate from the styrene monomer. These groups, having only one electron-withdrawing alkyl group present in the structure have a relatively electron rich delocalised (π) system. (Figure 4-3a) However the groups originating from the divinyl benzene monomer cause di-substituted phenyls to be present in the polymer. The benzene rings have a more electron deficient π system compared with that of the mono-substituted phenyl groups. (Figure 4-3b)

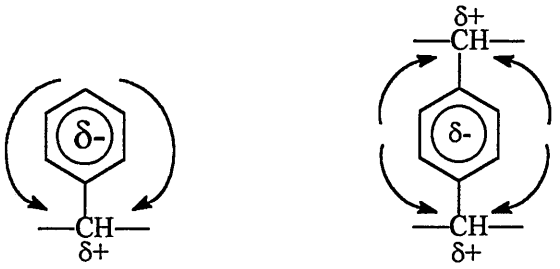


Figure 4-3 - Diagram Showing Styrene and Divinyl Monomers

The relatively polar character of these phenyl groups, caused by the π electrons systems, will allow trapping of compounds that also have some polar character. The major intermolecular forces on this part of the material will therefore be dipole-dipole and dipole-induced dipole bonding.

4.1.2.2 Results

Figure 4-4, shows a chromatogram of a dichloromethane extract from a sample of laboratory air. The sample was collected on a SDB cartridge over a period of 6:29 hours. This represents a total air sample of approximately 1000 litres .

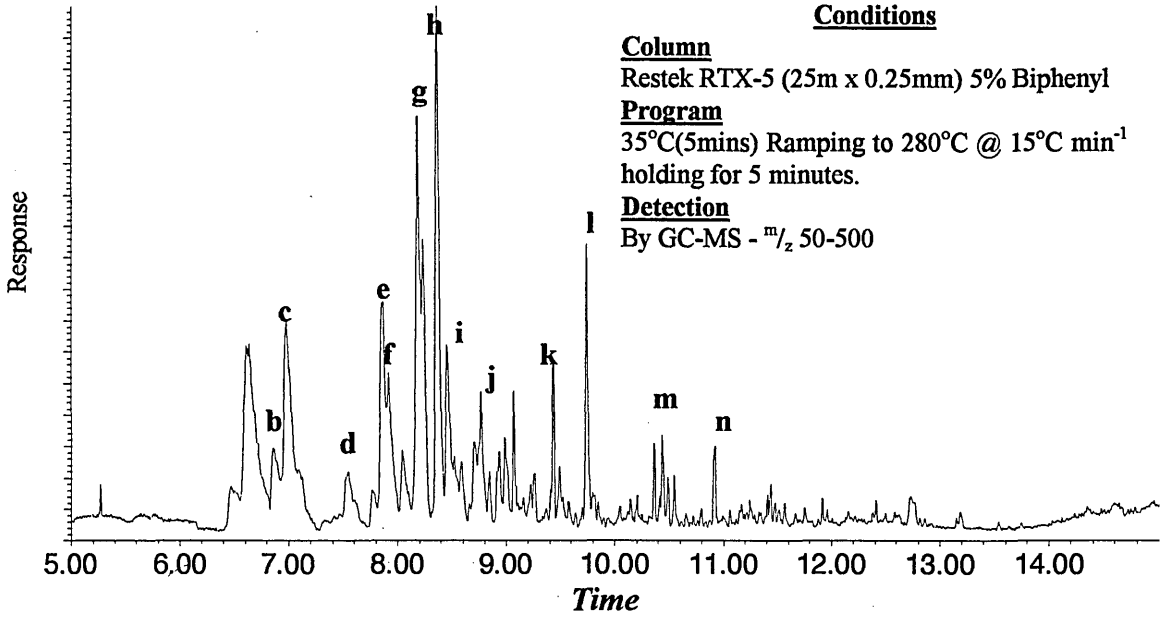


Figure 4-4 - Chromatogram of Dichloromethane Extract of SDB Sampled Indoor Air

This initial sample has 91 integrated peaks, representing compound classes aromatics, aliphatics, natural products and polyaromatic hydrocarbons. The initial identifications of the compounds were performed using the built-in library facility on the GC-MS equipment. Tentative identifications for individual compounds are shown in Table 4-1,

Table 4-1 - Identification of Compounds on SDB

Compounds Identified					
a	p-xylene	f	1-ethyl-3-methyl benzene	k	undecane
b	cyclohexanol	g	1,3,5 trimethyl benzene	l	naphthalene
c	o-xylene	h	1,4-dichlorobenzene	m	dimethylnaphthalene
d	α-pinene	I	1,2,4 trimethyl benzene	n	tetradecane
e	1-ethyl-2-methyl benzene	j	4-ethyl-1,2-dimethyl benzene		

A more general form of compound identification, using extracted ion chromatograms, is shown in Figure 4-5.

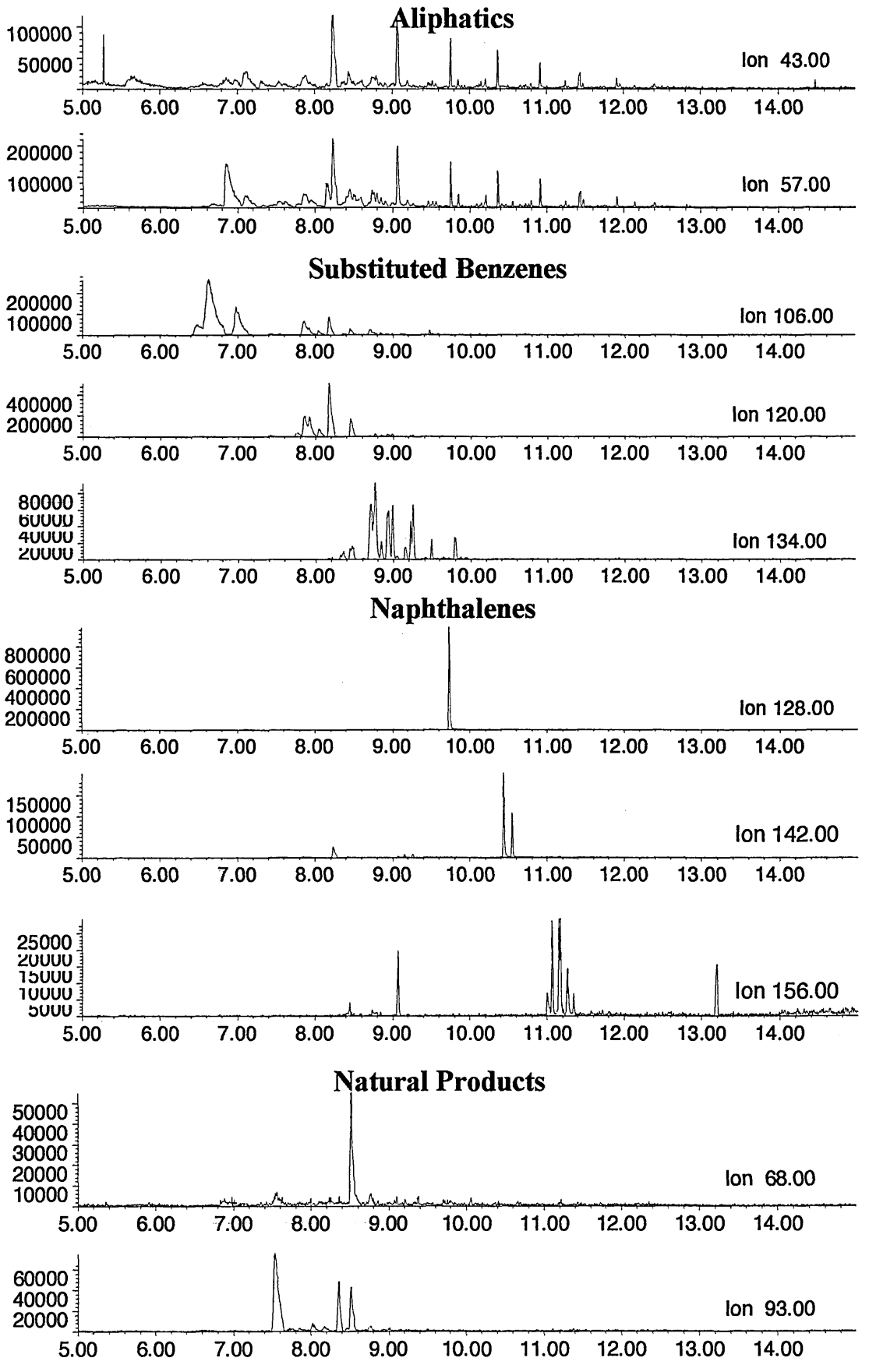


Figure 4-5 - Extracted Ion Chromatograms from SDB Sampled Indoor Air

By looking at mass fragment ions that are specific to certain compound classes, such as aliphatic alkanes, it possible to get an overall picture of the trapping capabilities of the SDB material. The groups of ions that were used for identification purposes are not an exhaustive list for all compounds but were chosen because they are representative of the classes being investigated.

4.1.2.2.1 Desorption Processes

The intermolecular forces of dispersion, dipole-dipole and dipole-induced dipole have very low bond energies of ~5 $\Rightarrow$ 30kJ mol^{-1}, compared to those of ionic and co-valent bonds which are ~100 $\Rightarrow$ 500kJ mol^{-1}. Although these forces are weak, they are strong enough to allow physical adsorption between the gas phase of the sample and the solid phase of the sorbent. Because of the nature of the polymer and the sorption processes that are occurring it was hypothesised that it should be possible to selectively desorb from the sorbent, compounds of different polarity. This could be achieved by extracting the sample from the cartridge using two or three different polarity solvents, and matching the polarity of the analyte with that of the solvent, in much the same way as one would use a gradient HPLC system.

A sequential solvent desorption protocol was devised to test this hypothesis. In order to analyse low boiling point VOC's, however, it was found to be necessary to extract the samples from the cartridges using low boiling point solvents (~40°C). Therefore the solvents investigated were *n*-pentane (bp 34-36°C) and dichloromethane (bp 40°C).

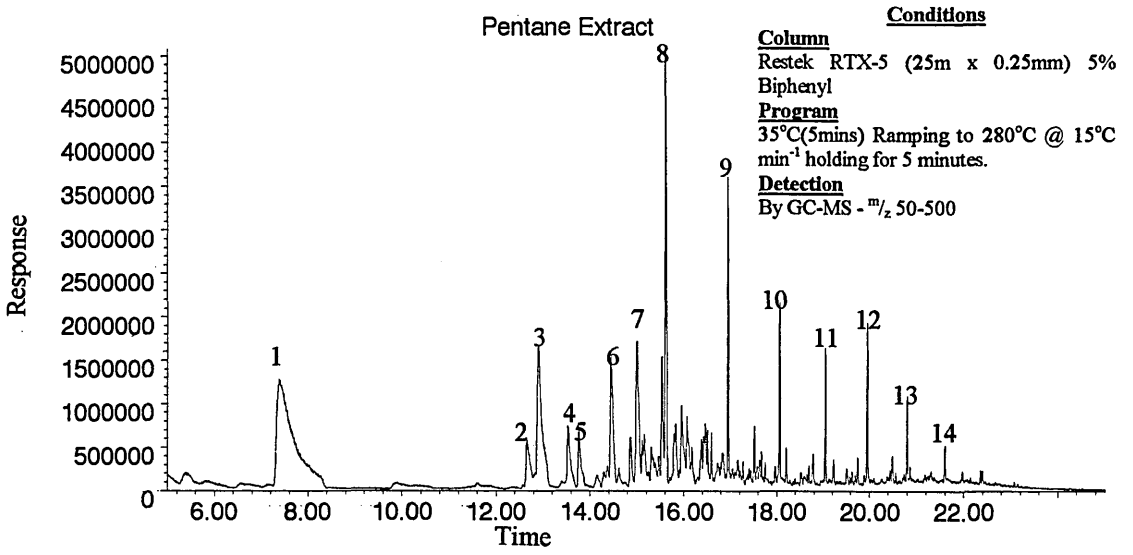


Figure 4-6 - Chromatogram Showing a Pentane Extract from SDB in A Sequential Desorption Experiment

1. Toluene, 2. Xylene, 3. Xylene, 4. Xylene, 5. Nonane, 6. α-pinene, 7. 1,4-Dimethyl cyclohexane, 8.Decane, 9. Undecane, 10. Dodecane, 11.Tridecane, 12.Tetradecane, 13. Pentadecane, 14. Hexadecane

It can be seen in Figure 4-6 that non-polar *n*-pentane generally extracts non-polar compounds, such as the *n*-alkanes. Some aromatic compounds are present however, namely toluene and xylene. This is due to an overlapping of the polarities between the analyte and solvent.

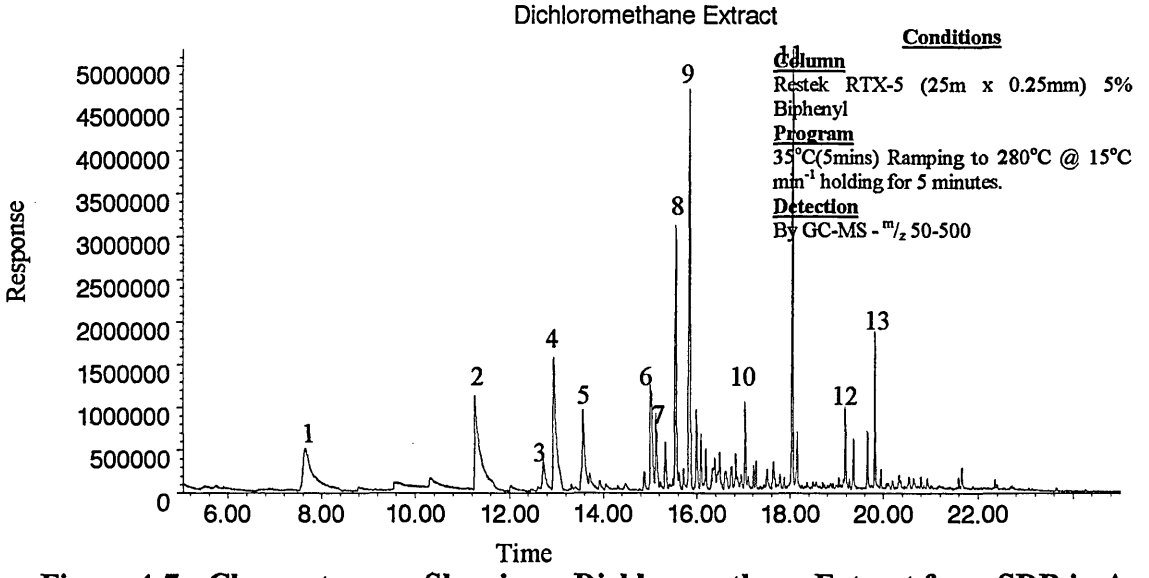


Figure 4-7 - Chromatogram Showing a Dichloromethane Extract from SDB in A Sequential Desorption Experiment

1. Toluene, 2. Acetic acid, butyl ester, 3. Xylene, 4. Xylene, 5.Xylene, 6.1-Ethyl-2-methyl-benzene, 7. 1-ethyl-2-methyl-benzene, 8. 1,2,4-trimethyl-benzene, 9. 1,4-

dichloro-benzene, 10. Nonanal. 11.Naphthalene 12. 1-methyl-naphthalene, 13. Butanoic acid, butyl ester

Figure 4-7 shows the chromatogram for the dichloromethane extract. Dichloromethane, having some polar character, extracts compounds from the sorbent which are of moderate polarity. The dichloromethane extract, therefore, tends to contain a higher proportion of alkyl-substituted benzenes.

By using a sorbent material in a system that will allow sequential desorption, such as the solid-phase extraction cartridge, it is possible to trap and analyse more effectively the compounds that are of interest to the analyst. Other benefits of the SPE system are described in a later section.

4.1.2.2.2 Sample Breakthrough

The styrene-divinyl benzene cartridge, when actively sampling, acts in a similar way to a GC packed column. Through the flow of air, compounds will pass through the cartridge, in effect being chromatographed. Eventually they will be eluted. The level of breakthrough is related to the sorbent's physical characteristics, to the individual analytes and also to physical factors such as air temperature and pressure. Breakthrough in this context is not a measure of the retention capacity of the sorbent but is a measure of the retention capability under sampling conditions. To study the breakthrough for all the compounds that were observed in our air samples would have been impractical and prohibitively time consuming. Hence the retention behaviour of just one particular compound was studied. 1,4-dichlorobenzene was chosen because it was found to be ubiquitous in all indoor air samples taken.

1,4-Dichlorobenzene is a compound, suspected as being carcinogenic, that is found with growing frequency in indoor air due to its use in commercial cleaning products and disinfectants. Using the assumption that, in the relatively closed system of an unused room, the levels of 1,4-dichlorobenzene present in the atmosphere would remain constant, it was, therefore, used as a marker compound. Using two SPE sampling tubes in series it was possible to test the breakthrough.

The chart in Figure 4-8 shows the level of build up of 1,4-dichlorobenzene on both the front and rear cartridges over a sampling period of several hours. By taking regular measurements over this time it was possible to obtain the data shown.

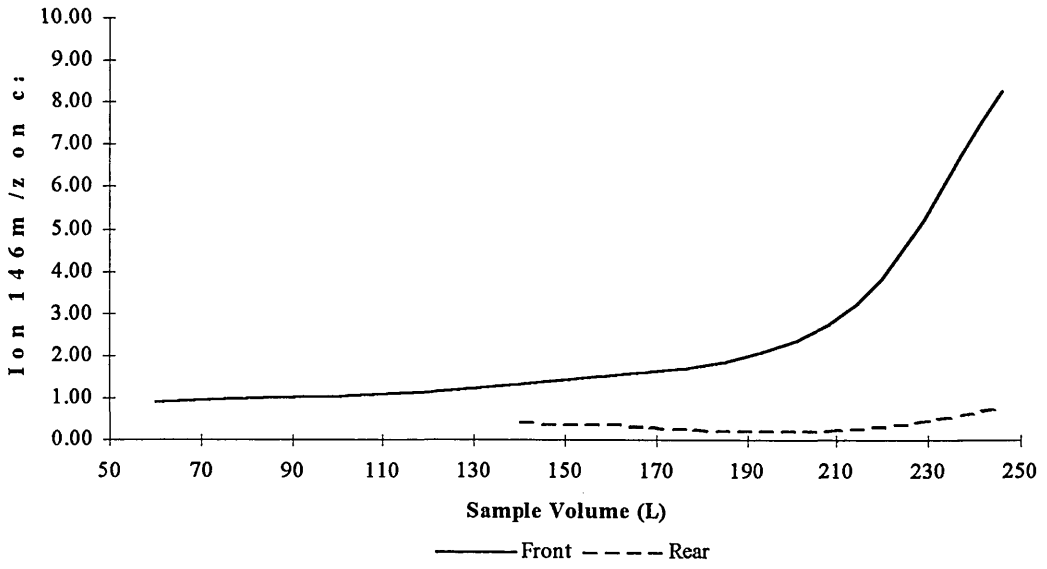


Figure 4-8 - Chart Showing SDB Breakthrough Results

It can be observed that for the 1,4-dichlorobenzene there was a steady build up of sample on the front cartridge, at a rate of approximately 13 pg L^{-1}, up to 200L of air sampled, after which time there is a more rapid rate of loading of 145 pg L^{-1}. The reasons for this change in loading rate are unclear. One possible explanation is that the primary sites on the sorbent matrix had become filled and there was a favourable change in the surface characteristics of the material. Another reason for the approximate 10-fold increase in loading rate could be attributed to a change of air quality in the sampling room over the period of study.

For the rear cartridge there was no increase in the amount of 1,4-dichlorobenzene present up to around 210L. In fact the results seem to suggest a slight decrease the concentration on the rear tube. This is in line with the chromatographic theory for sample breakthrough. After a sample volume of 215L, the concentration of 1,4-dichlorobenzene on the rear cartridge starts to rise steadily at a rate of 13 pg L^{-1}. In this series of experiments, it is at this point that breakthrough from the front cartridge to the rear cartridge is starting to be noticed.

Although sample loading is still occurring on the front of the first cartridge, there is some loss from the exit side. This chromatographic displacement potential should be

kept in mind when air sampling. It is only when a steady state has been achieved that the effects of breakthrough are eliminated. In a "real-life" sampling situation this steady state is never obtained.

4.1.2.2.3 Reproducibility

The reproducibility of the technique was studied by multiple sample collection. Using a closed room, samples of 300L were taken. Although this is a sample volume that is larger than the perceived breakthrough volume for 1,4-dichlorobenzene, it was assumed that equilibrium was reached between the compounds being trapped and those being eluted. Furthermore for the purposes of this experiment all the samples were taken under identical conditions and therefore any errors caused by this assumption would be minimised.

To take into account slight variations in pump speed, (a 5% variation in flow rate can cause a error of ±15L) it was necessary to ratio the relative peak areas for two known compounds that were found in the sample. Compounds of similar structure and polarity were chosen for the study to minimise variations in trapping and elution rates that may be present between different types of compound. Ratios of ethylbenzene/*o*-xylene and toluene/*o*-xylene were compared. Samples (n=6) were collected on two separate days (Experiments 1 and 2) and the cartridges extracted with dichloromethane and analysed by gas chromatography with atomic emission detection. The results from the two experiments are shown in Table 4-2.

Table 4-2 - SDB Reproducibility

		Ethylbenzene/o-xylene			Toluene/o-xylene		
EXPERIMENT	***n***	**MEAN, x**	**S.D., σ**	**%RSD**	**MEAN, x**	**S.D., σ**	**%RSD**
1	6	0.31	0.01	**3.4**	1.2	0.06	**5.7**
2	6	0.35	0.01	**3.0**	1.5	0.12	**8.1**

The results for the ratio of ethylbenzene and o-xylene show that for the two experiments the mean ratios were 0.31 and 0.36. This indicates that the concentrations of these components varied independently with time. However the ratio reproducibility within a batch of samples was 3.4% RSD (Expt. 1) and 3.0% RSD (Expt. 2).

For the toluene and o-xylene ratios we observed a similar difference between the mean of ratios, which were1.2 and 1.5. The reproducibility for the samples is 5.7% (Expt. 1) and 8.1% (Expt. 2). This reproducibility reflects the constancy of the pump speed, flow rate and the cartridge characteristics.

4.1.2.3 Applications

The developed procedure was applied to the sampling of domestic air. A long sampling time (equivalent to 815L) was used to trap a range of compounds trapped. The aim of this experiment was to identify as many components as possible that were present in the air sample. The concentration of the components found are considered to be the loading at equilibrium with some sample displacement occurring. The range of compounds trapped and eluted with *n*-pentane is given in Table 4-3. Amongst the chemical classes present are substituted benzenes (to C_5 i.e. tert-butyl dimethyl benzene), *n*-alkanes to C_{13} and the terpenes α-pinene and limonene, these latter two being common aroma compounds in domestic cleaning agents. No hydrocarbon profiles indicative of the presence of fuel or heating oils were observed.

1,4-dichlorobenzene was not observed. As 1,4-dichlorobenzene is, generally, not used in domestic cleaning materials this was used as a quality control. If the compound had been found it would suggest that the cartridge had been exposed to the compound either before or after the sampling.

Table 4-3 - Compounds Observed in Domestic Air (815 l)

Compound	*Pentane* ng/L	*DCM* ng/L
Benzene	1.33	-
Toluene	43.14	1.09
Ethylbenzene/m-Xylene	6.64	-
p-Xylene	6.91	-
o-Xylene	0.00047	1.88
1,3,5-Trimethylbenzene	-	2.22
a-Pinene	21.87	4.04
n-Propylbenzene	0.89	-
1-Methyl-3-Ethylbenzene	6.23	-
1-Methyl-2-Ethylbenzene	0.61	-
1,2,4-Trimethylbenzene	46.28	1.03
Decane	9.89	6.56
Isobutylbenzene	0.53	1.48
1-Methyl-3-isopropylbenzene	0.49	-
1-Methyl-4-isopropylbenzene	1.47	-
Limonene	97.86	13.69
1-Methyl-2-isopropylbenzene	-	1.99
1-Methyl-4-n-isopropylbenzene	-	0.28
1,2-Diethylbenzene	-	4.68
1,4-Dimethyl-2-ethylbenzene	0.05	-
1,2-Dimethyl-4-ethylbenzene	0.46	-
Undecane	5.53	-
1,2-Dimethyl-3-ethylbenzene	0.54	-
1,2,4,5-Tetramethylbenzene		1.57
t-1-Butyl-3,5-dimethylbenzene		0.19
t-1-Butyl-4-ethylbenzene	0.10	-
Dodecane	4.95	6.39
n-Hexylbenzene	-	0.57
Tridecane	3.10	1.05
Tetradecane	9.69	1.77

Using a "real" sample it was possible to confirm the earlier laboratory based results for the sequential solvent desorption. It was thought that the remnants of the pentane extract might be carried over into the dichloromethane extract. This would give misleading results for the second solvent. By measuring the ratios of masses of the compounds between the pentane and the dichloromethane extracts it was possible to show that certain compounds were selectively desorbed by the solvents.

The ratios obtained for the desorbed concentrations of toluene (pentane/DCM ratio = 39.5) through limonene (pentane/DCM ratio = 7.15) to dodecane (pentane/DCM ratio = 0.77) show differences that can only be explained through solvent selectivity.

Clearly the choice of desorbing solvent is influential on the recovery of the various components present and indicates that a degree of selectivity may be achieved by sequential elution with a range of solvents.

Table 4-4 presents the data for indoor workplace (office) air, sampled on two cartridges in series for 60 and 120 minutes respectively. Notable differences between this and the domestic air (Table 4-3) are the relatively low terpene content, and the similarity of the alkyl substituted mono-aromatics and the n-alkanes. Note also the dominance of benzene in the workplace (benzene/toluene = 20 and 46 against <1 shown in Table 4-3)

Table 4-4 - Compounds found in Workplace Air

Compound	Front	Rear	Front	Rear	180L
	120L		180L		
	ng L^{-1}	ng L^{-1}	ng L^{-1}	ng L^{-1}	
Benzene	1050.15	28.007	1058.57	-	
Toluene	53.64	-	20.94	-	
Ethylbenzene/m-Xylene	12.99	-	6.33	-	
p-Xylene	14.92	-	5.86	-	
o-Xylene	10.87	-	2.78	-	
n-Propylbenzene	0.69	-	-	-	
1-Methyl-3-ethylbenzene	10.40	-	5.16	-	
1,3,5-Trimethylbenzene	2.54	-	-	-	
1-Methyl-2-ethyllbenzene	2.50	-	1.18	-	
1,2,4-Trimethylbenzene	12.15	-	1.94	-	
Decane	66.05	97.82	44.94	58.45	
1-Methyl-4-isopropylbenzene	2.55	-	-	-	
Limonene	13.36	8.39	-	1.45	
1-Methyl-3-n-isopropylbenzene	0.93	1.90	0.41	-	
1,2-Dimethyl-4-ethylbenzene	4.44	4.36	1.12	-	
Undecane	20.11	29.45	8.78	12.05	
1,2-Dimethyl-3-ethylbenzene	2.45	-	-	0.88	
1,2-Dimethyl-3-ethylbenzene	2.68	-	1.51	-	
Dodecane	7.42	10.19	4.12	7.00	
Tridecane	6.50	9.67	4.34	5.83	
Tetradecane	10.04	19.99	8.37	12.06	

Table 4-5 lists the components found in a 325L sample of outdoor air. Note the absence of terpenes, the relatively low benzene and toluene concentrations and the absence of any profile associated with automobile exhaust. This suggests that a mass of clean air was passing the city centre sampling site.

Table 4-5 - Compounds Observed in Outdoor Air

Compound	*Pentane* ng/L
Benzene	9.55
Toluene	8.21
Ethylbenzene/m-Xylene	3.16
p-Xylene	3.37
o-Xylene	2.11
sec-Butylbenzene	1.34
Undecane	2.43
1,2-Dimethyl-3-ethylbenzene	0.59
Dodecane	2.66
Tridecane	1.77
Tetradecane	4.01

4.1.2.4 Conclusion

Styrene-divinylbenzene packed solid phase extraction cartridges have been shown to be capable of effectively trapping a wide range of organic compounds from both indoor and outdoor air. Also the use of different polarity solvent suggest that selectivity, if not of sampling then certainly of desorption, may be possible thus allowing the overall sampling operation to be targeted at a particular class of compounds. Sample breakthrough occurs after 200L of air has been taken but this is thought to be due to chromatographic displacement down the cartridge rather than exceeding the capacity of the cartridge itself. Hence, with long sampling times, an equilibrium concentration on the cartridge will be reached. In this respect the principle of the process has an analogy with solid-phase microextraction with coated fibres, whereby equilibrium with the surrounding air is reached over hours rather than minutes.

Various air samples were studied and revealed the presence of a complex mixture of substituted mono-aromatic, *n*-aliphatics and terpenes. 1,4-Dichlorobenzene was found to be a common contaminant of workplace indoor air.

4.1.3 Functionalised Silica

The previous section has shown that it is possible to sample directly onto polymer based solid-phase extraction cartridges with high degrees of success and efficiency. The next stage of the research investigates the functionality of cartridge packing materials (e.g. silica/cyano, silica/amino, silica/diol). This. coupled with sequential solvent desorption, presents the opportunity for both selectivity of trapping and selective desorption thus simplifying sample preparation and allowing specific classes of compound to be trapped and desorbed. Thus, for example, a diol functionalised cartridge

would be expected to selectively trap polar oxygenates such as small organic acids and alcohols, whilst a phenyl functionalised material would be expected to trap aromatic compounds.

4.1.3.1 Background

The functionalised silica materials that are used in solid phase extraction cartridges are basically the same as those used as HPLC column packings. The chemical composition of the silica starting material could be expressed as $SiO_2 xH_2O$, which means that water is chemically bound in non-stoichiometric amounts. Silica has a non-uniform surface comprising of a variety of different bonding structures. These are described in an earlier section. A point to note is that these surface variations are different between manufacturers and, in some cases, between batches.

4.1.3.1.1 Monochlorosilane Chemistry

The simplest procedure for the production of functionalised silica based materials is the reaction of silica with a monochlorosilane compound, such as trimethylchlorosilane.

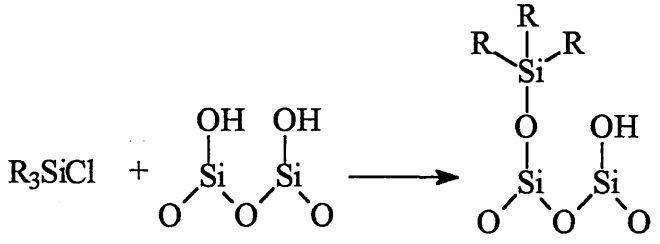


Figure 4-9 - Diagram Showing Simple Monochlorosilane Chemistry

The process involves a standard silylation reaction, that displaces a molecule of HCl for every silanol reacted (Figure 4-9) Due to the hydrophilic nature of the R_3SiCl, all such silylation reactions occur in a water free environment.

4.1.3.1.2 Trichlorosilane Chemistry

The use of a monochlorosilane effectively causes the addition of three functional groups per silanol.

A more complex procedure involves the reaction of the silica with trichlorosilane based compounds. This process is more involved and results in a 1:1 ratio of functional groups to silanol group.

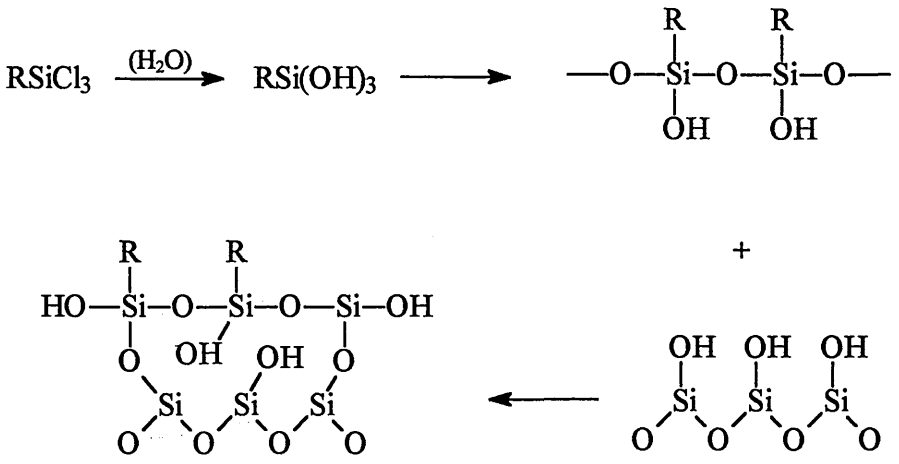


Figure 4-10 - Diagram Showing Trichlorosilane Chemistry

Using the reaction scheme shown in Figure 4-10, the trichlorosilane compound is first hydrated to form a short chain siloxane compound. This then reacts with the silica. Due to the spatial restrictions between the silica and the siloxane a 1:1 bonding ratio between the two compounds is not possible. This leaves residual silanol groups that can be effective in the extraction and/or sampling mechanisms.

4.1.3.1.3 Endcapping

"Endcapping" is a procedure that was introduced to reduce the effects of the residual silanols when it became obvious that some silanols were still accessible after surface modification with long-chain ligands.

Trimethylchlorosilane (TMS) is the most common reagent that is used to 'cover' accessible residual silanols. TMS is a relatively small molecule that can penetrate the silica surface and "cap" the areas of unreacted silanols. This generally reduces the effective polarity of the material. Even after endcapping though, the silica based sorbents can contain almost 50% of their original silanols.

4.1.3.2 Functional Groups

There are several major functional groups that are commonly used within the field of solid phase extraction. Each has its own characteristics that potentially allow the

user to obtain the maximum efficiency for the task to which it is employed. For the purposes of this study three different phases were studied.

4.1.3.2.1 Octadecyl Silica

The most commonly available material is octadecyl-silica (C_{18}), which is used in many applications involving both polar and non-polar compounds. The universality of this material makes it, theoretically, ideal for use as an air sampling sorbent.

The hypothesis being tested was that C_{18}-silica could be used to selectively sample non-polar aliphatic compounds in air without any interference from polar compounds.

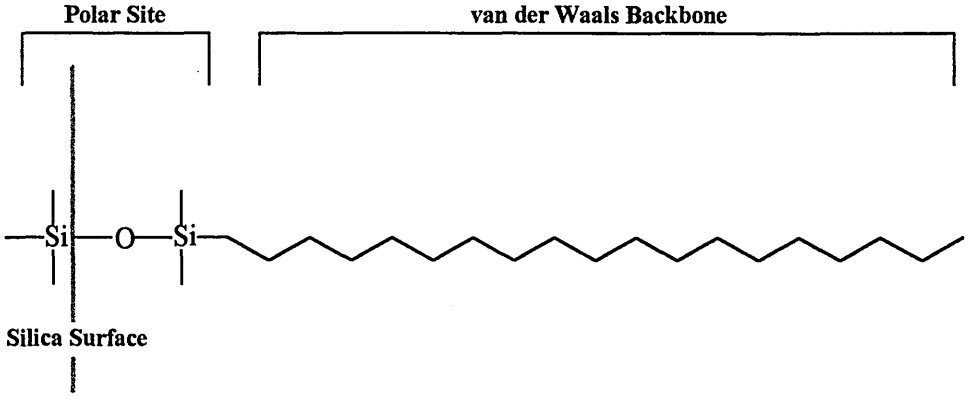


Figure 4-11 - Diagram Showing the Structure of Octadecyl Silica

As can be seen in the diagram (Figure 4-11 - Diagram Showing the Structure of Octadecyl Silica), the C_{18}-Silica functionality contains a large "van der Waals" backbone, suggesting that it should be suitable for use in the trapping of non-polar compounds. However, the large spatial area that the C_{18} functional group occupies means that, due to steric hindrances, not all the silanols will have reacted. As already suggested, even after end-capping, there will still remain a large proportion of residual silanols which, even though the overall material is classed as non-polar, might give some degree of polarity.

4.1.3.2.2 Propyl Amino Silica

Propyl amino functionalised silica has both a van der Waals backbone and a polar site within the same molecule. (Figure 4-12) This material has the same silica backbone as the octadecyl silica and therefore similar polar trapping is observed at the surface. Steric hindrances although not as great as those observed with the octadecyl silica

prevent the complete silylation of the silica surface leaving residual silanol groups. The polarity of the amino group and the associated hydrogen bonding mechanism also suggest that the selectivity of the sampling should be toward the polar compounds.

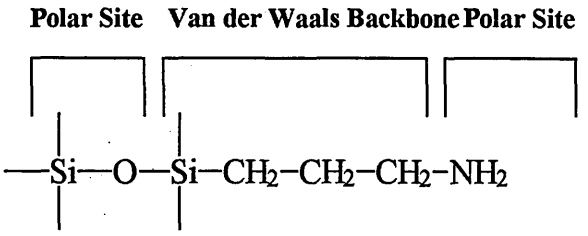


Figure 4-12 - Diagram Showing the Structure of Propyl Amino Silica

4.1.3.2.3 Diol Silica

2,3-Dihydroxypropyl is the functional group that is present with the diol silica sorbent material. As with the amino propyl silica, the diol silica has a small van der Waals backbone, along with the polar functional groups. Again residual silanol groups are present at the silica surface. However, for every functionalised silanol group there are two hydroxyl groups, suggesting that the overall polarity of the material is greater than that of the amino propyl silica.

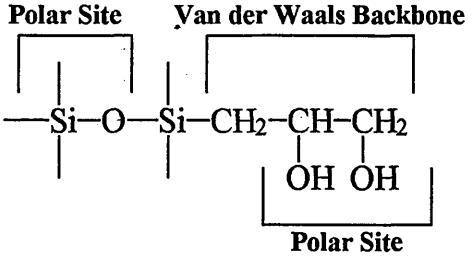


Figure 4-13 - Diagram Showing the Structure of Diol Silica

4.1.3.2.4 Results

The three phases chosen for study have different degrees of polarity. It was expected that each of the sorbent phases would use different trapping mechanisms and, therefore, show selectivity in sampling. The expected sampling mechanisms are shown in Table 4-6. To study the wide range of polar compounds that were expected, a three stage sequential washing protocol was adopted, using pentane, dichloromethane and methanol.

Table 4-6 - Expected Bonding Mechanisms

	Van der Waals	Dipole-Dipole	Dipole-Induced Dipole	Hydrogen Bonding
C_{18}	✓			
Amino	✓	✓	✓	✓
Diol	✓	✓	✓	✓✓

4.1.3.2.5 Residual Silanols

Based on the results from the SDB experiments, the pentane and dichloromethane phases extracted non-polar aliphatic compounds and some moderately polar aromatics, although the exact composition differed between phases. This will be discussed in more detail later. However, for all of the phases, the methanol extracts were found to contain organic acids, alcohols and other polar compounds.

The exact mechanism for the trapping of polar compounds on the C_{18}-silica is not known. However, there are two distinct possibilities. The first is that inter-molecular bonding is occurring, using dipole-dipole and hydrogen bonding. These types of bonding mechanism are to be expected and the possibilities of their use with other functional groups will be discussed later.

The second mechanism is the dissolution of the polar compounds in an aqueous layer that forms on the surface of the silica particles. Silica is well known for its hydrophilic properties, and even though these are reduced when the material is functionalised, the residual silanols already discussed will still be active. It is thought that the residual silanol groups attract atmospheric water molecules, which then form a thin film around the particle. It is then thought that the organic acids may dissolve in this film as they are passed through the cartridge.

Unlike the styrene-divinyl benzene co-polymer which was described in the last section, the silica based materials are much coarser in texture and thus air does not circulate around inside the cartridge with as much ease, thus causing reduced flow rates by providing a higher resistance to the flow. This reduction in flow rate has been observed to increase over a sampling period, which tends to validate the supposition that a water film is being collected, thus reducing the pore volume.

Other evidence to suggest that water affects the sampling efficiency of the silica based materials was found using the GC-AED. By monitoring the O_{777nm} channel, during

a run for the methanol extract, a large tailing peak was observed. Subsequent runs monitoring the H_{486nm} and C_{193nm} lines confirmed the identity of the peak as water.

4.1.3.2.6 Pentane Extracts

The compounds that were found in the non-polar or pentane phases were as expected, comprising mainly alkanes, both straight chained and branched, as well as alkyl benzenes. The surprising feature of the results was the parity between all three sorbent materials.

Table 4-7 - Pentane Extract Results

R.R.T.	Compound	Key	R.R.T.	Compound	Key
-0.656	Cyclohexane, methyl-	C A D	0.111	Dodecane	C A D
-0.585	Alk-Br	A D	0.113	Ar-C4	A
-0.280	Cyclotrisiloxane, hexamethyl-	C A D	0.114	Alk-C12	A D
-0.199	Ethylbenzene	D	0.116	Alk-C12	A D
-0.182	p-Xylene	C A D	0.118	Ar-C5	C
-0.143	p-Xylene	C A D	0.121	Decane, 3,8-dimethyl-	A D
-0.087	Alk-Br	D	0.124	Ar-C5	D
-0.052	Benzene, 1-ethyl-4-methyl-	C A D	0.128	Ar-C5	C D
-0.045	Benzene, 1,3,5-trimethyl-	A D	0.140	Naphthalene	C A D
-0.043	Alk-Br	D	0.144	Ar-C5	A D
-0.032	Ar-C3	D	0.149	Alk-C13	C A D
-0.023	Alk-Br	D	0.170	Alk-C13	A D
-0.019	Benzene, 1,2,4-trimethyl-	C A D	0.174	Alk-C13	C A D
-0.014	Decane	C A D	0.177	Alk-C13	C A D
	Benzene, 1,4-dichloro-		0.180	Alk-C13	C A D
0.005	Alk-C11	D	0.186	Decane, 2-methyl-	C A D
0.007	Alk-C11	C	0.191	Naphthalene,tetrahydro-6-met	C A D
0.008	Alk-C11	D	0.203	Tridecane	C A D
0.009	Ar-C3	A	0.211	Naphthalene, 1-methyl-	C A D
0.021	Alk-C11	C A D	0.222	Naphthalene, 1-methyl-	C A D
0.034	Ar-C4	A D	0.239	Alk-C14	C A D
0.040	Ar-C4	C A D	0.243	Alk-C14	C A D
0.042	Alk-C11	C A D	0.247	Alk-C14	C A D
0.047	Alk-C11	A D	0.255	Alk-C14	C A D
0.057	Ar-C4	C A	0.260	Tetradecane	C A D
0.058	Ar-C4	D	0.276	Naphthalene, 2,6-dimethyl-	C A D
0.062	Ar-C4	C A D	0.279	1,4-Methanoazulene, decahydro-4,8,8-t	C A
0.068	Alk-C11	C A D	0.284	Naphthalene, 1,6-dimethyl-	C A D
0.070	Alk-C11	C A D	0.286	Naphthalene, 2,6-dimethyl-	C A D
0.080	Ar-C4	D	0.291	Cyclohexane, 1,1'-(1-methyl-1,3-propa	A D
0.080	Alk-C12	C A	0.294	Dodecane, 2,6,10-trimethyl-	C A D
0.083	Alk-C12	C A D	0.313	Pentadecane	C A D
0.086	Ar-C4	C A D	0.364	Hexadecane	C A D
0.090	Ar-C4	C A D	0.412	Heptadecane	C A D

C = C_{18}, **A** = amino, **D** = diol

Table 4-7, above, shows the results from the pentane extract experiments. The compounds were identified using a relative retention time, against the ubiquitous 1,4-dichlorobenzene. The key identifies the cartridge on which the compounds were trapped with C as C_{18}, A as Amino and D as Diol. Overall for non-polar compounds it can be seen that there are no major differences in selectivity. This suggests that the van der Waals backbone in both the amino and the diol cartridge is trapping non-polar compounds.

This lack of selectivity tends to indicate that the hypothesis that surface functionality will lead to selectivity, is incorrect.

Another question that the results shown in

Table 4-7 raise is: 'why does the selectivity of the C_{18}-silica show no significant difference to that of the van der Waals backbone in the amino and diol sorbents.'

One likely answer is that of cartridge conditioning. When these sorbent materials are being used for liquid phase extractions, cartridges are conditioned with a volume of extraction solvent. This serves the two purposes of cleaning the cartridge and activating the surface.

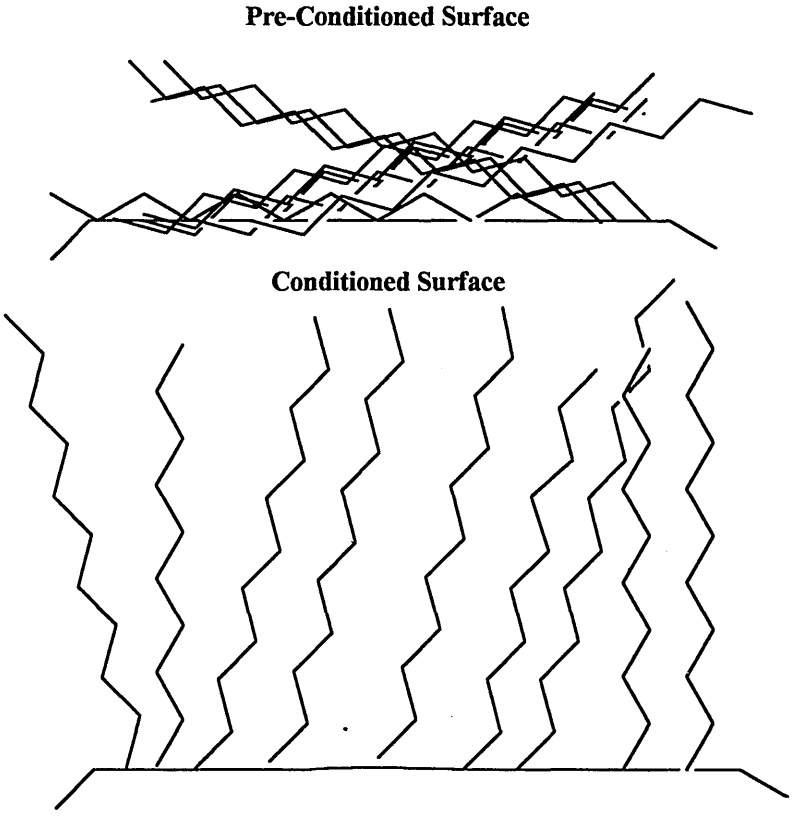


Figure 4-14 - Schematic Diagram of the Silica Surface

Before conditioning, the functional group chains are laid flat against the surface of the silica. After being washed with a conditioning solvent, the strands are held upright by the inter-spatial solvent molecules thus allowing a greater surface area to be exposed. When sampling air, however, the conditioning solvent will be blown off almost immediately leaving the functional groups in what is, in effect, the unconditioned state. This effectively reduces the surface area of the sorbent to that of the silica particle. For the short chain van der Waals backbones of the amino and diol functionalities this has no real detrimental effect to the sampling efficiency, but for the octadecyl silica the effect of reduced selectivity is noticeable.

4.1.3.3 Dichloromethane Extracts

Identification of the majority of the compounds in the DCM phase is very poor (i.e. %fit < 70) The suggested explanation for this is that the concentration of the compounds in the sample was too low as to give sufficient mass spectral data to aid identification. This was confirmed by the low ion abundance readings given by the even the largest peaks. However, given this, it is still possible to draw some conclusions regarding the selectivity of the sorbent phases from these results.

The most noticeable feature of the results was the presence of alkanes in the DCM phase. From physical observations, it was seen that not all of the pentane phase was removed from the cartridge. The drying of the cartridge with an inert gas such as nitrogen between desorption washes has been considered and rejected on the grounds that the gas flow will chromatograph the analytes through the cartridge, thus losing sample. Also, removal of the solvent through drying, will leave the some of the non-polar analytes on the cartridge. It was, therefore, decided that the pentane carry over was a known quantity and could be accounted for when interpreting the results.

In studying the results for the DCM phase it can be seen that there are differences in composition between the different sorbent phases, although not as dramatic as the initial hypothesis suggested.

Table 4-8 - Dichloromethane Extract

R.R.T.	*Compound*		*R.R.T.*	*Compound*	
-0.712	Cyclohexane	C	0.050	2,3-Heptadien-5-yne, 2,4-dimethyl-	C
-0.650	Cyclohexane, methyl-	C D	0.069	Undecane	C
-0.521	Heptanal	D	0.069	Nonane, 5-(1-methylpropyl)-	A
-0.514	Toluene	C D	0.069	Tetradecane, 1-chloro-	D
-0.275	Acetic acid, butyl ester	C	0.075	Nonanal	C D
-0.269	Cyclotrisiloxane, hexamethyl-	C	0.116	Cyclohexanone, 5-methyl-2-(1-methyl)	C
-0.183	p-Xylene	C A D	0.139	Dodecane	A
-0.143	Benzene, 1,2-dimethyl-	C A	0.145	Decanal	C
-0.129	Cyclohexanone	C	0.170	Pyridine, 2,4,6-trimethyl-	D
-0.118	Heptanal	C	0.185	Nonane, 3-methyl-	A
-0.049	Benzaldehyde	C	0.201	Tridecane	C A
-0.038	1-Heptanol	C D	0.211	2,6-Octadienal, 3,7-dimethyl-, (E)-	A
-0.026	Phenol	C	0.221	Naphthalene, 1-methyl-	A
-0.018	2-Octanone	A D	0.240	Propanoic acid, 2-methyl-, 2,2-dimeth	C A D
-0.007	Octanal	C D	0.250	Propanoic acid, 2-methyl-, 3-hydroxy-	C A D
0.015	1-Hexanol, 2-ethyl-	C D	0.259	Tetradecane	C A D
0.020	1-Ethyl-2,2,6-trimethylcyclohexane	C	0.312	Pentadecane	C A D
0.033	1-Dodecanol, ethoxy-	D	0.363	Hexadecane	C

The results shown in Table 4-8 tend to indicate that compounds with some polar character such as carbonyls were being trapped alongside alcohols. The results tend to show that the diol-silica has more selectivity toward the alcohols than do the other two phases. Although these results are only qualitative, they give a good indication of the overall sampling capabilities of the silica materials.

Although giving similar results to the other phases, the amino-silica showed disappointing selectivity. This does not rule out the use of this phase for air sampling just that similar results could be obtained using other materials.

4.1.3.3.1 Conclusions

Overall the results obtained from the functionalised silica materials were disappointing, in that the desired selectivity of sampling was not achieved. This was due to a number of factors such as the effects of the silica base material.

Because of the lack of overall selectivity, the usefulness of the functionalised silica materials was limited. Having materials such as SDB in the cartridge format means that similar, if not better, results can be obtained more easily than with the silica.

Due to the structure of the silica particles the flow of air through the cartridge was less than that obtained using the SDB material. This restricted air flow causes lower sampling rates and thus eventually lower sample yields.

4.1.4 Conclusion

In respect of a single method approach to air analysis the use of solid-phase extraction cartridges, especially with styrene-divinyl benzene co-polymer as sampling medium, meets the general criteria laid down in section 5.1.

The surface area of the sorbent material is critical when discussing sampling efficiency. With the functionalised silica particles it is only the outside of the particles that have been reacted. So in effect it is only the outside of the material that is used in the sampling mechanism.

With the SDB material, as there are no additional surface functionalities, the surface area that is used for sampling is therefore greater. This translates to a higher sampling efficiency. Evidence for these effects is given by the ion abundance values from the GC-MS results. In general, the values for compounds absorbed by SDB are 4-5 times greater than those for compounds absorbed by C18, using the same air mass.

The small particle size of the SDB material when packed in the cartridge allows a turbulent movement around the cartridge body which, as well as maximising the surface area that is in contact with the sample, tends to allow an increased flow rate. Although not widely used, high flow rates allow the rapid sampling of an air mass, which is usually in a state of constant change. Hence a more accurate picture of the composition of the air can be obtained. Also high flow rates allow the sampling of larger volumes, leading to higher analyte concentrations and thus increasing the instrumental limits of detection.

As was shown in the results, the range and types of compounds that were being trapped were wide, covering alkanes, alkyl benzenes, PAH's, alcohols, aldehydes and organic acids. These compounds could not have been determined without the sequential solvent desorption (SSD) procedure which allowed narrower ranges of compounds to be desorbed and thus analysed. By making the composition of each analytical run less complicated it was possible to interpret the results more fully. All of the SPE based sorbent media allowed the use of SSD and thus satisfied the given criteria. It was however the SDB co-polymer that absorbed the widest range of compounds. This was due to the greater efficiency of the sampling medium. Although the results for the silica-

based sorbents were more than acceptable it was the co-polymer that gave the better results.

For the analyst the use and disposal of solvents needs to be considered when designing experiments, for the reason of both health, safety and finance. Using large volumes of solvents and secondary glassware all add to the risk of end sample contamination which, when performing trace analysis, is not desirable.

The procedures developed for use with the solid phase extraction cartridge used the minimum amounts of solvent. For a standard three stage SSD, 5ml of each solvent was used for the cleaning and conditioning of each cartridge. Only 1ml of solvent is used per desorption step, and with the process taking place on the cartridge the risk of external contamination of the sample is small.

By desorbing directly into the analytical solvent it is possible to use this sampling technique with most analytical procedures. For example, the use of aqueous impingers for the sampling of organic acids, implies that the analytical technique should be some form of liquid chromatography. By desorbing organic acids in methanol, for example, it is possible to use either GC or LC for analysis. Hence we suggest that this analytical technique can be adapted to match the needs of the analyst. Also it is possible to use these samples with instrumental techniques that require multiple sample injections such as GC-AED. This makes the technique as quick, yet more flexible, than thermal desorption.

Another advantage of using small solvent volumes is that the preparation time taken per sample is approximately 1 minute. By reducing the time taken for sample preparation, it removes this step from being the limiting factor in the experimental design.

The desorption procedure is simple and easy to use, enabling the most junior of laboratory personnel to perform the task. The simple act of using positive pressure from a gas syringe, to force the solvent through the cartridge and into an autosampler vial means that this technique meets the given criteria. Sample preparation procedures that involve multiple steps are not only time consuming but are often technically prohibitive. By using a simple technique the opportunity to experiment and further develop the procedure to suit the needs of the analyst is afforded. Such simple techniques are suited for in-field analysis work as well as routine and screening protocols.

By using this simple non-destructive desorption technique it is possible to re-use the cartridges many times. Results have shown that by cleaning the cartridges, with 5ml

of desorption solvent, before sampling. it is possible to condition the cartridges ready for use, thus saving the laboratory the expense of the more traditional one-shot methods.

Another positive feature of the solid phase extraction cartridge that makes it attractive as a sampling technique is the polyethene cartridge body. Many air sampling media are marketed in glass vials, which to use require the removal of the sealed ends. This task is hazardous, even under ideal laboratory conditions, but when used in the field the risk factor multiplies. By using the SPE cartridge, a physically robust and relatively unbreakable system is acquired. Although this benefit is secondary to those of sampling efficiency and breakthrough volume, it can be described as the "icing on the cake" for the procedure.

Therefore, with the solid phase extraction cartridge air sampling technique we feel that we have developed a method that makes it ideal for use in both routine and compound specific trace analysis.

4.2 Analysis

4.2.1 Introduction

After developing an air sampling technique that would enable the analyst to prepare samples in a form ready to be used by the majority of the available analytical techniques it was decided to adopt a single instrumental technique that would allow the analysis of the majority, if not all, of the compounds in a given sample. Although this was now no longer a necessity it was considered to be the ideal.

The obvious technique to use was gas chromatography, but as can seen from the earlier literature review, with the number of different air analysis publications already available there were no ground breaking discoveries left to be made. However, one area within the field of air analysis, with which we encountered difficulties was that of confirmatory analysis of compounds in our samples.

Using gas chromatography with flame ionisation detectors, mass spectrometers and atomic emission spectroscopy we examined the ways in which we could utilise the data from all three to provide information that would help in the study of volatile organic compounds in air.

Initial work on obtaining a single analytical method was directed at examining and optimising the various GC options that were available, before developing a more unified technique. The working hypothesis was that, by using three identical

chromatography columns with three different GC detector systems, it should be possible to obtain comparable results. With these goals in mind, it was therefore necessary to look at some of the fundamentals of chromatography.

4.2.2 Chromatographic Optimisation

Gas chromatography is a separation technique that was developed in the mid-20th century, initially using packed columns, similar in efficiency to HPLC, but then evolving to utilise the superior separating and resolving power of the wall coated open tubular (WCOT) column, or as is more commonly known the capillary column. The continuous development of column technology means that from year to year the tools of the analyst are improving. The science, which underpins the chromatographic separation, has, however, remained constant for the last century, so for a more complete investigation into the optimum analytical conditions it was necessary to perform some simple, yet fundamental experiments.

4.2.2.1 Basic Column Theory

The quality of a separation is determined by several functions including the visible factors of peak shape and resolution. The higher the separating efficiency of the column, the better the peak shape and resolution. The band broadening theory is expressed mathematically by the Van Deemter equations, as functions of theoretical plate height.

There are two main theories regarding chromatographic separations: plate theory and rate theory. Plate theory was derived from the early separation techniques of distillation and solvent-solvent extraction. The underlying principle of plate theory was that the separations occurred at distinct zones or plates within the column. In a simple distillation system, Figure 4-15, the separation occurs at the reflux condenser where there is an equilibrium established between the gaseous and liquid phases.

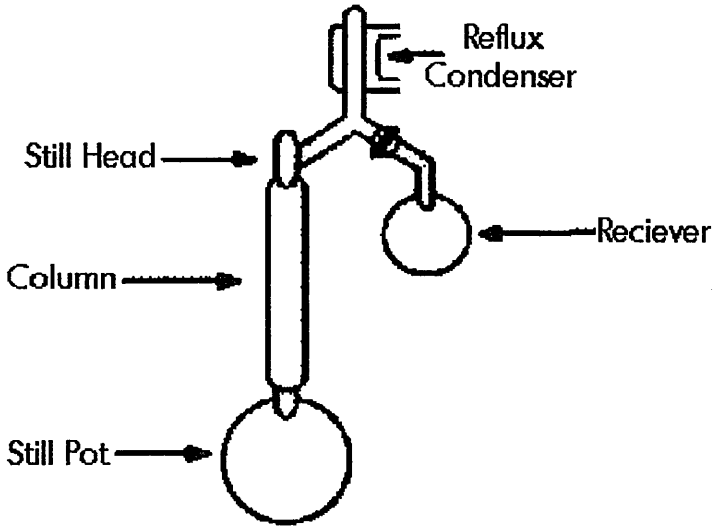


Figure 4-15 - Diagram Showing a Laboratory Distillation System

In more complex distillation apparatus, such as that used in oil refineries, the separations occur at many separate physical stages, or plates, up through the column. The effect is similar to having several simple distillation apparatus in series. It is recognised that better separations occur with larger numbers of plates. Using the plate model for chromatography, the column is divided into imaginary segments known as theoretical plates. The mathematical description of the number of theoretical plates is based on the calculating peak being of Gaussian band shape. This is expressed by the following equation:

$$N = \frac{t_r^2}{\sigma^2} = \frac{16t_r^2}{w^2}$$

where t is the retention time of the peak, σ is the standard deviation and w is the width of the peak measured at its base. Alternatively, N, can be calculated using the width of the peak at its half height. This is expressed in the formula:

$$N = \frac{5.55t_r^2}{w_{½}^2}$$

Another way of expressing the number of theoretical plates is as the height equivalent. The value of H.E.T.P. is determined from the simple formula:

$$H.E.T.P. = \frac{L}{N}$$

Where L is the length of the column.

These formulae are at the heart of plate theory, however, although plate theory can give an adequate description of the separations, it fails to account for the entire band broadening phenomena that is observed. In 1956 the publication of J.J. Van Deemter's, now famous equation, gave a more realistic view of chromatographic separation. This indicated that the concept of rate theory, which suggests that band shape is related, not just to equilibration, but also to the rate of elution of the mobile phase.

4.2.2.2 Van Deemter Equation

Van Deemter built on plate theory by using the height equivalent to the theoretical plates as an indication of column efficiency. However, he recognised that band broadening had three main sources within the chromatographic column. These are: multiple paths of the analyte as it passes through the column packing; longitudinal molecular diffusion; effect of mass transfer between phases.

4.2.2.2.1 Multiple Paths

The velocity of the gas phase through the column may vary significantly across the column diameter, depending on the particle shape, porosity, and the whole bed structure. Band broadening is caused by differing flow velocities through the column, i.e. the front end of the analyte band could be moving faster than the rear. This is expressed in the equation:

$$\mathbf{H_p = 2\lambda d_p}$$

Where H_p is the HETP arising from the variation in the zone flow velocity, d_p is the particle diameter (average), and λ is a constant which is close to 1. This equation shows that Hp may be reduced (efficiency increased) by reducing the particle diameter. The constant λ depends on the particle size distribution. In WCOT columns where the particle size is effectively zero, it can be seen that dp has no significant effect on the band broadening and hence column efficiency.

4.2.2.2.2 Longitudinal Molecular Diffusion

It is well known that molecules disperse or mix due to diffusion. The longitudinal diffusion (along the column long axis) leads to the band broadening of the analyte band. This process may be described by equation:

$$H_d = 2\frac{\gamma D_m}{V}$$

Where D_m is the aggregate diffusion coefficient in the mobile phase, γ is the factor which is related to the diffusion restriction by column packing and V is the gas flow velocity.

It can be seen from the above equation that the higher the gas flow velocity, the lower the diffusion effect on the band broadening. Molecular diffusion in the liquid phase is about five orders of magnitude lower than that in the gas phase Thus this effect is almost negligible at the standard HPLC flow rates.

4.2.2.2.3 Kinetics of the Mass Transfer.

Mass transfer is the most questionable of the three parameters. For the modern types of packing materials it may combine two effects: adsorption kinetics and mass transfer (mainly due to diffusion) inside the particles. Because WCOT columns have no particles diffusion inside the particles will be negligible, so it is the time taken for the analyte to reach equilibrium between the mobile and stationary phases at any give place along the column which is inportant. The relationship is expressed by the equation:

$$H_m = \frac{8}{\pi^2}\frac{k\, d_f^2}{(1+k^2)D_i}V$$

where: d_f is the stationary phase film thickness, D_i is the diffusion coefficient of the analyte in the mobile phase, k is the capacity ratio, and V is the linear flow velocity.

The above equation describes the linear dependence of HETP on the flow rate. The slower the velocity, the more uniformly analyte molecules may interact with the stationary phase.

4.2.2.2.4 Total Band Broadening

Each term discussed above, plays a part in the total band broadening equation, therefore the sum of all of them will give the total column plate height.

$$\mathbf{H = H_p + H_d + H_m}$$

A more simplified version of this equation is:

$$\mathbf{H = A + B/V + CV}$$

Where A represents the multiple path term, B represents the molecular diffusion and C the kinetics of mass transfer. It can be noted that the B and C terms are dependent on the flow rate of the carrier gas.

From this equation it can also be determined that for WCOT columns the A term will have little or no effect on the total HETP. Also the C term, which is dependant on film thickness, will have a reduced effect. The C term is only significant when thick film stationary phases are being used, but these tend to be used more for specialist applications.

4.2.2.3 Results

Van Deemter plots were obtained for the various systems being used. The columns that were being used had a stationary phase of 5% diphenylpolysiloxane (d_f = 0.25μm). Each was 25m in length, with an internal diameter of 0.25mm. The characteristics of the column enabled the separation of both non-polar and slightly polar compounds, thus suiting the sample compositions being obtained using the method described in the previous section.

Three different detectors were being investigated: FID, AED and MS. The AED and MS had similar electronic flow control systems thus allowing a more "accurate" control of the flow rate of the carrier gas. Furthermore, the MS and AED were both using helium as the carrier gas. Due to the sensitivity of the filament used in the MS it was not possible to run comparable experiments on this instrument. Assuming that by using identical GC systems it should be possible to transpose the results between instruments, the experiments were only performed using the AED instrument. The FID instrument had only manual flow control and was using nitrogen as the carrier gas.

Although the FID instrument was not as technologically advanced, as will be shown shortly, the results obtained were superior. In the case of the electronic flow controlled instruments, it was only possible to obtain flows that the instrument would allow. By measuring the retention times of the unretained methane peak (t_{meth}) it was possible to calculate the actual flow rates of the carrier gas. From

Table 4-9, it can be seen that there are some discrepancies between the set and actual values.

Table 4-9 - Set and Actual Flow Rates

Set Flow Rate ml min^{-1}	Actual Flow Rate ml min^{-1}
0.020	0.242
0.050	0.273
0.075	0.293
0.100	0.317
0.200	0.401
0.300	0.482
0.400	0.553
0.500	0.612
0.600	0.683
0.700	0.737
0.800	0.789
0.900	0.839
1.000	0.894
1.100	0.940
1.200	0.960
1.400	1.091
1.800	1.246
2.000	1.303

The difference in values was only noticeable at the low flow rates. This caused problems when calculating the Van Deemter plot for this column, because the flow rates obtained were not actually low enough to show the effects of the B term. A minimum value was obtained however.

Figure 4-16 shows the Van Deemter Plot obtained for the He carrier gas. The superimposed lines for the B and C terms show that the values obtained match the expected values quite closely. It can be noted though, that because the instrument was unable to allow the low flow rates the values for the exponential part of the B term plot cannot be accurately predicted.

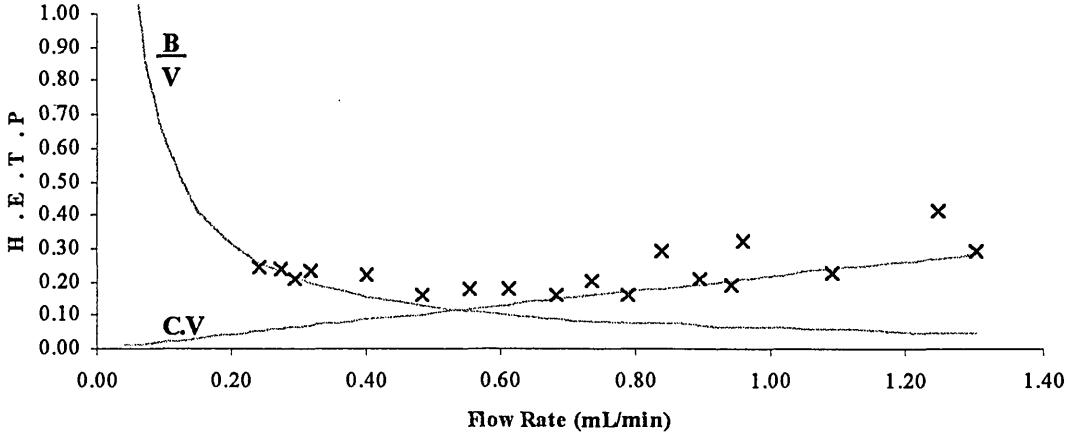


Figure 4-16 - Chart Showing the Van Deemter Plot for He Carrier Gas

The plot for the N_2 carrier gas can be seen in Figure 4-17, below. Again it can be seen that the actual and theoretical values for the C term closely match.

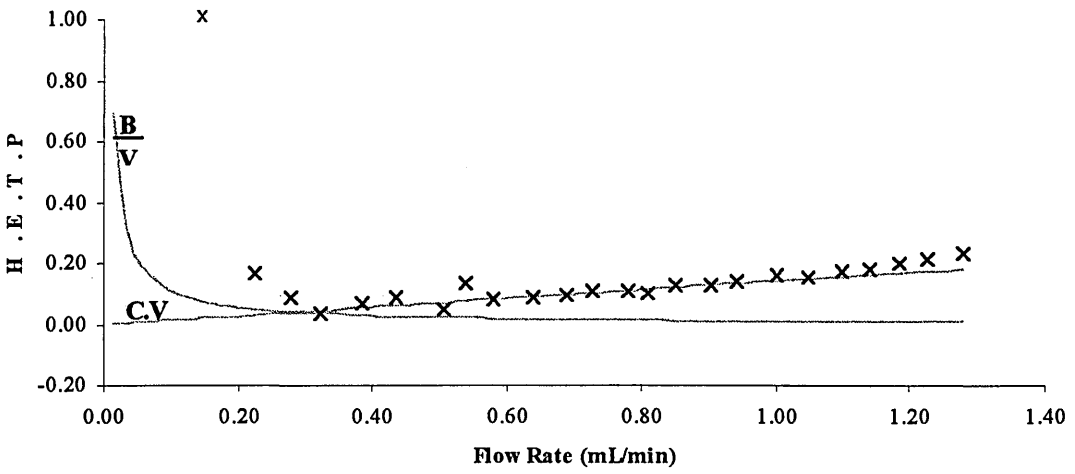


Figure 4-17 - Chart Showing the Van Deemter Plot for N_2 Carrier Gas

With both carrier gases the A or multiple path term has little or no effect as a band broadening mechanism. From theory this is to be expected, as the term is a function of the packing material which is absent in capillary columns.

The optimum values for the flow rates that were obtained from these experiments are shown in Table 4-10.

Table 4-10 - Optimum Flow Rates

	N_2	He
Minimum Value (H.E.T.P.)	0.072 mm	0.161 mm
Flow Rate	0.39 mL min^{-1}	0.68 mL min^{-1}

Although the optimum values are shown in the table, it should be noted that due to the limited effects of the C term, the flow rates for each of the carrier gases can be increased somewhat without significant loss of efficiency. In actuality the flow rates were set at approximately 1mL min^{-1} for both gases giving a H.E.T.P. of 0.292 mm and 0.161mm for helium and nitrogen respectively.

By using the "optimised" flow rates for the carrier gases it was, theoretically, possible to transfer the method from instrument to instrument, thus enabling a crude, yet workable, "unified" detector.

4.2.3 Total Air Analysis

4.2.3.1 Introduction

The necessity of a unified technique was highlighted when results from the thermal desorption-GC-MS analysis, (Figure 4-18 & Figure 4-19) of certain air samples gave results that could not easily be confirmed. The main example being that of the long chain alkyl carbonyl compounds that were being identified by the instrument, yet when examining the mass spectra of the compounds it was found that they were similar to those of the corresponding alkanes.

Below are shown the mass spectra of both decane and decanal, (Figure 4-18 & Figure 4-19). It can be seen that although there are differences, namely ions at $^{m}/_{z}$ 67 and 70 in the decanal spectra, the similarities are more significant.

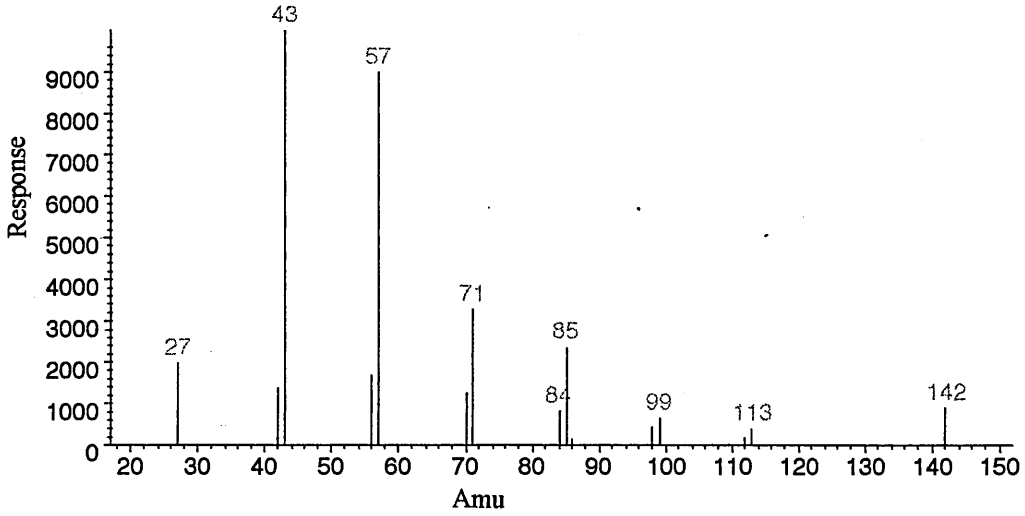


Figure 4-18 - Library Mass Spectra of Decane

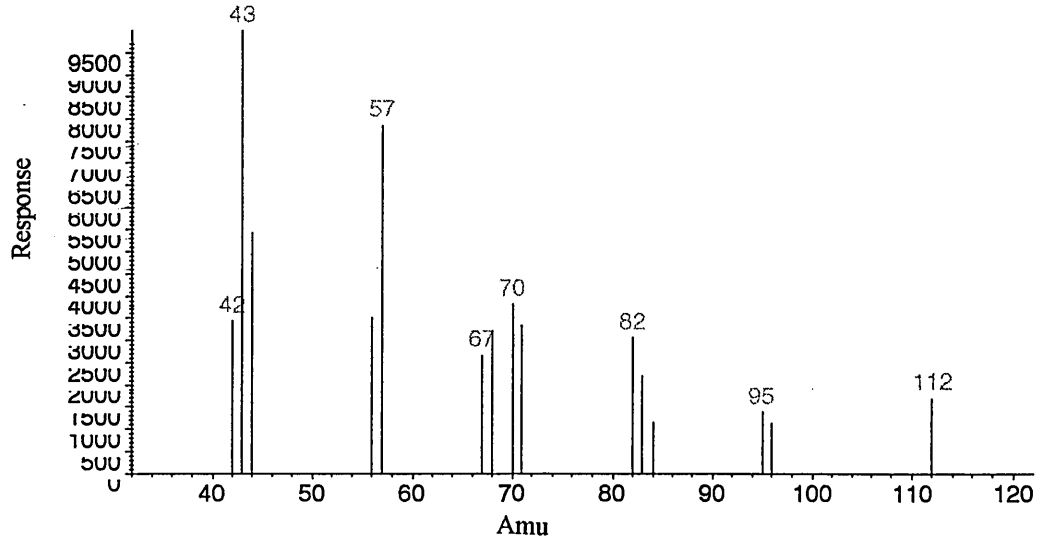


Figure 4-19 - Library Mass Spectra of Decanal

Samples that contain trace amounts of an analyte will have reduced signal to noise ratios, and therefore will often give spectra with peaks that are, in reality, just noise.

Using the example of decane and decanal, to positively identify between the two we need to be able to either detect the oxygen or use retention time data, which for a sample containing 150 different compounds can prove very difficult. From this example, it is possible to see that this identification problem can have serious consequences regarding the validity of the results that analytical scientists produce.

Several different methods of optimising the data obtained from the various GC experiments to produce valid results were investigated, bearing in mind that the primary purpose of the research was to study VOC's in urban and indoor air and their effects on air quality.

4.2.3.2 Elemental Detection

Initial work on the SPE sampling method showed that 1,4-dichlorobenzene was ubiquitously in the test environment. Using the mass spectrum (Figure 4-20) it was possible to identify the compound because of the unique fingerprint fragments that halogens produce.

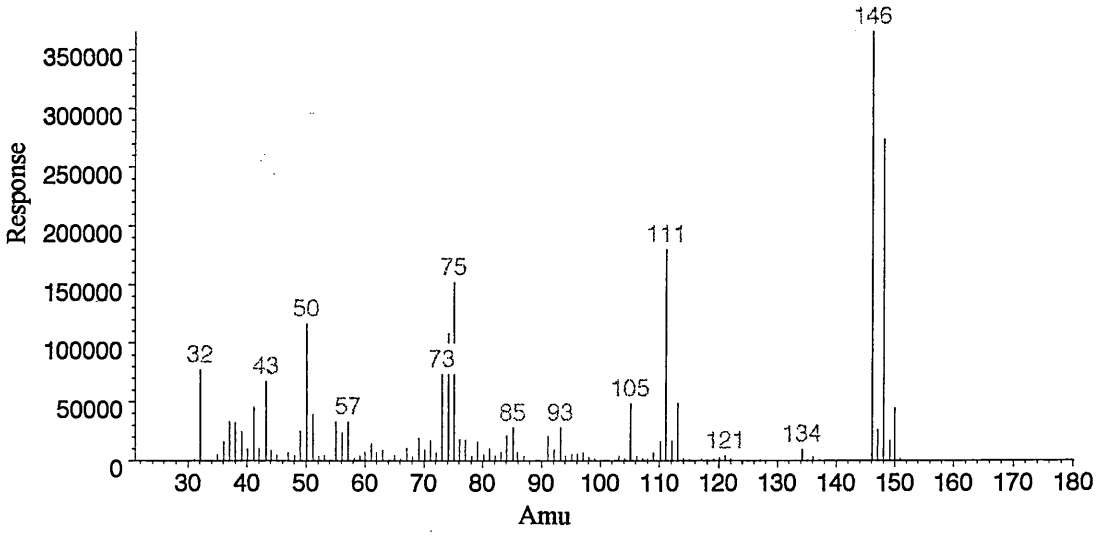


Figure 4-20 - Mass Spectrum of 1,4-dichlorobenzene obtained from an Indoor Air Sample

However, the poor resolution that was observed around the peaks in the spectrum ($^{m}/_{z}$ 35-90) is indicative of the potential problems faced by relying on one identification method.

Another compound that was tentatively identified from the mass spectra of the air sample was cyclohexanone. This was thought to be co-eluting with xylene and thus could only be identified after several background subtraction steps. Figure 4-21 shows the spectrum for the peak. The mass fragments at $^{m}/_{z}$ 91 and 106 are indicative of xylene, however the peaks at $^{m}/_{z}$ 55, 69, and 98 suggest cyclohexanone.

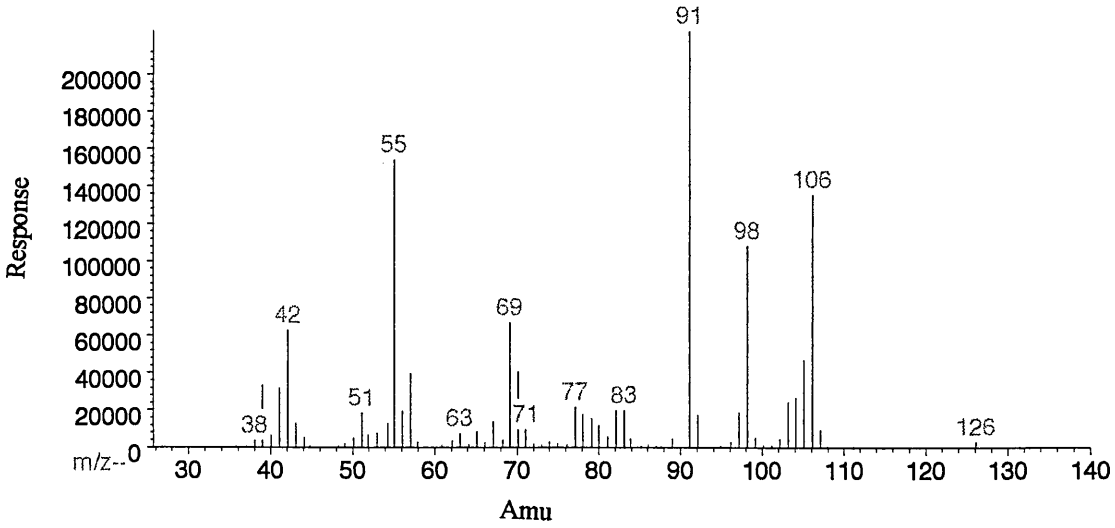


Figure 4-21 - Mass Spectrum of Cyclohexanone - Xylene Peak

The possible presence of cyclohexanone was of particular interest, as it is thought to be a photodegradation product of either benzene or toluene.

Although there were other potential compounds of interest such as sulphonates and nitrogenates, it was the identification of oxygenated organic compounds using the O_{777nm} emission line on the AED that was of most interest.

4.2.3.2.1 Results

Using the sampling method described earlier in section 4.1.2, an investigation using the atomic emission detector was performed as a means of confirming the earlier GC-MS results.

Using an elemental suite of C_{193nm}, S_{181nm}, N_{174nm}, O_{777nm}, C_{496nm}, H_{486nm}, Cl_{479nm} and Br_{478nm}, the basic composition of the compounds that were found in air was determined. Although the manufacturers of the AED claim that compound independent calibration is possible, work by Webster[180], showed that this is not the case. Therefore only qualitative results could be obtained.

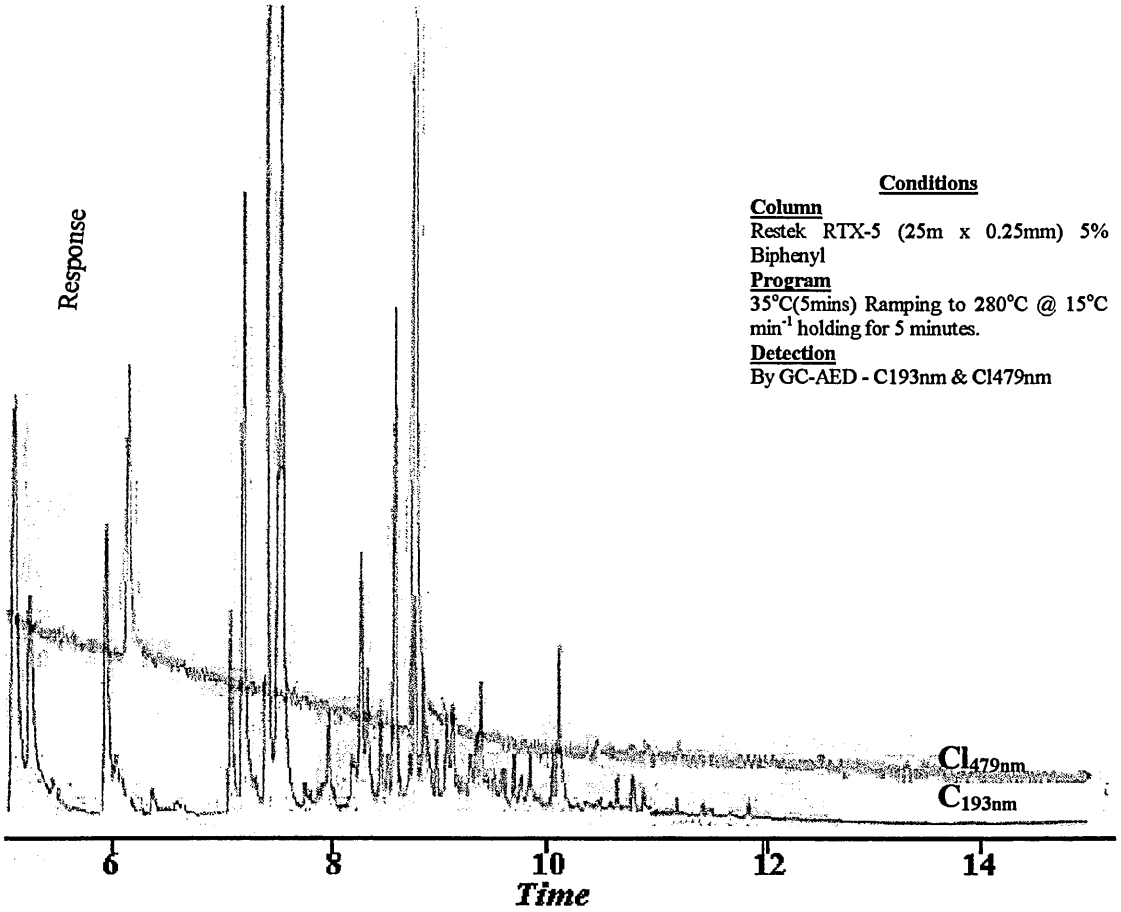


Figure 4-22 - Atomic Emission Chromatograms for Indoor Air Sample looking at the C_{193nm} and Cl_{479nm} Emission Lines

The chromatograms in Figure 4-22, show the emission lines for C_{193nm} and Cl_{479nm}. Although, as indicated, a tentative identification was obtained from the GC-MS data, the peak at t_r = 8.80min on the Cl_{479nm} line confirms the presence of 1,4-dichlorobenzene in indoor air.

The mass spectrum already discussed (Figure 4-21) showed problems with identification of that peak, due to the co-elution of the cyclohexanone with xylene. Used in conjunction with AED data, it was possible to confirm that the tentative identification of cyclohexanone was correct. The chromatogram below (Figure 4-23) shows two distinct peaks on the O_{777nm} emission line. It can also be seen that the peak at t_r = 7.75min does co-elute with the xylene, although a slightly better resolution can be obtained, resulting in two peaks.

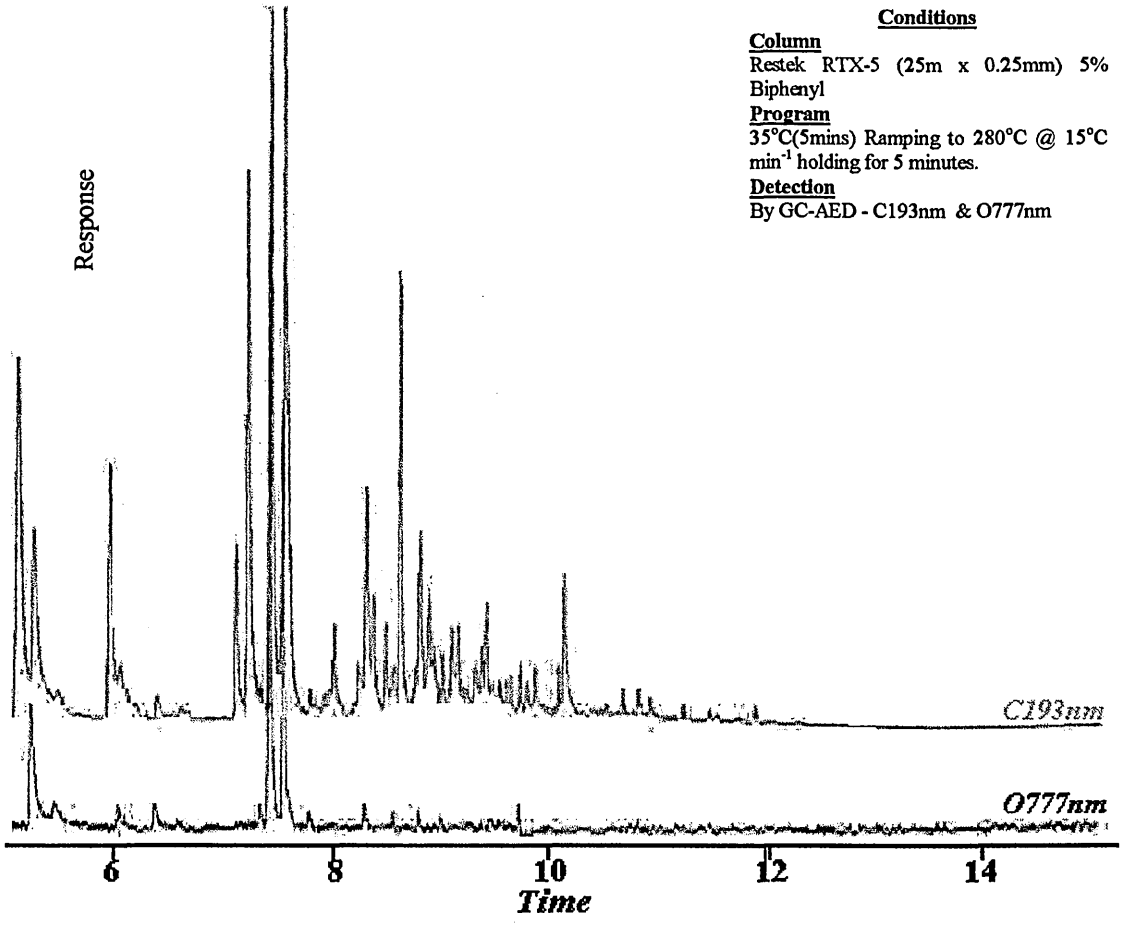


Figure 4-23 - Emission Chromatograms for an Indoor Air Sample looking at the C_{193nm} and O_{777nm} Emission Lines

Using either of the techniques alone would not have allowed the identification and confirmation of the compounds yet used in parallel the usefulness of both techniques was greatly improved.

It should also be noted that from the same sample, the S_{181nm} line gave several peaks that could not be identified using either technique. The S_{181nm} line is in a region that is often affected by carbon molecular emissions, i.e. sometimes there are peaks that do not relate to sulphur thereby reducing the integrity of the line.

Although it can be seen that using two advanced detection techniques in parallel is preferable for the increased identification "power", some caution still needs to be exercised in the interpretation of the results obtained.

In only one sample did we observe peaks from the Br_{478nm} emission line. As this could not be reproduced this result was tentatively called "experimental error" and ignored, although it could have been a bromine containing species present in that air sample alone. However, the sensitivity of the Br_{478nm} line does not preclude its use.

Figure 4-23 also showed a series of small peaks (t_r= 8.00 - 10.00min). Due to the weakness of the O_{777}nm signal and the relative strength of the hydrocarbons from the C_{193}nm emissions it can be seen that identification by GC-MS would be difficult. However, using a series of standards it was suggested that the compounds indicated as these peaks are a series of esters. This type of series has also been observed in other indoor air samples. The sources of the compounds that are present will be discussed later.

4.2.3.2.2 Conclusion

From the results and discussion above it is clear that, in order to identify the individual compounds that are found in a given air sample, is a complicated task. It has been suggested that the use of standards and GC-MS data alone does not give sufficient data to allow positive identification of the compounds. It has also been shown that using confirmatory techniques can, in some cases, still leave ambiguities. This problem could be investigated further by looking at the chemistry or the results from a different point of view.

4.2.3.3 Hetero-Atom Tagging

4.2.3.3.1 Introduction

Up to now the techniques that have been discussed have been noted for their simplicity. However, it became clear that for certain compounds, use of AED, was not entirely suitable.

Although the C_{193nm} emission line is extremely sensitive, the lines of the common hetero atoms found in VOC's tend to be very weak. This is especially the case for O_{777nm} that has a sensitivity of 250 times less than that of C_{193nm}.

Other atoms can be determined using other detectors, i.e. Cl using ECD, S using FPD and N using NPD. However, it is the oxygenated compounds that are the most difficult to determine.

The use of derivatives to change the physical characteristics of the samples is commonly used in both liquid and gas chromatography. It was decided, therefore, to experiment with the idea of fluorine tagging. Although a single fluorine atom has a similar sensitivity to that of a single oxygen atom, by using derivatives with multiple

fluorine atoms, this would theoretically increase the overall sensitivity of the compounds being investigated.

The compounds under initial investigation were carbonyls. As mentioned several times already, these compounds play an important role in the function of the atmosphere and therefore are suitable for further study.

Although the method was to be used on the AED, during the development process both GC-MS and GC-AED were used. It was found, therefore, that the unique nature of the fluorine tag made it suitable for with use both techniques.

4.2.3.3.2 PFBOA Determination of Carbonyls

It has been noted that carbonyls may be reacted with 2,4-dinitrophenyl hydrazine for use in LC determinations. The derivatives obtained are not suitable for use with GC. However, a similar type of reaction involving, *o*-pentafluorobenzyl hydroxylamine, can be used to prepare volatile derivatives. The methodology for this reaction is described in Chapter 2. The reaction scheme is shown below in Figure 4-24.

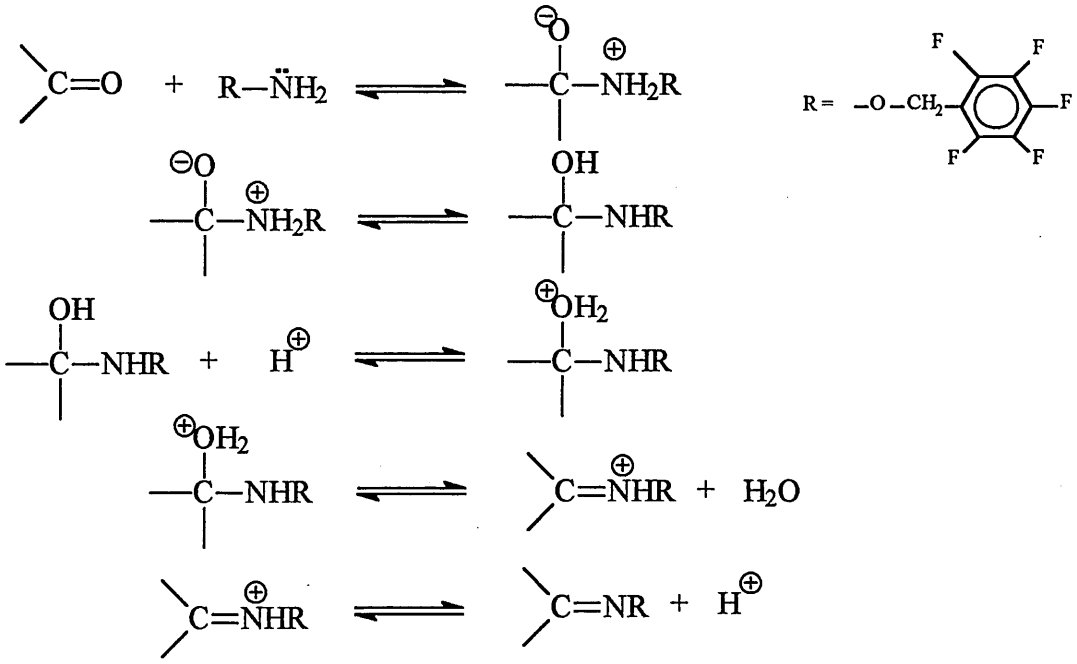


Figure 4-24 - Reaction Scheme for the Derivatisation of Carbonyls using PFBOA

The derivatives that are formed have three different hetero atoms, O, N and F, present. However, it is the five fluorine atoms that are of interest in this work.

The reaction takes place in acidic aqueous conditions, therefore before analysis the samples need extracting into a non-polar organic solvent, drying and neutralising, if necessary. Early runs indicated that the drying and neutralising process was not being

performed efficiently as there appears to be sulphur breakthrough, from the H_2SO_4, onto the C_{193nm} channel.

4.2.3.3.3 Results

Initially using 100ppm(mg L^{-1}) standards, experiments were performed to establish the optimum time for the reactions. By measuring abundance's relative to the internal standard, decafluorobiphenyl, it was possible to determine that a reaction time of two hours gave the optimum yield. After two hours there was an apparent reduction in yield.

The diagram below (Figure 4-25) shows a chromatogram obtained from a **100ppm(mg L^{-1}) aldehyde standard**. Above formaldehyde, each component shows as a doublet caused by the cis-trans isomerism across the C=N bond in the derivative, although poor resolution at the end of the run does not show this for heptanal. The peak at t_r = 13.80min is for acetone which is another compound that is commonly present at detectable quantities in the laboratory environment.

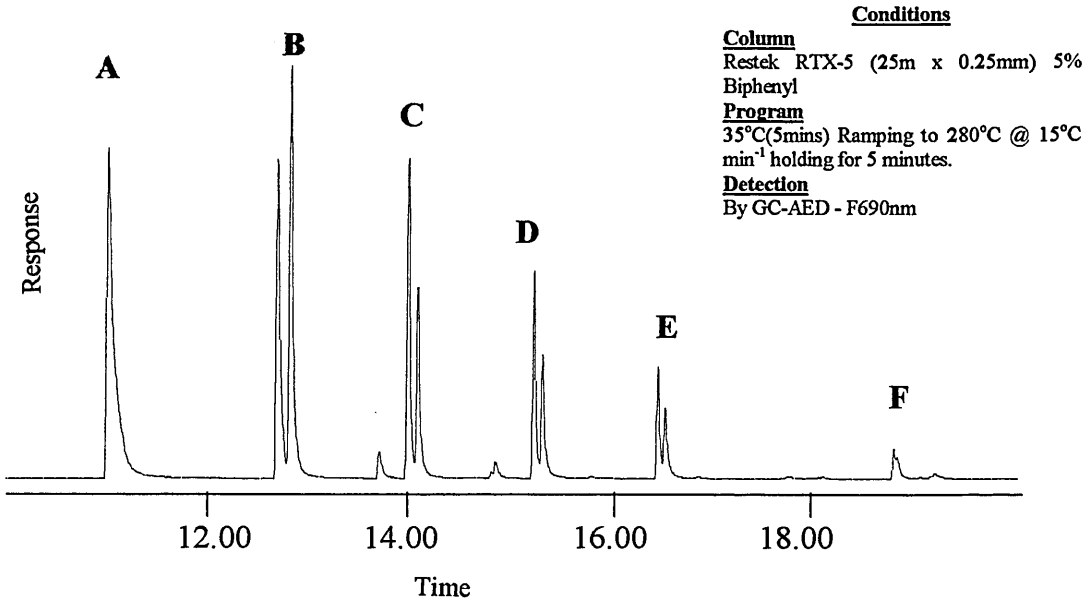


Figure 4-25 - Chromatogram of a Series of PFBOA-Aldehyde Derivatives

A - Formaldehyde **B** - Acetaldehyde **C** - Propanal **D** - Butanal **E** - Pentanal **F** - Heptanal

The experiments were also performed for ketones. The results of which are shown in Figure 4-26.

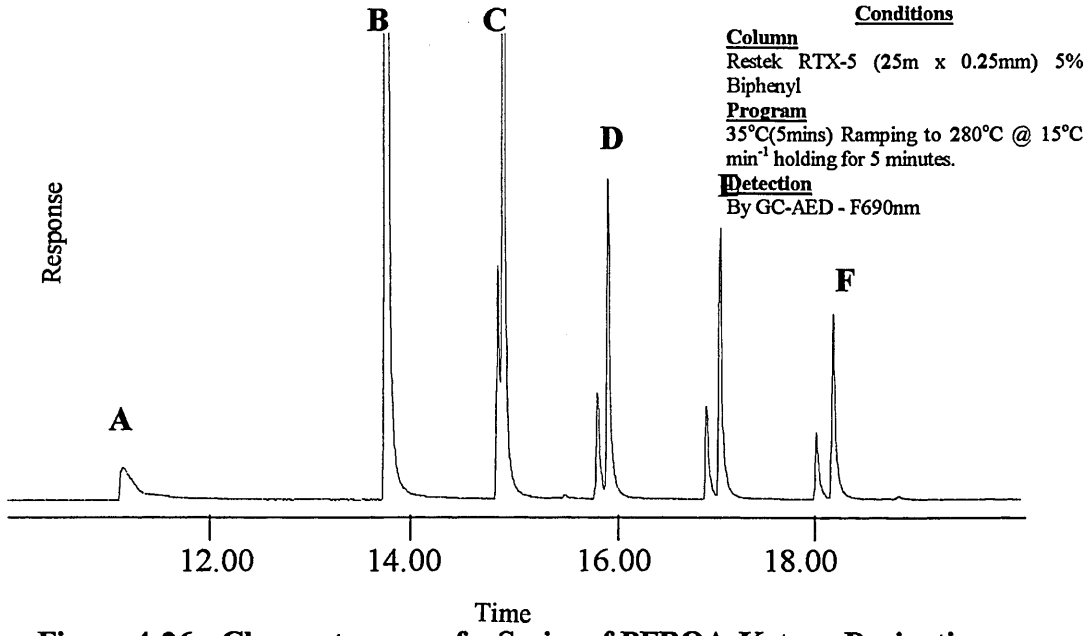


Figure 4-26 - Chromatogram of a Series of PFBOA-Ketone Derivatives

A - Formaldehyde **B** - Acetone **C** - 2-Butanone **D** - 2-Pentanone **E** - 2-Hexanone **F** - 2-Heptanone

In this experiment contamination from atmospheric formaldehyde can be seen (Peak A).

The experiments with the standard solution show that using the F_{690nm} emission line for samples that are of sufficient concentration give results that are acceptable, at least for qualitative analysis of an air sample.

Using the SPE cartridge air sampling method it is possible to obtain quite concentrated samples. The cartridges were extracted with H_2O/methanol and the eluent reacted with the PFBOA. Analysis of the extracted cartridges showed that various carbonyl compounds were being trapped and then derivatised.

Below are two chromatograms (Figure 4-27) from indoor air samples, for one air was spiked with propanal and pentanal. The un-spiked sample can be seen to contain a mixture of both aldehydes and ketones of the composition that is to be expected in such a sample. Whereas the spiked sample shows strong responses to both compounds.

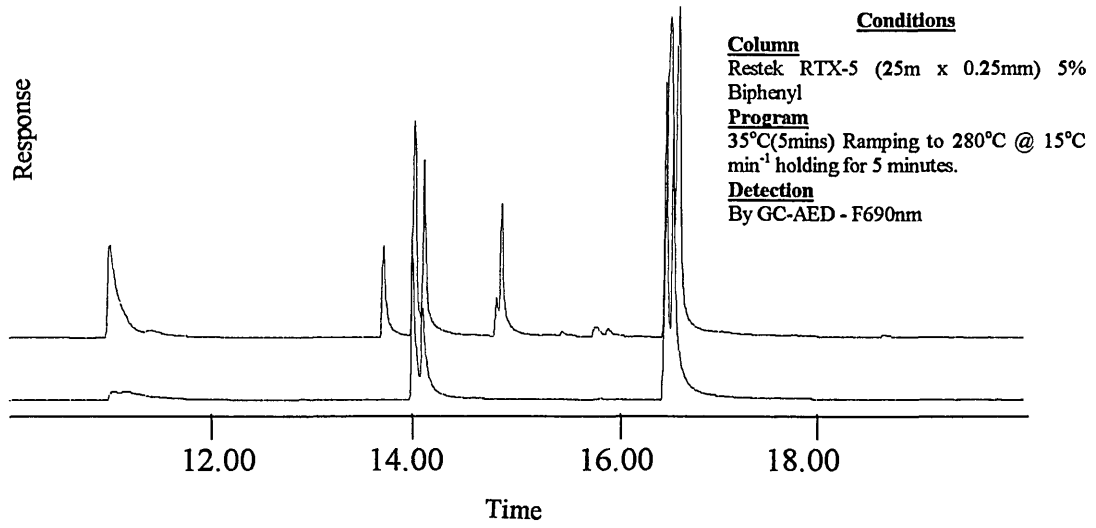


Figure 4-27 - Chromatograms showing PFBOA Derivatives of Carbonyls in Real and Spiked Air Samples

The compounds qualitatively identified in the real sample were formaldehyde, acetone, propanal, butanone, pentanone, and pentanal.

At this development stage the confirmation of the compound identity came from GC-MS results of the samples. By measuring the mass fragment at $^{m}/_{z}$ = 181, it was possible to determine which compounds contained the pentafluorobenzyl-group, and therefore had reacted.

4.2.3.3.4 Conclusions

The results described above suggested that the tagging of carbonyl compounds with a pentafluorobenzyl group, which can then be selectively detected using instruments like the AED, is a useful technique for the confirmatory identification of such compounds.

Although the results gave a good qualitative indication of the types of compounds present in an air sample for quantitative determinations the protocols examined gave very poor results.

An internal standard of decafluorobiphenyl (DFBP) was used for the work, yet there were problems with the introduction of this compound into the analytical sample. Two approaches were investigated, and in both cases were not suitable for use in routine analysis.

The first method involved having the internal standard present in the extraction solvent. This, in theory, would have been the preferred choice of introduction. However, it was found that the DFBP was extracted from the solution by the SPE cartridge, and thus was not present in the eluate.

The second technique involved extracting the derivatives from the reaction solution into the analytical solution using solvent containing the internal standard. Again, quantities of the internal standards were lost in the process due to the extremely small quantities of solvents that were being used.

It was decided, therefore, that for use with the SPE sampling technique, the results obtained could only be used for qualitative identification, air profiling and air "fingerprinting". The latter two techniques will be discussed in the next chapter.

4.2 Conclusions

This chapter has discussed the major analytical issues that were investigated during the course of the research project. In a sample, however selective the sampling process, there will be a large number of different compounds present.

As analytical techniques become more sensitive it is possible to determine lower levels of analyte, and although this is good for science, in general, for air analysis this causes more problems than it solves. Although different ways of determining and quantifying these compounds were examined, the same general conclusion was reached, i.e. the results were becoming to complicated to interpret simply.

For target compound analysis the currently used techniques are more than adequate for the results that are required. But for the examination of total air quality it was found that although the analytical techniques that we had investigated were producing results it was the interpretation of these results that was open to many questions. Although good analytical practice and method development is essential, the modern analyst needs to be looking further than the end of the analytical process, to be able to produce effective and meaningful results.

Chapter 5

Data Analysis

5.1 Introduction

For the researcher, the decision has to be made of which compounds are important and which aren't. As analytical and environmental science crosses the manmade political borders of the world we find that the results we produce will cause conflicting views somewhere.

As already discussed air is a complex and continually interacting mixture of compounds, and many of the compounds that are present are found in all three phases.

How do we define good air quality? At present the key indicators for air quality are ozone, NO*x*, SO*x* and PM_{10}. Some organisations also measure benzene and 1,3-butadiene. The question is, do these compounds represent 'air quality'? Take for example a street market place, the levels of ozone and NO*x* might be within the given parameters for good air quality but the smells of fruit, fish and human activities can sometimes make the air feel thick and unpalatable. The compounds that cause these odours, however, are not considered when calculating air quality. It is impossible to be able to monitor the variations in air quality across a small area such as a town centre, but the question that needs to be asked is: 'are we using the correct compounds as indicators of air quality'? Or 'are the ones used politically motivated'?

Air quality is very subjective. What is considered good air quality? A country dweller will probably find city air to be of poor air quality. Yet many city dwellers find the smells of the country offensive. A study by Fanger *et al.*[181] has shown that the quality of indoor air in various buildings as perceived by a panel of judges varies dramatically. This begs the question: If "experts" can't agree on what is good air quality how can we expect the public to believe what we say?

Terms like ppm(mg L^{-1}), LOD and 'action thresholds' are frequently used by scientist to describe results. Yet these same fundamental words are responsible for the impression that scientists live in "ivory towers" and do not relate to reality for the 'man in the street'. At the end of the day it is our responsibility to make the relevant results accessible and understandable to the man or woman in the street.

So, in this chapter we will be discussing two techniques for interpreting the analytical data to give results that have some meaning for the non-scientific community. We will also be examining some of the problems associated with the interpretation of air quality results, especially those concerned with indoor air quality.

5.2 Air Fingerprinting

5.2.1 Introduction

Until recently blood grouping was used as a reliable way of medically identifying people. With the development of DNA fingerprinting, scientists can be much more specific with the identifications, and an accuracy of 1 person in 14 million is commonly quoted. With DNA fingerprinting, the scientists are not looking at individual genes, but at large fragments of DNA which are characteristic of the person in question.

By using this analogy, and transposing it to air analysis, it can be seen that as analysts we are at the two extremes. We are either producing results that are not specific enough, i.e. the target compound approach. Or we are looking at every compound present in the air, which is in a way like cataloguing specific genes, and making judgements based on that. Air analysis has yet to take the step into looking for the characteristic features of the compounds in air.

5.2.2 Background

Many of the air samples that were being obtained generally had the same qualitative composition. Hence it was decided that, instead of trying to quantify each of the individual components, it would be advantageous to group them together according to the characteristic mass fragments of the compounds. For example alkanes have the characteristic ions of $^{m}/_{z}$ 43, 57, and 71. Whereas alkyl aromatics have ions of $^{m}/_{z}$ 91, 106, 120 and 134.

So by initially investigating several general classes of compounds it was possible to build up pictures or fingerprints that could be used to show the composition of a particular air sample.

5.2.3 Results

5.2.3.1 Initial Experiments

The compounds that were chosen to be part of the initial fingerprint were alkyl aromatic compounds (often associated with indoor air but also traffic fumes!), naphthalenes (associated with diesel fumes), small terpenes or natural products (associated with both personal and environmental perfumes), and 1,4-dichlorobenzene

(PDCB). Although PDCB is an individual compound its reason for inclusion in the basic set will become apparent.

Samples from both indoor and outdoor air were taken using the SPE air sampling method and then analysed using GC-MS. The data was processed so that the ion abundances for each of the 'target' mass fragments were collated. The ions used are shown in the table below.

Table 5-1 - Mass Fragment Ions used for Initial Fingerprints

Ion $^{m}/_{z}$	Group
91	Alkyl Aromatics
105	Alkyl Aromatics
106	Alkyl Aromatics
120	Alkyl Aromatics
128	Naphthalenes
142	Naphthalenes
156	Naphthalenes
146	PDCB
68	Natural Products
93	Natural Products

Using these basic ions it was, therefore, possible to build up a picture of the some of the key components in the samples.

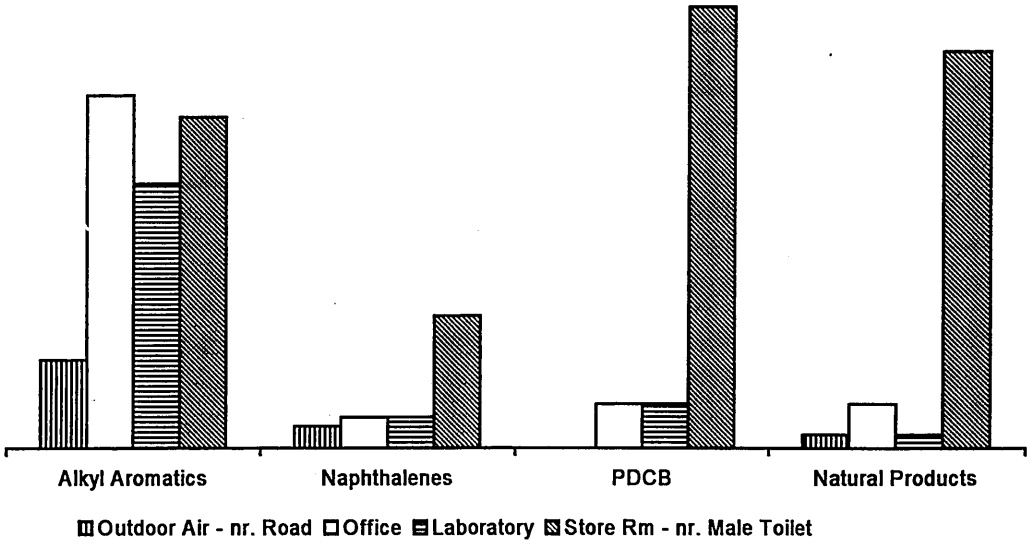


Figure 5-1 Basic Fingerprints of Urban and Indoor Air Samples

Figure 5-1 shows the basic fingerprints for four different air samples that were taken and analysed using the same protocol. By looking at this simple picture the information that can be obtained is more meaningful than many chromatograms.

All four samples contained alkyl aromatics, though the Office sample contained levels that far exceeded the other three samples. Because of this it was necessary to recalculate the results using a standardising factor. This applied across all four categories allows the 'pictures' that the results create to be compared. The importance of the standardising factor will be discussed later.

The office air and laboratory air samples were very similar in profile except that the office air had slightly higher levels of natural products.

The sample that gave the most interesting set of results was the store room sample. This room was used for storing old or disused analytical instruments and was formerly an office. The location of this room next to the male toilets is the reason for the high levels of PDCB and natural products.

The outdoor air sample has moderate levels of both alkyl aromatic compounds and the naphthalenes but very low levels of the natural products and the PDCB.

5.2.3.1.1 Conclusion to Initial Experiments

The results of initial experiments suggested that it was possible to use such a presentation technique to produce workable fingerprints of various air samples. It can also be seen that the different air samples had quite different fingerprints, i.e. Indoor air is different from outdoor air.

The use of the standardisation factors was necessary to account for the differences in the sample volumes and concentrations of the compounds in the air. It should be recognised that with this technique we are creating 'pictures' of the air, the results are not quantitative, though they can be used as indicators to the levels of the compounds that are present. Therefore these initial experiments have shown that the fingerprinting technique is a good way of presenting complex information that layman and scientist alike can interpret it.

5.2.3.2 General Development

5.2.3.2.1 Results

The number of compound classes that can be used in the fingerprint is dependent of the wishes of the analyst, however, by using the widest range of compound classes it is possible present a more accurate picture of the sample. It was decided therefore to include alkanes in the fingerprints as well as using a wider range ions to represent the alkyl aromatic compounds.

Another feature that was added was 'compound weighting'. By simply multiplying the values for a compound by a given factor it is possible to obtain greater detail for certain compounds. In the following example compound weightings were given to several compounds. and the alkyl aromatics. Positive weightings were given to the PDCB and the natural products. This, in effect, magnifies their portion of the fingerprint, giving more emphasis. The alkyl aromatics were given a negative weighting thus reducing their impact on the picture. It is essential however, that what the same weightings are given regardless of sample.

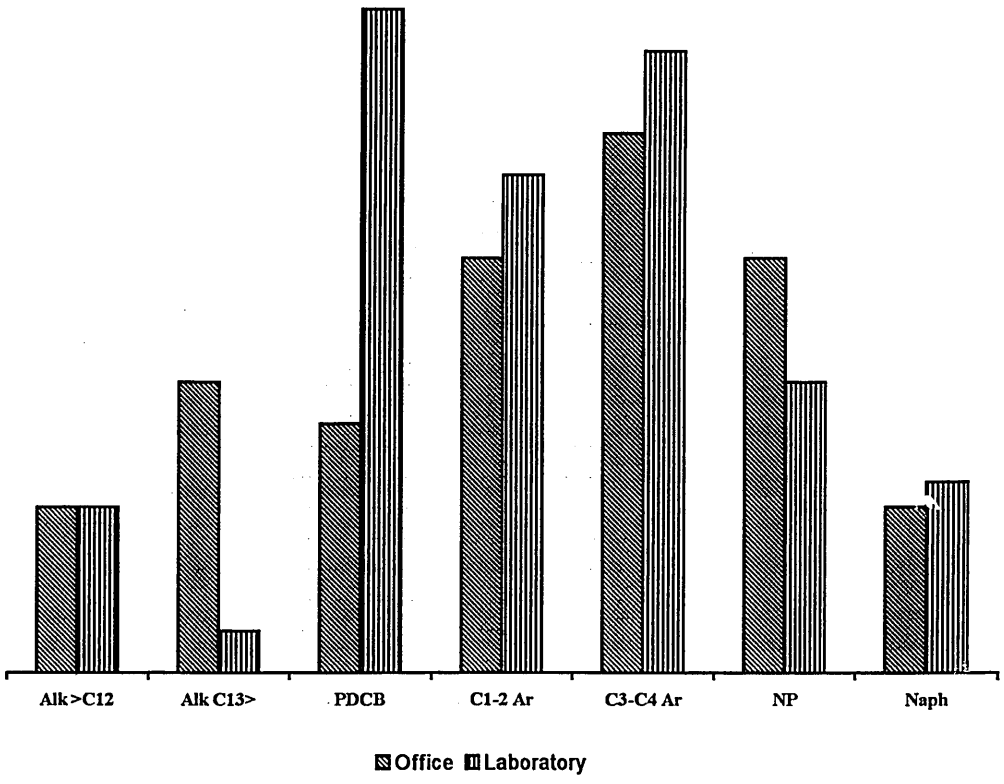


Figure 5-2 - Fingerprints of Two Different Indoor Air Samples

Figure 5-2 shows two apparently very different fingerprints for indoor air samples. By expanding the range of compounds investigated it is possible to give more detail to the final results. On closer examination it can be seen that there are some fundamental similarities to the fingerprints, i.e. lower alkanes, alkyl aromatics and naphthalenes. Major differences are seen in the other three factors. The reason for higher levels of PDCB in the laboratory on that day were never determined but are probably related to cleaning regimes and rotas.

The reasons for the levels of the higher alkanes and the natural products that were found in the office were attributed to the presence of a female secretary. Other rooms studied never showed the same profile for these compounds. Analysis of the secretaries' perfume showed that it contained the compounds that were present in the room as a whole.

Another experiment performed compared domestic indoor air with that from the workplace.

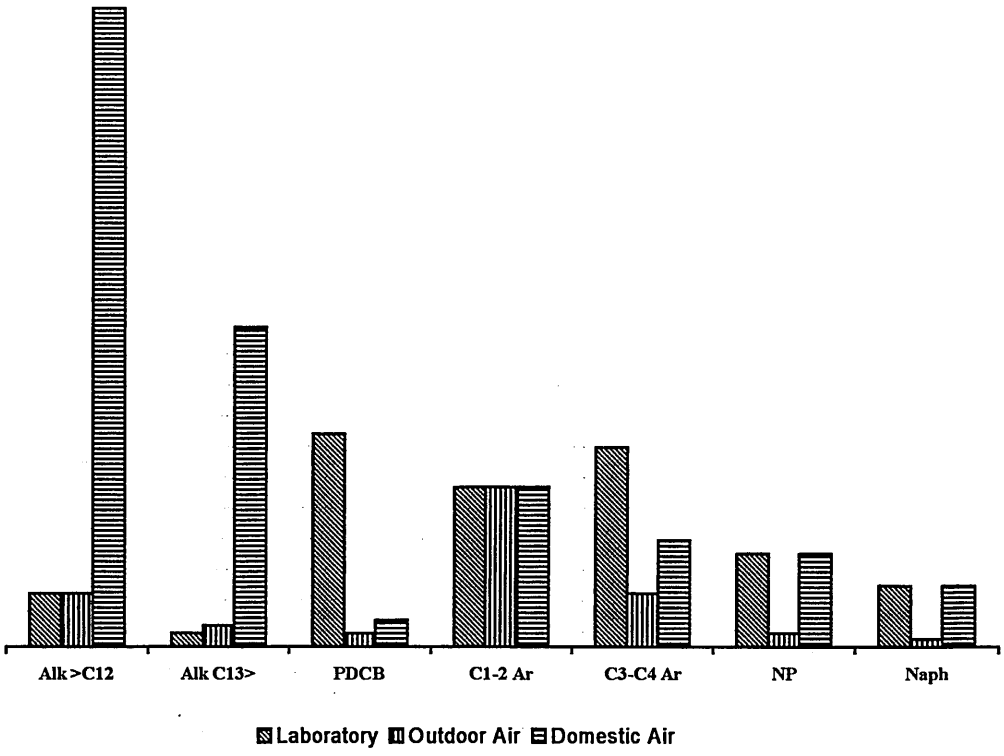


Figure 5-3 - Comparison of Indoor and Outdoor Fingerprints

The fingerprints shown above (Figure 5-3), are standardised to the C_1-C_2 Aromatic factor. As already suggested increased levels of C_3-C_4 alkyl aromatics is indicative of indoor air. This is seen here with the outdoor air have significantly less.

Also compared to the out outdoor air sample, both indoor samples have raised levels of natural products. In general the outdoor air sample has low levels of all the factors except C_1-C_2 alkyl aromatics, this group contains toluene and xylenes, which are ubiquitous in the environment, and are often related to vehicle exhausts and fuel escapes.

The only anomaly is the raised levels of lower alkanes in the domestic sample. This could originate from various sources such as cooking, or cleaning products, or even suburban pollutant sources. As expected the relative levels of PDCB are higher in the workplace sample than in the domestic as there are fewer domestic products that contain it.

5.2.4 Conclusion

Using the expanded fingerprint, it was possible to present a picture of the air that could allow meaningful and sensible conclusion about the air mass to be made. Although air fingerprinting is just a qualitative technique, when examining air quality it is not necessarily the final 'number' that is important. In understanding how an air mass came to be polluted we can then arrange ways of dealing with it, this is especially true for indoor air. It can be seen then from these particular results that although, in general, indoor air is uniform in composition, local factors such as human activity can change the local air composition quite radically. It was shown from the results in Figure 5-2 that just *one* person changed the composition of the air to a noticeable degree. By measuring the legislative target compounds however, the air quality in that room would have been the same as in any of the room that were used for sampling. It is important therefore, to analyse for toxic compounds but not all of the compounds that affect air quality are toxic!

Although the fingerprinting technique is an excellent way of presenting the air quality data in an understandable, yet still meaningful form, it does not answer the questions of how good the air quality of a particular air mass is. This is a very subjective issue. There have been no real attempts to quantify air quality other than the measure of the 'big' target compounds. However, would the impact that, for example, benzene makes on air quality be the same in summer as in winter? These questions are not answered by the present way of monitoring air quality, because they are not asked.

Policy makers have found it to easy to place values on compounds without really understanding what those values mean. By trying to understand and take into account factors such as the effects of UV light, the atmospheric lifetime of a compound, and it's

toxicity, it should be possible to obtain a value that reflects the effect of a particular compound on air quality.

5.3 Air Quality Index (AQI)

5.3.1 Introduction

As already mention air quality is difficult to define objectively. At present, air quality is defined and measured in terms of the concentrations of ozone, oxides of nitrogen and sulphur and particulate matter. These parameters, although having a firm scientific basis, fail to give an accurate picture of total air quality. In an urban situation there are other factors and sources that will affect air quality but will not affect the levels of O_3, NO_x, SO_x and PM_{10}. E.g. sewage treatment works, incinerators, road laying (tar), heavy industry etc.

To define an objective value for air quality we need to understand what is happening to compounds that are in the air and we also need to decide which compounds are useful markers of air quality

As discussed in Chapter 1, air is a dynamic and complex mixture of both organic and inorganic compounds. Due to the extreme conditions that are found in air there is a constant interaction between the compounds of the air. The actions of ozone, NO_x, the hydroxyl radical and sunlight mean that most compounds have a finite atmospheric lifetime. In many cases the atmospheric conditions and lifetime of the target compounds tend to be neglected when air quality or pollution levels are defined.

In examining the possibilities of an index for air quality it was decided therefore to consider factors other than the atmospheric concentration at the point of sampling. To do this we developed the Individual Component Weighting (ICW) and the Individual Component Air Quality Index (ICAQI). Like the Richter Scale for earthquakes and the Beaufort Scale for wind speed, which give a simple value to a complex phenomenon, the ICAQI was designed to give a number that, although based on scientific knowledge, was simple, yet relevant, for everyone to understand.

5.3.2 Individual Component Weighting

The ICW is the starting point for the air quality index. It is at this stage, just a theoretical model, that takes into consideration the toxicity, atmospheric lifetime and UV exposure of individual compounds in the air. None of the operands that are expressed in

the formula have definite values, but it is the merits of those operands that will be discussed in this section. The ICW is expressed by the formula:

$$\frac{t}{x} \cdot \frac{1}{w}$$

Where t is atmospheric lifetime, x is toxicity and w is "UV" exposure.

5.3.2.1 x-Factor

The x-factor represents the toxicity of the component being measured. The values that have been chosen to represent toxicity are the Exposure Levels from various statutory bodies. However, even on what might be considered 'safe' ground there is a wide variation between countries and bodies in allowed values.

For the purposes of the examples illustrated in this section the values that are being used are taken from the Minimum Risk Levels issued by the Agency for Toxic Substances and Disease Registry, Atlanta, Georgia. These values are given in $\mu g\ L^{-1}$, and appear to give a fair and average value. Some bodies give what appear to be excessively tight regulations whereas others take and unusually lenient view.

5.3.2.2 t-Factor

This value is based on the lifetime of the individual compound in the atmosphere. This value is a theoretical value obtained from kinetic data. Again values like this will need to be set by convention. However, 'ball park' figures will be sufficient, if the information going into the formula is too complex it seems to defeat the purpose of what the ICW is designed to achieve. For the purposes of this discussion approximate values will be used.

5.3.2.3 w-Factor

This value is the most approximate of the three components. It represents the "UV" exposure that the compound will receive. The action of ultra-violet light in the

atmosphere is the likely initial 'sink' to most organic compounds. This value is an attempt to quantify this effect.

For example: On a sunny day compound X will survive, on average, 6 hours. On a cloudy day it will last 12 hours. Indoors compound X will have a lifetime of 36 hours. This means that the potential exposure time will be twice as long on a cloudy day as it will be on sunny day and 6 times as long indoors.

∴ Potential "UV" Exposure: Sunny Day>Cloudy Day>Indoor

Although this is may seem very ambiguous at first, by including a operand that can account for the removal of the pollutant from the atmosphere it possible to obtain a clearer picture of the air than is otherwise allowed.

The table (Table 5-2) below shows theoretical examples of the Individual Component Weighting's for several of the compounds that have been found in the indoor air samples during the experiments performed during the course of this research project.

Table 5-2 - Individual Component Weighting Examples

Component	x - μg L^{-1}	t - hrs	w - hrs	I.C.W. μg L^{-1}
Toluene	3.715	15	6.5	0.621
Xylenes	4.281	26	6.5	0.934
Benzene	0.1595	12	6.5	11.5746
p-Dichlorobenzene	1.185	36	6.5	4.674

Using a w-value that is representative of the UV exposure for an average spring or autumn day, theoretical values were obtained for the ICW. Although the toxicity of the xylenes was less than that for toluene, because of the atmospheric life time factor it can be seen that the ICW values for xylene are higher. This, therefore, represents more accurately the effects that xylene would have on air quality. It might be less toxic, but because it lasts longer in the atmosphere it can be effective for longer. Also to be noted is that the I.C.W. for benzene is significantly higher than that for toluene even though it's atmospheric lifetime is not greatly different from the toluene.

The I.C.W. is a simple way of characterising and classifying the various organic compounds that are found in air and their effects on the air quality. However, it is not

quantitative. To quantify the air quality it was necessary to take the ICW one step further to develop the Individual Component Air Quality Index.

5.3.3 Individual Component Air Quality Indices

The ICAQI is a way of quantifying the components in an air sample with relation to their Individual Component Weighting. The ICAQI is expressed in the equation below:

$$\frac{t}{x} \cdot \frac{1}{w} \cdot c$$

where c is concentration of the component in the air with units of $\mu g\ L^{-1}$. The result of this equation is a number, without units. This number then, is similar in effect, to the Richter and Beaufort scales, the larger the number the more "toxic" the air sample. Although that is an over simplification of the type of results that are obtained, that in essence is what is achieved.

Using the ICW data from Table 5-2, the ICAQI values were calculated for a theoretical air sample containing $0.005 \mu g\ L^{-1}$ of both benzene and toluene.

$$ICAQI_{benzene} = 11.5740 \times 0.005 = 0.0579$$
$$ICAQI_{toluene} = 0.621 \times 0.005 = 0.003$$

It can be seen from the two equations that although the benzene and toluene were present in the same concentrations the ICAQI values are vastly different reflecting, more accurately, the effects that each of the compounds has on the quality of the air. Additionally, these results are in line with current thinking, and thus, are not controversial.

For a more comprehensive value of air quality the summation of the Individual Component Air Quality Indices (ΣICAQI) of various compounds has been investigated. This will give a value that is more representative of the air quality of the particular sample in question. Which compounds to use in the summation though, brings us full circle with this problem.

Using data obtained from an indoor air sample it was possible to calculate the ICAQI and then the Σ(ICAQI) values for the sample. This data is shown in Table 5-3.

Table 5-3 - ICAQI

Compound	Sample $\mu g\ L^{-1}$	Indoor I.C.A.Q.I.	Outdoor I.C.A.Q.I.
α-Pinene	0.008	0.001	0.000
β-Pinene	0.000	0.000	0.000
Limonene	0.033	0.003	0.001
Benzene	0.153	1.674	0.473
Toluene	0.107	0.063	0.018
Xylene (2)	0.074	0.065	0.020
Heptane	0.000	0.000	0.000
Octane	0.000	0.000	0.000
Nonane	0.000	0.000	0.000
Decane	0.070	0.049	0.015
Undecane	0.011	0.005	0.001
Dodecane	0.007	0.003	0.001
Tridecane	0.007	0.003	0.001
Tetradecane	0.016	0.007	0.002
Σ(I.C.A.Q.I.)		**1.87**	**0.53**

Two scenarios were investigated using these results. The first is for the actual sample, i.e. indoor air, the second is if similar results were obtained from an outdoor sample. The arbitrary *w*-terms that were used were 2 hours for the indoor air and 6.5 for the outdoor. These values reflect the realistic levels of UV light that were experienced at the time the sample was obtained.

In this particular example it can be seen that the benzene concentration was rather high but this was then reflected in the ICAQI. The major point to note is that outdoor sample has a lower value than the indoor sample even for the same composition. This describes a more accurate picture of the air quality than just a single measure of concentration.

5.3.3.1 Conclusion

By using a realistic yard stick by which to measure air quality it should be possible to assist the people who need the information, both the public and the policy makers, to a greater degree. It is felt that the ICAQI approach to the measurement of air quality, although still at the theoretical stage is a step in the right direction. By taking well thought out steps to present the information that is really required, it has been shown that a simple formula can produce meaningful results.

There is still a much work that needs to be done on the ICAQI approach such as which values to adopt for toxicity, exposure and so forth, but this works need to be done

by consensus, taking into account the wide body of experience of the scientific community, both in the UK and abroad.

The air fingerprinting technique and ICAQI are just starting points to making the results of our science accessible and meaningful to the people whom rely on our results.

Chapter 6

Conclusion

6.1 Introduction

There were three aims for the research work described within thesis: to examine the role that organic compounds play in the atmosphere and air quality, to develop analytical methods that are simple yet efficient, and to examine ways of presenting the data, especially air quality, so that they are more easily understood. This final chapter examines all three aims and how they were met throughout the work and the thesis.

6.2 The Role of Organic Compounds...

6.2.1 ...in the Atmosphere

The role of organic compounds in the atmosphere was described in chapter 1. The traditional view of air, that is taught all the way to degree level, is that air is 79% nitrogen, 19% oxygen, with small percentages of noble gases and carbon dioxide, does not do justice to the real complexity of the atmosphere. The traditional picture might be accurate on a macro scale but in reality falls short. Air is a complex and dynamic mixture of organic as well as inorganic compounds that is constantly changing and interacting.

The literature review in chapter 1 examines the roles of many compounds in the air but focuses on two specific classes: organic acids and carbonyls. These compounds are both highly oxidised and are basically at the end of the carbon cycle. But by just concentrating on the measurement of these two classes of compounds are we in danger of losing sight of the bigger picture?

It was shown that many classes of hydrocarbon break down to produce carbonyls and acids as by-products, and other by-products further break down to produce yet more carbonyls and acids. So by focusing on just oxygenates it was possible to give misleading information about the composition of air. That is not to say that oxygenates are not important but they are just one small part of a much larger and complex picture.

It should be noted that many components of the atmosphere are linked to each other in cycles in much the same way as we find the cycles within the living cell. Measuring pyruvic acid, for example, does not give an indication of the well being of a body. So in the same way the measurement of individual compounds does not give an accurate picture of the air. Hence it is essential to look at the air as a whole and not just of a small sub-set of compounds.

The aim of examining the role of organic compounds in air therefore was shown that: they play a more important role than is often assumed. Many of the compounds that we call pollutants have natural sources as well. This means that for most compounds the natural chemistry of the atmosphere will deal with it. (The Gaia Theory)

6.2.2 ...in air quality

The fact that there are many compounds present in the atmosphere suggests that they all might play an important role in defining air quality. However air quality is now a political issue, and it has been decided that only 8 compounds should be used as targets for air quality. Unlike clean water, which is provided as a paid service, air is free, and as such is difficult to legislate for. Only by global legislation will it be possible for us to improve air quality, because the wind does not recognise political boundaries. Control of the use of motor car will play an important step in this process, but once we have that under control the process will start again. Good air quality is for everyone's benefit, but who decides what is good?

The other major political minefield that scientists face is that of tobacco smoking. No science is needed to say that tobacco smoke adversely affects air quality. However, many of the compounds that are found in an air sample are also thought to originate from other sources. Also many of the carcinogens that are found in tobacco smoke are also found in many other types of smoke. This does not suggest that smoking is safe. Clearly it is not, but if people want to partake in dangerous activities then that is their choice. The scientist, theoretically, should remain objective at all time.

It was found that, for the issue of air quality, to date there are not many answers to any of the air quality issues, and the answers that are provided are complex and difficult to understand. This was to be expected but was still disappointing to find. However, it meant that we could still address our third aim.

6.3 Development of Analytical Techniques

Many analytical techniques were investigated throughout the course of the project both theoretically and practically. Some were deemed suitable for use, whereas others were not. What was noticeable was the complex diversity of techniques for similar analytes. Many laboratories are limited by what techniques they can use, a set of uniform protocol would not go amiss although the EPA approach seems unnecessarily bureaucratic. It was from this point that we approached the analytical phase of the

research. Of all the techniques that we attempted it was only the capillary electrophoresis that proved successful. The results of the various experiments that we performed are well documented in Chapter 3.

The use of so many different techniques only complicated the objectives that we were trying to achieve. Hence it was decided that a single analytical method approach was more desirable.

With the successful development of the Solid Phase Extraction cartridge sampling technique the use of a simple gas chromatography analysis proved adequate to obtain the majority of the results that were required. The selectivity that the SPE method allowed us was far more beneficial than the multi-method approach.

By using hyphenated techniques such as GC-MS and GC-AED it was possible to confirm the analytical results. Also by using GC-MS it was possible to be selective in the interpretation of the results thus allowing the development of the fingerprinting technique that was described in Chapter 5.

Analytical scientists have a tendency to be preoccupied with developing methods, instead of looking ahead to see what results are required. In this respect scientists should apply the standard test of quality to their results i.e. are they 'fit for the purpose?' If this happened more often air analysis would be much simpler. Reviewing many of the recent analytical journals it seems that all we are doing is repeating or incrementally developing the same concepts. Radical thinking seems to be unacceptable these days though some might argue (James Lovelock for example) that it always was.

Over the years we have made analytical science to complicated. Instead of taking steps forward, we have been taking too many steps sideways. The Star Trek vision of the all seeing analytical instrument of the Tricorder, might seem like a fantasy but at present we are not even trying.

By using a simple and reusable technique, that is also efficient, quick and cheap, we feel that we are in some way going against this trend. The SPE sampling method gave efficiency and reliability that could not be matched by many of the traditional sampling techniques. With this technique alone we feel that we have addressed the second aim. Furthermore by looking at the results that were required before we developed the methods we obtained exactly what we wanted. Backing this up with the use of different detectors some simple some complex, we confirmed our findings in simplest possible way.

6.3.1 Data Presentation

The majority of the research conducted in the United Kingdom, is carried out using public money in the form of research grants. In the age of accountability it seems that the research scientists, especially those dealing with air analysis, have slipped through the net of public scrutiny. The results that we produce are often complicated and not easily understood by the layman.

It was with this in mind that we developed both the Air Fingerprinting technique and the Individual Component Air Quality Index. These were attempts at expressing complex data in a form that was easily understandable to everyone.

The use of a pictorial interpretation of the composition of the air to produce the Air Fingerprint is based on an old idea. Graphs have long been used to express visually complex equation, whether for financial or medical data. So, with this fundamental background, we approached air. The examples shown in Chapter 5, showed that from simple pictures the correct conclusions can easily be reached. We therefore believe that Air Fingerprinting has great possibilities in the field of data presentation.

The ICAQI also has great possibilities. Although expressed in it's theoretical form we have shown that it too can be used to present complex data. To the layman being told that a high number means poor air quality whereas a low one means good is more beneficial than being told that ozone is present at 100ppb for example.

It can easily be imagined in the not to distant future that air quality will become quite an emotive issue that is as much a part of everyday life as the weather is today. Having a convenient way of presenting air quality is one possible way to ease the situation. After all it works for temperature.

6.3.2 Conclusion

This chapter is not a crusade against the scientist but is aimed at raising some of the issues that we, as scientists, must face. Many of the problems that we face are of our own making, being too complicated in our approaches and so on. Others are not. It is not necessarily our entire fault that we are not understood. It is our responsibility. Throughout this thesis we have constantly strived to stress the importance of simplicity.

By keeping our sampling simple, our determinations simple and then our results simple it is possible to see more than we otherwise could. The old saying "you can't see the wood for the trees" is very true at times for analytical science.

Appendix A - Water Sample Electropherograms

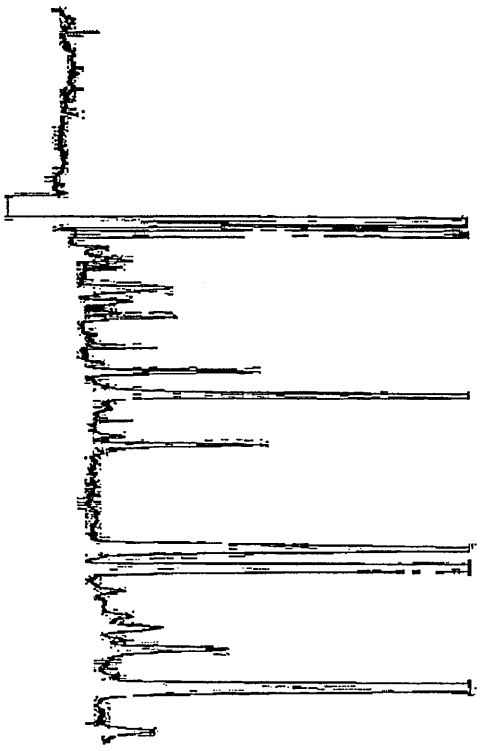


Figure 1 - Electropherogram of AnalR Water (Aldrich)

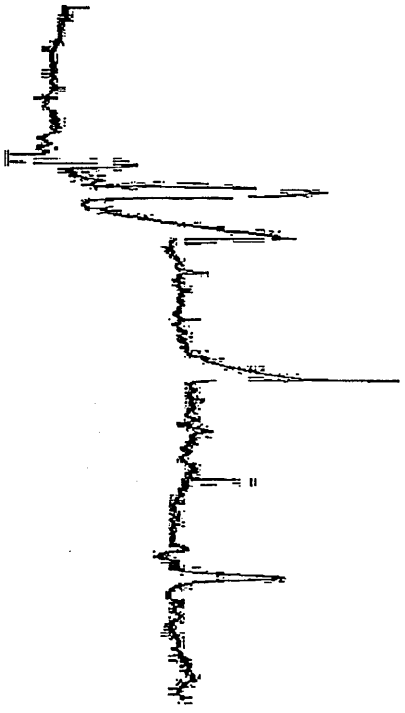


Figure 2 - Electropherogram of AnalR Water (BDH)

Figure 3 - Electropherogram of Laboratory Glass Distilled Water

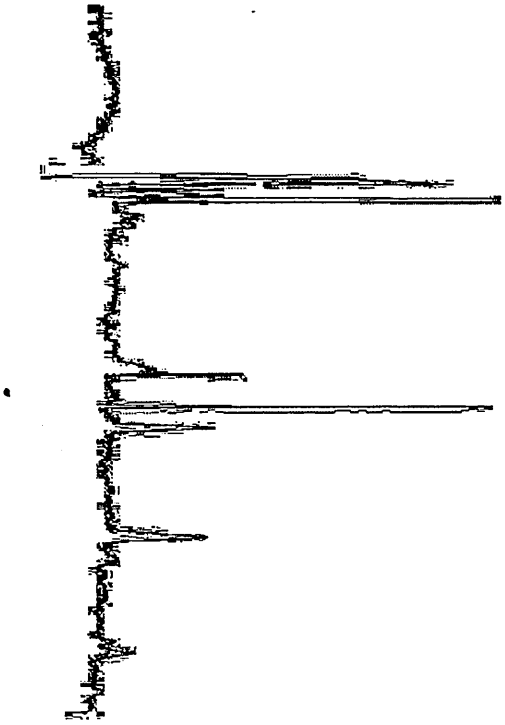
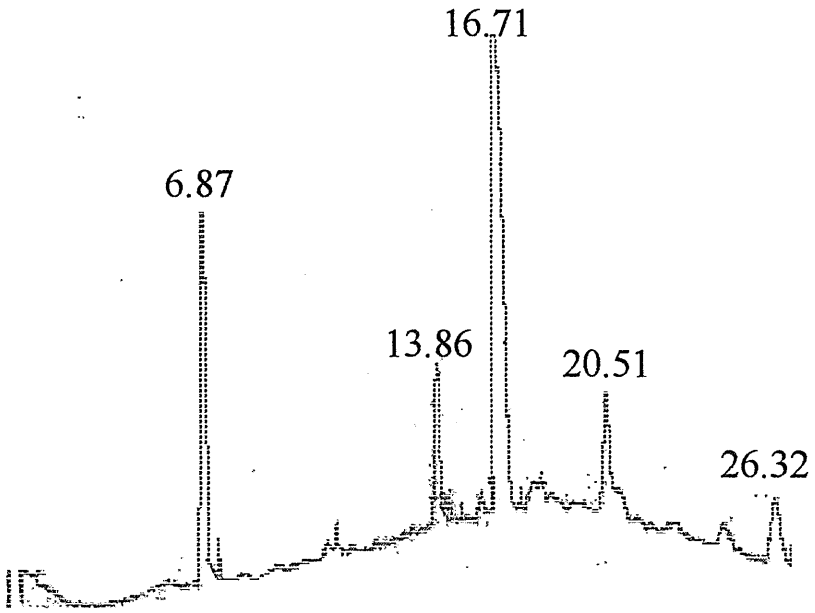


Figure 4 - Electropherogram of Laboratory Prepared Milli-Q Water

Appendix B - Urine Sample Electropherograms

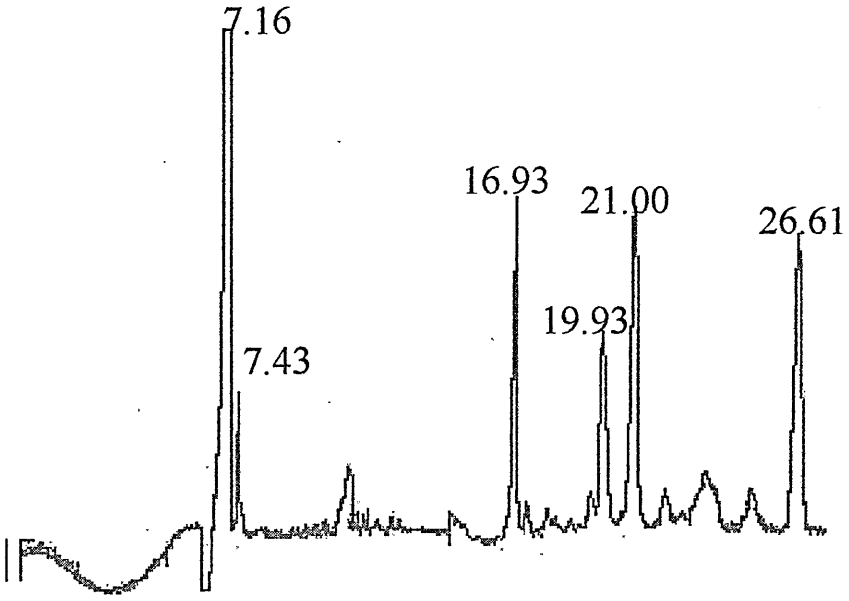
SAMPLE 20 (1:7 Dilution) :

2 yr Old - Profound Metabolic Acidosis + β-Ketothiolase Definciency

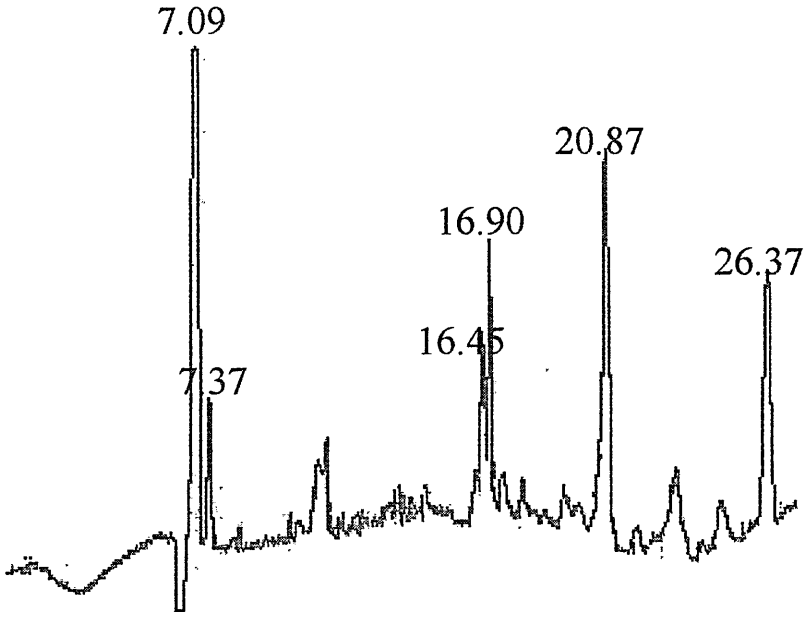


SAMPLE 16 (1:7 Dilution)

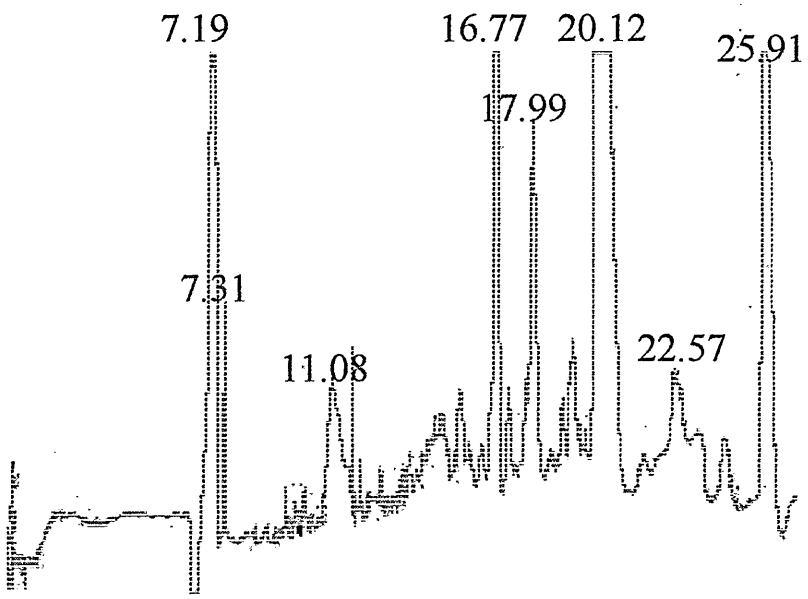
2yr Old - Hypotonia, hepatosplenmegaly Developing Mevalonic Aciduria



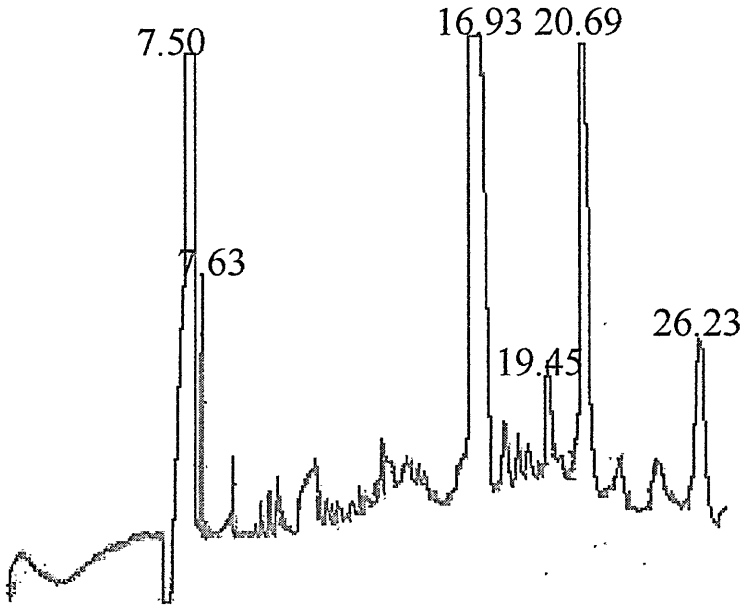
SAMPLE 18 (1:7 Dilution)
3yr Old - Seizured during febrile illness, dev delay, Valpruate metabolites



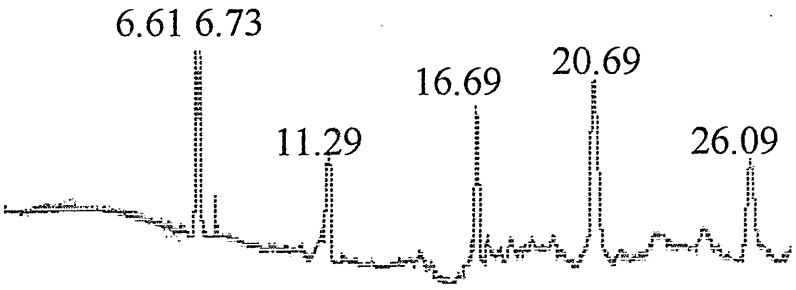
SAMPLE 21 (1:7 Dilution)
2yr Old - Afebrile Fits



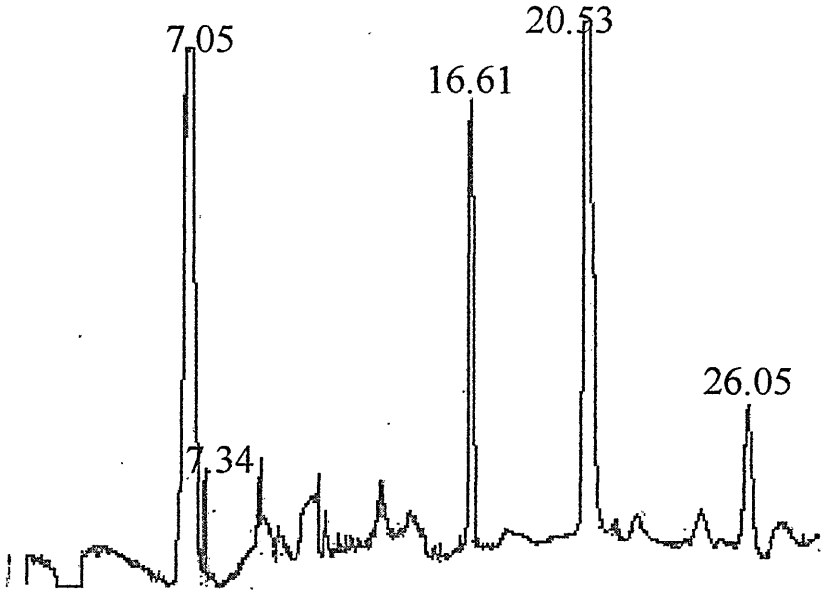
SAMPLE 25 (1:7 Dilution)
8yr Old Male - Adoption Screen - NORMAL



SAMPLE 26 (1:7 Dilution)
8mth Old Female - Seizures



SAMPLE 27 (1:7 Dilution)
3yr Old Female - Failure to Thrive



Appendix C - Course and Conferences Attended

10th-11th July 1995

Research and Development Topics

University of Hull

15th March 1995

HPLC Troubleshooting and Tips

Hewlett-Packard, Stockport

22nd March 1995

GC-MS for the Chromatographer

Hewlett-Packard, Stockport

9th October 1995

SPE Method Development Seminar

RSC, London

24th January 1996

Advances and Applications in Capillary Electrophoresis and Related Techniques

University of Sunderland

5th March 1996

1st Annual Young Environmental Chemists Meeting

Leicester DeMontfort University

July 1996

Research and Development Topics - 1996

Nottingham Trent University

23rd September 1996

Symposium of Environmental Analysis

University of Lancaster

18th March 1997

2nd Annual Young Environmental Chemists Meeting

Leicester DeMontfort University

18th - 22nd May 1997

19th International Symposium on Capillary Chromatography and Electrophoresis

Wintergreen, VA

Appendix D - Publications

Papers

The Use of Capillary Zone Electrophoresis to Determine Lactate, Pyruvate and Other Organic acids in Neonatal Urine.

M. Willets, P. Clarkson, M. Cooke

Chromatographia, 43(11/12), (**1996**), 671-674,

The Identification of an Unusual Volatile Component in Processed Tobacco by Gas Chromatography with Mass Spectrometry and Atomic Emission Detection

Paul J Clarkson and M. Cooke

Analytica Chimica Acta, 335, (**1996**), 253-259

Enhanced Recovery of Chlorophenols from Surface Waters Using Polymer Based Extraction Cartridges

Ricarda Schilling, Paul J Clarkson, and Michael Cooke

Fresenius J. Anal. Chem., 360, (**1998**), 90-94

Posters

The Selectivity of Functionalised Silica Solid Phase Extraction Cartridges in Air Sampling

Paul J Clarkson, Malcolm R Clench, Michael Cooke

19th Intern. Symposium on Capillary Chromatography and Electrophoresis,

18/22 May 1997

Wintergreen, VA, USA,

The Use of F-685nm Atomic Emission Spectroscopy with GC for the Analysis of Fluorine Containing Derivatives of Carbonyls in Environmental Samples

Paul J Clarkson, Christof C. E. Simons, M.R.Clench and M. Cooke

19th Intern. Symposium on Capillary Chromatography and Electrophoresis,

18/22 May 1997

Wintergreen, VA, USA,

The Use of Styrene-Divinyl Benzene Copolymer Based Solid Phase Extraction Cartridges for General Purpose Air Sampling

Paul J Clarkson, Malcolm R Clench, Michael Cooke

19th Intern. Symposium on Capillary Chromatography and Electrophoresis,

18/22 May 1997

Wintergreen, VA, USA,

Modifications of the Extraction Procedure for Chlorophenols in Water for Use with Polymer Based Extraction Cartridges

Ricarda Schilling, Paul J Clarkson, and Michael Cooke

19th Intern. Symposium on Capillary Chromatography and Electrophoresis,

18/22 May 1997

Wintergreen, VA, USA,

Air Quality and Fingerprints

Paul J Clarkson, M.R.Clench and M. Cooke

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The Determination of the Structure of Tobacco Additives using Thermal Desorption Gas Chromatography- Mass Spectrometry and Direct Headspace Gas Chromatography-Atomic Emission Spectroscopy.

Paul J. Clarkson and M. Cooke

R&D Topics,

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Appendix E - COSHH

Introduction

In accordance with the COSHH regulations, risk assessments were carried out for the compounds that were used in the experiments described within this thesis. Table Appendix E - 1 and Table Appendix E -2, show the health and safety criteria that were used for the assessments.

Table Appendix E -1 - Risk Phrases

R1 Explosive when dry.
R2 Risk of explosion by shock, friction, fire or other source of ignition.
R3 Extreme risk of explosion by shock, friction, fire or other sources of ignition.
R4 Forms very sensitive explosive metallic compounds.
R5 Heating may cause an explosion.
R6 Explosive with or without contact with air.
R7 May cause fire.
R8 Contact with combustible material may cause fire.
R9 Explosive when mixed with combustible material.
R10 Flammable.
R11 Highly flammable.
R12 Extremely flammable.
R13 [no number 13!]
R14 Reacts violently with water.
R15 Contact with water liberates extremely flammable gases.
R16 Explosive when mixed with oxidising substances.
R17 Spontaneously flammable in air.
R18 In use, may form inflammable/explosive vapour-air mixture.
R19 May form explosive peroxides.
R20 Harmful by inhalation.
R21 Harmful in contact with skin.
R22 Harmful if swallowed.
R23 Toxic by inhalation.
R24 Toxic in contact with skin.
R25 Toxic if swallowed.

R26 Very toxic by inhalation.

R27 Very toxic in contact with skin.

R28 Very toxic if swallowed.

R29 Contact with water liberates toxic gas.

R30 Can become highly flammable in use.

R31 Contact with acids liberates toxic gas.

R32 Contact with acid liberates very toxic gas.

R33 Danger of cumulative effects.

R34 Causes burns.

R35 Causes severe burns.

R36 Irritating to eyes.

R37 Irritating to respiratory system.

R38 Irritating to skin.

R39 Danger of very serious irreversible effects.

R40 Possible risk of irreversible effects.

R41 Risk of serious damage to the eyes.

R42 May cause sensitisation by inhalation.

R43 May cause sensitisation by skin contact.

R44 Risk of explosion if heated under confinement.

R45 May cause cancer.

R46 May cause heritable genetic damage.

R47 - R48 Danger of serious damage to health by prolonged exposure.

R49 May cause cancer by inhalation.

R50 Very toxic to aquatic organisms.

R51 Toxic to aquatic organisms.

R52 Harmful to aquatic organisms.

R53 May cause long-term adverse effects in the aquatic environment.

R54 Toxic to flora.

R55 Toxic to fauna.

R56 Toxic to soil organisms.

R57 Toxic to bees.

R58 May cause long-term adverse effects in the environment.

R59 Dangerous to the ozone layer.

R60 May impair fertility.

R61 May cause harm to the unborn child.

R62 Risk of impaired fertility.

R63 Possible risk of harm to the unborn child.

R64 May cause harm to breastfed babies

Table Appendix E -2 - Safety

S1 Keep locked up.

S2 Keep out of the reach of children.

S3 Keep in a cool place.

S4 Keep away from living quarters.

S5 Keep contents under ... (there follows the name of a liquid).

S6 Keep under ... (there follows the name of an inert gas).

S7 Keep container tightly closed.

S8 Keep container dry.

S9 Keep container in a well-ventilated place.

S12 Do not keep the container sealed.

S13 Keep away from food, drink and animal foodstuffs.

S14 Keep away from ... (a list of incompatible materials will follow).

S15 Keep away from heat.

S16 Keep away from sources of ignition.

S17 Keep away from combustible material.

S18 Handle and open container with care.

S20 When using, do not eat or drink.

S21 When using do not smoke.

S22 Do not breathe dust.

S23 Do not breathe vapour.

S24 Avoid contact with skin.

S25 Avoid contact with eyes.

S26 In case of contact with eyes, rinse immediately with plenty of water and seek medical advice.

S27 Take off immediately all contaminated clothing.

S28 After contact with skin, wash immediately with plenty of soap-suds.

S29 Do not empty into drains.

S30 Never add water to this product.

S33 Take precautionary measures against static discharges.

S35 This material and its container must be disposed of in a safe way.

S36 Wear suitable protective clothing.

S37 Wear suitable gloves.

S38 In case of insufficient ventilation, wear suitable respiratory equipment.

S39 Wear eye / face protection.

S40 To clean the floor and all objects contaminated by this material, use .... (there follows suitable cleaning material).

S41 In case of fire and / or explosion do not breathe fumes.

S42 During fumigation / spraying wear suitable respiratory equipment.

S43 In case of fire use ... (there follows the type of fire-fighting equipment to be used.)

S45 In case of accident or if you feel unwell, seek medical advice immediately (show the label whenever possible.)

S46 If swallowed, seek medical advice immediately and show this container or label.

S47 Keep at temperature not exceeding...

S48 To be kept wet with (there follows a material name).

S49 Keep only in the original container.

S50 Do not mix with ...

S51 Use only in well ventilated areas.

S52 Not recommended for interior use on large surface areas.

S53 Avoid exposure - obtain special instructions before use.

S56 Dispose of this material and its container at hazardous or special waste collection point.

S57 Use appropriate container to avoid environmental contamination.

S59 Refer to manufacturer / supplier for information on recovery / recycling.

S60 This material and its container must be disposed of as hazardous waste.

S61 Avoid release to the environment. Refer to special instructions / safety data sheets.

S62 If swallowed, do not induce vomiting; seek medical advice immediately and show this container or label.

COSHH Assessment

During the course of the project, many compounds were used as standards and markers. Due to the small quantities of each of the compounds used it has been decided to summarise the risk assessments for each of the compounds classes taking the most hazardous compound as the baseline. So by following the safety practices required for the most hazardous compounds used, and treating all compounds with care we should reduce any of the risks and hazards.

The following data, is a summary of the compounds used and the risk and hazards related to them. This data is shown in Table Appendix E -3.

Table Appendix E -3 - Assessment Data

Compound Name	COSSH Assessment
Carbonyl Compounds	**Formaldehyde**:
	Acetaldehyde: Harmful by inhalation, ingestion and through skin absorption. Some experiments with animals suggest that this substance may be anticipated to be a carcinogen. Contact with skin or eyes may cause severe irritation or burns.
	Butaldehyde: Harmful if swallowed, inhaled or absorbed through skin. Extremely destructive of mucous membranes, eyes and skin. Stench! Possible sensitiser. Corrosive - causes burns. High exposure may cause a build-up of fluid in the lungs (pulmonary oedema), a medical emergency.
	Risk: R11, R20/21/22, R35, R36/37/38, R41, R42/43, R45 **Safety**: S25, S36, S37, S51
Organic Acids	**Acetic Acid**: This material is strongly corrosive and causes serious burns. No evidence of carcinogenic, mutagenc or teratogenic effects.
	Risk: R21/22/23, R35, R41 **Safety**: S25, S36, S37, S51

n-Aliphatic Compounds	**n-Pentane**
	Low toxicity, Mild Irritant, Narcotic in High Doses, Sore throat, Shortness of Breath, Abdominal pain. Highly Inflammable
	Risk: R11,
	Safety: S2, S9, S16, S29, S33
Dichloromethane	Highly toxic, Moderate Irritant, Possible Systemic, Possible Long Term Effects, Animal Carcinogen.
	Nausea, Abdominal Pain, Burning and Redness of Skin, May Cause Pain, Redness and Watering of Eyes, May cause headaches, dizziness and Unsteadiness.
	Risk: R34, R38, R40, R47-48
	Safety: S2, S23, S24/25, S36/37
Methanol	Highly toxic, Mild Irritant, Possible Systemic, Possible Long Term Effects.
	May cause dizziness, abdominal pain, diarrhoea, and headache.
	May cause redness of skin. May be absorbed through skin.
	May cause redness of eyes. May affect optic nerve and retina.
	Headaches, cough and shortness of breath.
	Risk: R11, R23/25
	Safety: S(1/2), S7, S16, S24, S25
Acetonitrile	Highly Toxic, Moderate Irritant, Possible systemic effects.
	May be absorbed through the skin.
	Severe respiratory irritant.
	Cyanide effect, nausea, vomiting, shortness of breath.
	Risks: R11, R23/24/25
	Safety: S(1/2), S16, S27, S45

1,4 Dichlorobenzene	Moderate Toxicity, Moderate Irritant, Possible Long Term Affects. Nausea, Vomiting, Abdominal Pain. Mild Skin Sensitiser, May be absorbed through the skin. May cause Pain, Redness and Watering of Eyes May cause Non-Specific Injury to Liver and Kidneys. **Risks:** R22, R36/38 **Safety:** S(2), S22, S24/25, S46
Sodium Tetraborate	Moderate Toxicity, Mild Irritant
Sodium Hydroxide	High Toxicity, Corrosive. **Risks:** R35 **Safety:** S(1/2), S16, S27, S35

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e Use of Capillary Zone Electrophoresis to Determine ctate, Pyruvate and Other Organic Acids in Neonatal Urine

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y Words

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determination of the organic acids oxalic, malonic, eic, succinic, pyruvic, lactic, 3-hydroxybutyric and uric was investigated using capillary zone electroresis. They were separated in a fused-silica capillary cm × 75 μm id) which was filled with 50 mM sodium aborate (pH 10) containing a cationic surfactant as electroosmotic flow modifier and Ca^{2+} in the buffer id separation of closely migrating peaks and imve peak shape. The developed method was successapplied to the determination of organic acids in e. The effect of passing samples through a C-18 solid se extraction cartridge was investigated briefly, to to simplify the sample prior to injection. Finally the eloped screening procedure was used to study a set rine samples some of which were obtained from dren with metabolic errors resulting in the excretion n abnormal organic acid profile. Discrimination be-en normal and abnormal samples was achieved. The lts were in good agreement with information ob-ed by a GC-MS study of the same urine samples.

roduction

ary organic acids are short-chain carboxylic acids are intermediates or ultimate products in the radative metabolic pathway of amino acids, fats and ohydrates [1]. The accumulation of particular or-c acids in blood and/or urine can be an indication of certain metabolic disorders. The determination of organic acids in urine has been used to diagnose numerous inborn errors of metabolism known as organic acidurias.

Over thirty organic acidurias have now been recognised which have a collective incidence of probably one to two per 10,000 live births [2]. These conditions can be life-threatening but may respond to dietary treatment or cofactor supplementation, providing fast, efficient diagnosis can be achieved.

The organic acid composition of urine is very complex with over 30 organic acids identified in neonates [3]. A comparison of the organic acids in the urine of adults and neonates [4] has shown that neonatal urine may contain high levels of succinic, fumaric, 2-ketoglutaric and 3-hydroxy-3-methylglutaric acids. These are only present in small amounts in adult urine. Conversely, adults show large amounts of hippuric acid, which is a relatively minor constituent of neonatal urine. Studies by Chalmers and co-workers [5–7] have shown that the variations in excretion pattern are large. Extreme dietary alterations showed only small changes in the pattern, and overall their data suggested that variations in excretion depend mainly on the metabolism of the individual rather than dietary input.

The current method of choice for analysing organic acids in urine is gas chromatography/mass spectrometry (GC/MS) [1] This method usually involves a preparation step such as solvent extraction, or column chromatography to remove the organic acids from the aqueous phase. Derivatisation to form, for example, the trimethylsilyl derivative, is followed by separation and identification by capillary GC-MS.

High-performance liquid chromatography (HPLC) has also been employed [8] for the separation of organic acids in untreated urine by direct injection HPLC-positive ion thermospray (i.e. with mass spectrometric detection). Kajita and co-workers [9] have described a method of analysing organic acids in urine by HPLC-atmospheric pressure chemical ionisation mass spectrometry, (APCI-MS). Both these approaches are complex

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nd hence are unsuitable for screening large numbers of amples. Recently there have been several methods ublished in the literature that use CE for the analysis f organic acids in a variety of matrices. For example, öder and Bächmann [10] describe a method of deterining organic acids in rain water, and Lalljie [11] escribes a method of analysing organic acids in sugar efinery juices. However these methods use indirect UV etection which suffers from a lack of sensitivity due to he small change in the absorbance which occurs. In the etermination of organic acids by indirect UV, the aborbing electrolyte is usually an aromatic acid such as -hydroxybenzoate or phthalate [11, 12]. For this aplication the use of a phthalate buffer has been invesigated [13] but was rejected because it was not possible o obtain a baseline suitable for the determination of he trace amounts of the organic acids that are present n urine although this detection mode has proved aplicable elsewhere [14, 15] in methods based on HPLC.

method of analysing organic acids in urine by capilary electrophoresis that would be suitable for diagnosng problems such as organic acidurias could be exremely beneficial and would be particularly useful for creening large numbers of samples or for operation in routine laboratory environment. In this short comunication we describe such a procedure.

Experimental

Equipment

All electropherograms were generated using a Crystal CE 310 with a ATI UNICAM 4225 UV/VIS detector (ATI Unicam, Cambridge, UK) measuring at 196 nm. Fused silica capillaries (Composite Metal Services, Hallow, Worcs., UK) of 75 μm (i.d.), 375 μm (o.d.) of total length 70 cm were used. The detection window was 10 cm from the end of the column. The signal was recorded on a Spectra-Physics 4290 integrator (Spectra-Physics, UK). The sample was introduced onto the column using hydrostatic injection.

Chemicals

Lactate and pyruvate (Aldrich, Gillingham Dorset, UK) malonate, maleate and succinate (BDH, Poole, Dorset, UK) were obtained as the sodium salt. 3-Hydroxybutyric acid (Lancaster, Lancaster, UK) was obtained in liquid form. CIA-Pak OFM Anion-BT (Waters-Millipore, Milford, MA, USA) and sodium tetraborate (BDH, Poole, Dorset, UK) were used for the buffer. All solutions were prepared using Milli-Q water, and were stored at 4 °C prior to use.

Procedures

The fused silica capillary column was initially conditioned by rinsing through with 0.1 M NaOH for 30 min, and Milli-Q water for 10 min, before being flushed through with buffer solution for 20 min. Before each run the column was rinsed with 0.1 M NaOH for 20 s then with Milli-Q water for 30 s and then finally with buffer for 2 min. The buffer was prepared to the composition 50 mM Borax, 0.4 mM Ca^{2+}, and 1 mL of OFM per 50 mL of buffer solution. The pH was then adjusted to pH 10 using 0.1 M NaOH.

SPE (C_{18}/silica) (J T Baker, Milton Keynes, UK) cartridges were first washed with water, and then the sample was passed through under moderate vacuum and the resulting extract recovered and analysed.

Samples

Samples of urine were taken from seven children with the following conditions:

Sample 16:	2 yr old	– Hypotonia
Sample 18:	3 yr old	– Seizured during febrile illness
Sample 20:	2 yr old	– Profound metabolic acidosis and β-ketothiolase deficiency
Sample 21:	2 yr old	– Afebrile fits
Sample 25:	8 yr old	– Adoption screen – normal
Sample 26:	8 mth old	– Seizures
Sample 27:	3 yr old	– Failure to thrive

Normal urine samples were obtained from both adults, and children hospitalised for medically unrelated reasons.

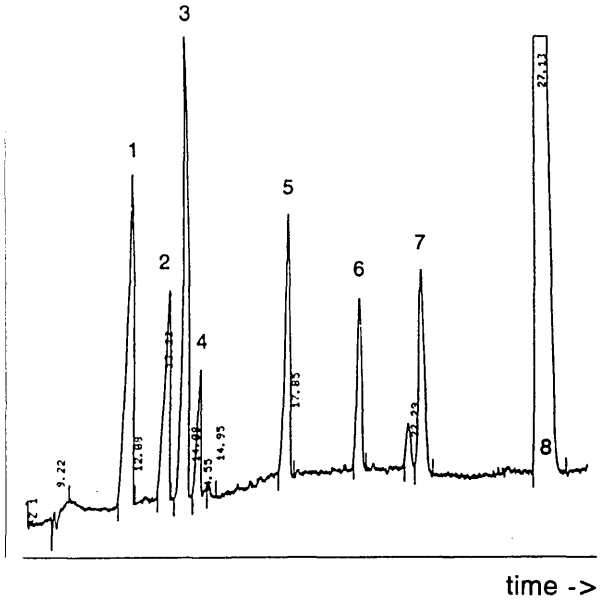
Results and Discussion

Separation Development

The instrument was configured with the detector situated at the anode end of the capillary. The simplest method of optimising the separation was to change the surface characteristics of the capillary and this was achieved by using an osmotic flow modifier in the buffer.

The osmotic flow modifier used was CIA-Pak Anion-BT which is a commercial product based on TTAB. Its effect on the separation of seven acids was investigated by keeping the borate concentration at 50 mM and the pH constant at 10.0 and a ratio of 1 mL to 50 mL of buffer was adopted.

The choice of detection wavelength was made by studying the UV spectra of a dilute standard of the organic acids and a diluted urine sample, over the range of 190 to 380 nm. The standard showed a maxima at 196 nm and the sample at 198 nm. Hence a detection wavelength of 196 nm was chosen. The choice of sodium tetraborate as the background electrolyte has several advantages. Tetraborate is a weak acid and has an electrophoretic mobility that is matched to the organic acids being investigated. Borate, as well as buffering the



re 1

tropherogram of a standard solution of seven organic acids. k identification: **1** = oxalic; **2** = malonic; **3** = maleic; **4** = succinic; pyruvic; **6** = lactic; **7** = 3-hydroxybutyric; **8** = hippuric.

tion at pH 10, is also UV transparent in the relevant ion of the spectrum.

instrument was operated in the constant current de allowing the voltage to fluctuate to keep the tropherograms more consistent. Migration times e remarkably constant with the largest variation ng associated with the shortest migration time 2 % RSD).

effect of pH was investigated by running a standard even organic acids at three different pHs (9.5, 10.0,) (the borate concentration was kept constant at mM, as was the OFM volume at 0.5 mL per 50 mL er). A pH of 10.0 was chosen as a reasonable com- mise between separation, runtime and signal-to- se ratio. Several workers [12, 19] have described the ition of calcium to the run buffer to aid the separa- of acids which have similar structures or electro- retic mobilities.

thought that addition of calcium operates by affect- the relative mobilities of the ions through the nge of their charge state due to complexation with Ca^{2+} ions. Hence 0.4 mM Ca^{2+} was added to the run fer, resulting in an improvement of peak width and metry.

summarise, therefore, the optimum conditions were a mM sodium tetraborate buffer, (pH 10), with 1 mL M per 50 mL buffer and 0.4 mM Ca^{2+} present, a ection wavelength of 196 nm and the current set at – μA. Under these conditions an eight acid standard fully separated (Figure 1).

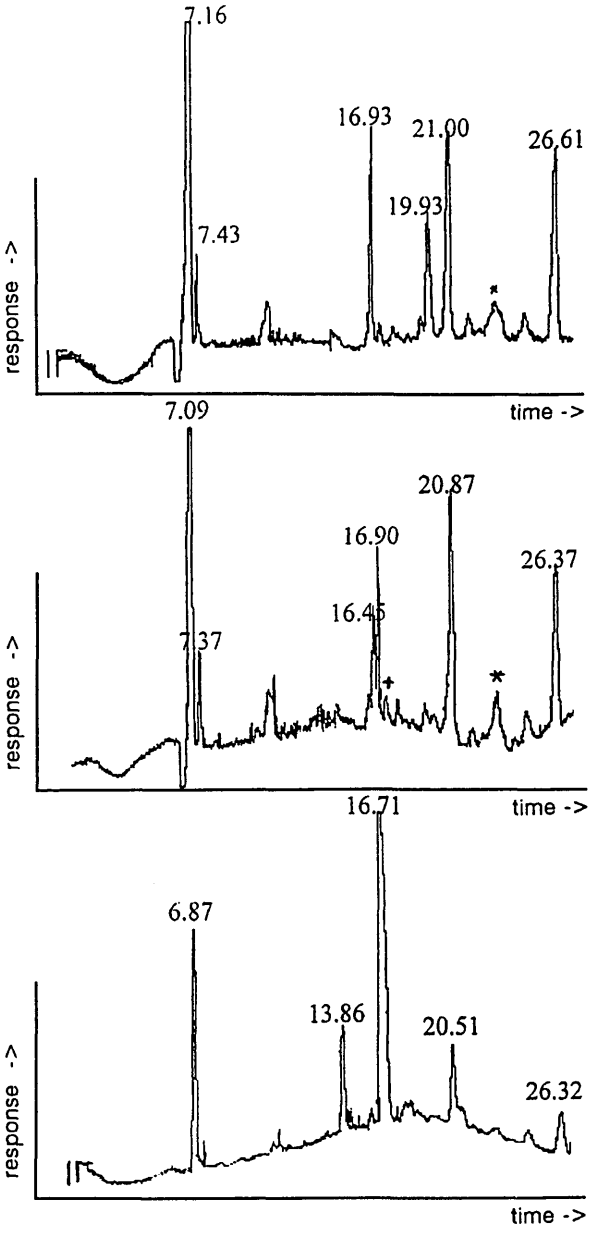


Figure 2

Upper trace: Urine sample of patient with mevalonic aciduria; middle trace: urine sample of patient suffering from seizures and delayed development; lower trace: urine sample of a patient suffering profound metabolic acidosis. All samples diluted 1:7 before analysis.

Application to Urine Samples

A range of urine samples from either patients or donors with normal urinary acid profiles or from patients with specific diagnoses (see Experimental Section) were studied. Typical results are shown in the three eletropherograms shown in Figure 2. The upper trace was obtained from a 2-year old who was diagnosed as developing mevalonic aciduria. Dominant acids are hippuric (t = 26.61), lactic (t = 21.00) and unknowns at t = 19.93 and 16.93. In this sample the lactate:hippurate area ratio

s approximately 1 whereas, in a normal sample, the hippurate concentration would be expected to dominate. It s possible that a low concentration of 3-hydroxyutyrate (*) is present in this sample.

ıe middle trace was obtained from the urine of a 3ear old suffering seizures and delayed development. actate and hippurate are present, pyruvate (+) and 3ydroxybutyrate (* identified by co-injection) are also resent. The peak at t = 19.93 is absent and several other omponents are present between t = 17.00 and t = 26.00. n this sample the lactate:hippurate area ratio is greater han 1, which is abnormal.

n the lower trace the unknown component at t = 16.71 ominates. Pyruvate is undetectable and the lactate:hippurate ratio approximates to 1. For comparison in a noral urine sample (not shown) the pyruvate:lactate was f the order of 1:10 and the hippurate response was aproximately five times that of lactate.

ıe reproducibility of migration times in these urine amples gave relative standard deviations ranging from .44 % to 1.82 %. We consider this level of reproucibility to be sufficient to avoid mis-identification if his method is to be used for the routine screening of rine samples.

ome samples studied were both complex and highly oncentrated. Dilution brings some simplification but he effect of passing the urine through a silica-based C_{18} loaded solid phase extraction (SPE) cartridge was briefy studied. Although some selective removal of nonionic components (and coloured components) was achieved selective retention of certain organic acids (particularly lactate) was also apparent. As the simplification achieved did not compensate for the selective removal of some acids this procedure was considered inappropriate in a screening method and hence dilution only is recommended.

Conclusions

The optimum conditions for separation of the eight organic acid standards available (oxalic, malonic, maleic, succinic, pyruvic, lactic, 3-hydroxybutyric and hippuric) were found to be: sodium tetraborate (pH 10), 1 mL CIA PAK Anion-BT 50 mM electroosmotic flow modifier per 50 mL buffer and 0.4 mM Ca^{2+} with direct UV detection at 196 nm. The addition of Ca^{2+} was found to improve resolution and make the peaks sharper and more symmetrical. Adjusting the run buffer to pH 10 was found to be a good compromise between the better quality baseline but poor separation at pH 9.5 and the better separation but poorer baseline at pH 10.8.

In the analysis of the urine samples the major peaks identified were lactate, and hippurate but only one contained elevated pyruvate. Several samples contained low levels of pyruvate and 3-hydroxybutyrate. In addition, individual abnormal samples contain unidentified components which behave as anions and are thus likely to be other organic acids. As it is only the relative intensities of the peaks and the profile of the organic acids present that are of interest diagnostically the concentration of the sample is not very important. Hence sample dilution can be used as appropriate to reduce the need for instrumental changes during routine use. Overall this method shows the promise of being a possible routine method of monitoring organic acids in urine.

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The identification of an unusual volatile component in processed tobacco by gas chromatography with mass spectrometry and atomic emission detection

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Abstract

Three types of tobacco products have been analysed for their volatile components which constitute the aroma of the product. Automatic thermal desorption gas chromatography–mass spectrometry (GC–MS) and direct headspace sampling gas chromatography–atomic emission detection (GC–AED) have been used. One product was found to contain three unusual volatile components which were not present in the other two. By combining information from both mass spectrometric and atomic emission detection (AED), elemental composition and partial molecular structures were obtained. Final identification was achieved by comparing, both chromatographically and spectroscopically, with an authentic sample. The three components were isomers of dipropyleneglycol methyl ether and were present in the product in the same ratio as in the authentic sample. Direct headspace sampling offered several advantages over the thermal desorption approach.

Keywords: Aroma analysis; Gas chromatography; Mass spectrometry; Atomic emission spectrometry; Headspace sampling

1. Introduction

Over the past twenty years gas chromatography with mass spectrometric detection (GC–MS) has become the main analytical tool for the determination of the structure and elemental composition of the components of complex mixtures. With the advancement of computer technology, libraries of compounds may be installed with most instruments, thus promoting unambiguous identification of the compounds present in many, but not all, cases. The identification of compounds that are similar in structure and composition can sometimes be difficult when GC–MS alone is used. This is particularly the case when isomers are present. In such cases a complementary method of identification is needed. The comparison and correlation of data from mass spectrometry and other detection systems often gives information which confirms the presence of a certain compound. Conventional gas chromatographic detectors such as the nitrogen specific or electron capture detector usually give selective data about composition and seldom provide the definitive data required for identification of the compounds under investigation. Thus the electron capture detector is selective

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for electrophilic compounds and hence respond to halogens as well as nitro-groups and cannot distinguish between these. Element specific detectors that can give a positive identification of the elements present are now available. Used in combination with GC–MS, however, these detectors have applications in many fields such as pharmaceuticals [1], petrochemicals [2] and environmental analysis [3,4]. The use of GC–MS with complementary detection techniques has been employed in the identification of components in foodstuffs [5–8].

With the emergence of a commercially available atomic emission detector (AED) for gas chromatography in 1990 the ability to provide confirmatory elemental information on a compound has been utilised particularly in the field of environmental analysis [9]. The study of organometallic compounds in environmental samples, especially organotin compounds, has been widely reported [11–13].

The study of complex mixtures of compounds in the gas phase presents particular problems of sampling. Conventionally a trapping mechanism involving an adsorption cartridge is used to obtain the sample which is then transferred after thermal desorption into the analytical system [14]. Such a procedure can often be selective both in what is trapped and what is recovered. An alternative is to use a direct headspace sampling method utilising a large volume (ca 1 ml) gas tight syringe combined with an injection device capable of receiving such a volume of gas and then focusing it into a suitable capillary column to maintain chromatographic efficiency.

The combination of GC–MS with GC–AED coupled with either thermal desorption or direct headspace sampling to facilitate the positive identification of three components of a complex mixture is reported herein.

2. Experimental

Three commercially available cigarette brands were used for this study. The samples were kept fresh by storing in closed containers to minimise loss of volatile (aroma) components.

2.1. Sampling by thermal desorption

The tobacco from five cigarettes was placed in a 500 ml wide-mouth glass bottle. Into the bottle were suspended three, pre-cleaned, thermal desorption tubes each packed with 0.16 g of Tenax (60–80 mesh) and the top replaced on the bottle. These tubes were exposed to the tobacco aromas for seven days. Hence the headspace was sampled passively.

Thermal desorption (TD) was achieved via a Perkin–Elmer ATD-50 thermal desorption unit and sample vapours were transferred directly to a Hewlett–Packard 5890 gas chromatograph via a heated, deactivated, fused silica transfer line held at 260°C. Separation was performed on a 5% phenyl: 95% methyl silicone gum column (30 m × 0.32 mm i.d., d_f=0.25 μm) using a temperature programme as follows: initial temperature, 35°C; initial time, 2 min; ramp rate 15°C to 210°C then 25°C to 280°C.

Detection was either by a Trio-1 mass spectrometer (VG Masslab, Wythenshaw, UK) or by mass selective detection (Hewlett–Packard, Model No 5971). Total ion chromatograms were obtained for each of the samples studied.

2.2. Direct headspace (DHS) analysis

Into a 25 ml septum-capped vial was placed the tobacco from two cigarettes and the samples allowed to equilibrate at room temperature. Using a gas tight syringe, 1 ml of the headspace vapour was removed through the septum. A compensating 1 ml of dry nitrogen was injected. This volume of sample was injected at a steady rate through an Optic injection system (AI-Cambridge, UK) interfaced to a Hewlett–Packard 5890 II gas chromatograph. Separation was achieved as for thermal desorption studies. Cryofocusing was found to be unnecessary. The gas chromatograph was interfaced to a Hewlett–Packard Model 5921A microwave induced plasma-atomic emission detector (MIP-AED) which was used to monitor the response for carbon (193 nm), nitrogen (174 nm), oxygen (777 nm) and sulphur (181 nm). Chromatograms were obtained for each of the three tobaccos used and for a spiked sample using the authentic sample.

3. Results and discussions

The results from the thermal desorption GC–MS analysis of the three tobacco aromas are displayed in Fig. 1. Each aroma profile is relatively complex yet there are several areas of similarity between them. For example all reveal the presence of nicotine (t_R=20.50±0.05) which is sufficiently volatile to suffer slow loss by evaporation from the product once the packaging had been opened. Each product also contains one or more highly polar compounds (note the poor peak shape) which elute after some 8–10 min. These are glycols (ethylene and propylene

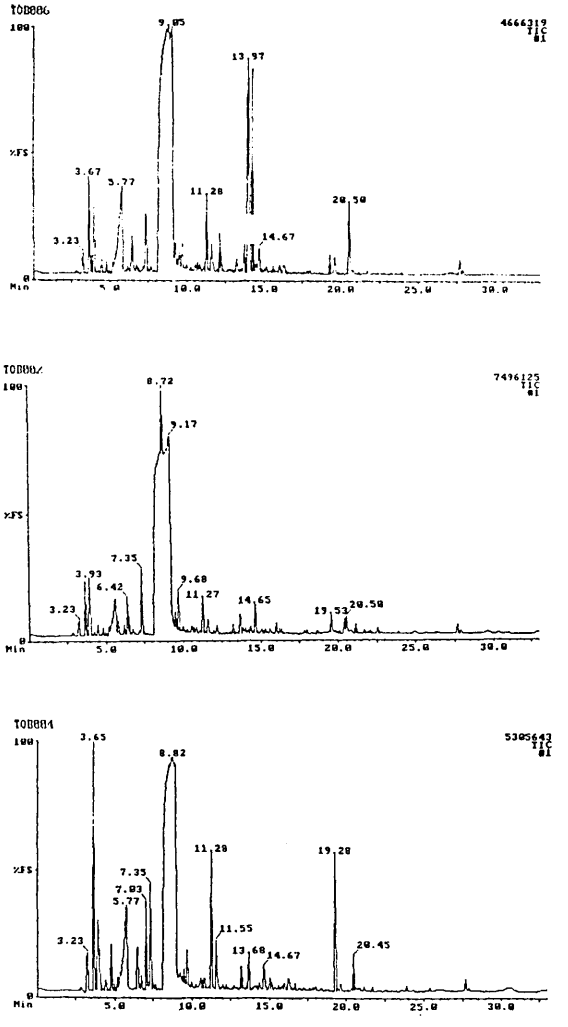

Fig. 1. Total ion chromatograms of the three tobacco samples studied. (A=upper trace, B=centre trace, C=lower trace).

are commonly used) and are added to the tobacco to conserve moisture and hence preserve texture. An incidental property of these components may be to reduce evaporative losses by acting as a "keeper" solvent. Some components are common to all three samples. For example ethanol (t_R=3.65±0.05 min) is present in all three as are a C_5 aldehyde (t_R=7.35± 0.05 min), a C_3 hydroxyketone (t_R=6.43±0.05 min) and a C_3 ester (t_R=11.28±0.05 min). One sample contains a significant amount of a compound eluting at ca t_R=19.28 min. Mass spectral data suggest that this is an anisole *para*-substituted with a C_3 fragment (most probably isopropyl). Sufficient commonality exists between the three chromatograms to suggest an overall similarity of major flavour components.

Given that the sampling procedure was standardised with respect to the amount (weight) of tobacco used, the time of exposure to the sampling tubes and the temperature of the sampling containers, the intensity of the response for each sample can be taken to approximate to the amount of volatile material desorbing from each type of tobacco product. Hence it would appear that whilst all three products release a wide range of similar volatile compounds the amount of these compounds desorbed is approximately the same from types A and B but is less for type C.

The major difference occurs with cigarette A at ca t_R=14 min (Fig. 1). Three major peaks occur which are not present in the other two products. This is clearly shown in Fig. 2 in the upper trace (A) at $t_R \cong 10.5$ min. (Fig. 2 represents an expansion of the central part of the chromatograms in Fig. 1. The temperature programme was varied to highlight these three components. Hence the change in retention time.) The chromatograms for (B) and (C) do not show these components. It could be argued that two of these components (t_R=10.35 and t_R=10.48 min respectively) are present in both A and C (but with a slight retention shift) and that it is the component at t_R=10.87 min which is the only major difference. For the reasons discussed below this is not thought to be the case.

The mass spectra of each of these three components (Fig. 3) were essentially the same and rather simple giving no reliable indication of identity. No clear parent ion was observed and each component

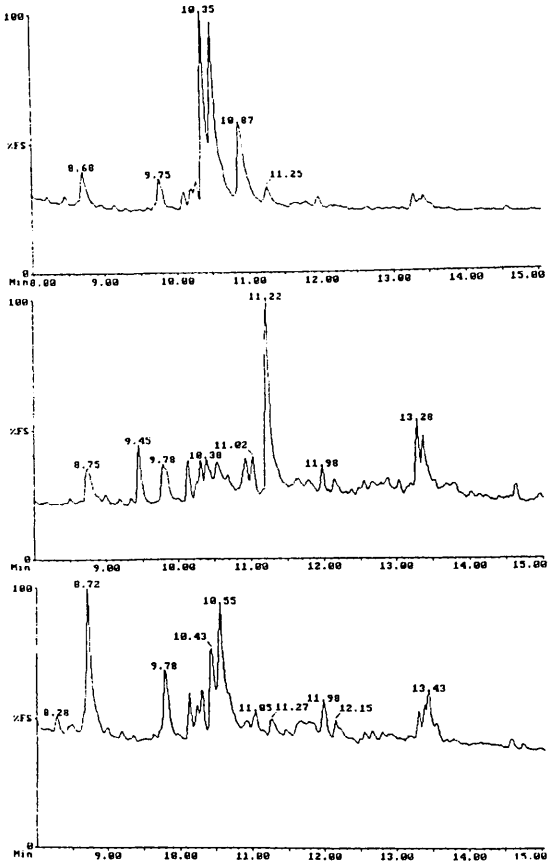

Fig. 2. Expansion of the region of the chromatogram from 8–15 min showing the three major consituents of sample A at t_R=10.35, 10.48 and 10.87 min.

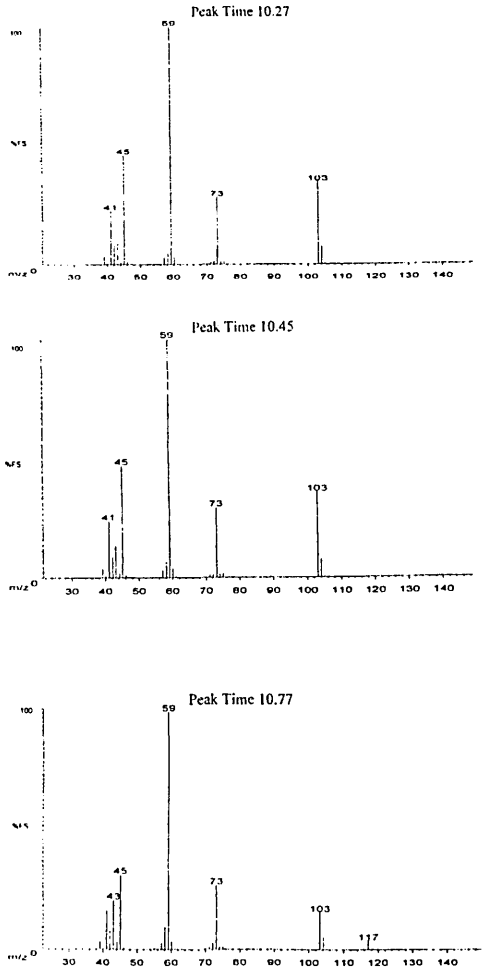

Fig. 3. Mass spectra of the three components present in sample A.

had a base peak at M^+/z=59. Library search routines suggested that the compounds possibly contained a tertiary alcohol group and/or an ethoxy moiety. A minimum of 7 carbon atoms and 1 oxygen atom was indicated by this data. The fragment ions of masses M^+/z 45, 59 and 73 are characteristic for alcohols and ethers and indicate that partial structures such as those shown in Fig. 4 are present. However, no unambiguous identification was possible using the mass spectral data only.

An alternative technique for deriving structural information about unknown compounds is AED linked to high resolution capillary gas chromatography [9–13]. In atomic emission spectroscopy, atoms are excited by an external energy source and, upon returning to the ground state, emit energy at

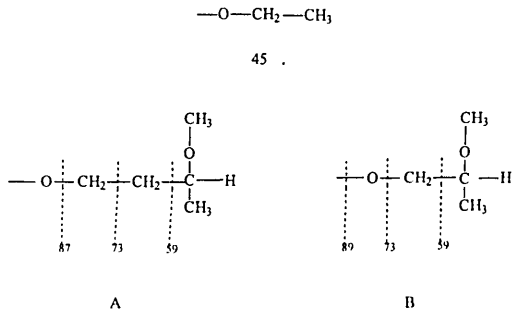

Fig. 4. Partial structures present in the unknown components. '*' denotes an optically active centre.

wavelengths characteristic of the element involved. Coupling of a capillary column to a MIP cavity permits components which elute from the column to be atomised and to emit characteristic line spectra. Analysis of this data gives information about the elemental composition of the eluate and facilities calculations of empirical formulae.

The headspace vapours from product A were subjected to analysis by GC-MIP-AED. Appropriate emission lines for carbon (193 nm), oxygen (777 nm), nitrogen (174 nm), sulphur (181 nm) were monitored. Although the GC–MS data suggested that only carbon, hydrogen and oxygen were present, with the AED it was possible to confirm that nitrogen and sulphur were absent from the compounds and that carbon, hydrogen and oxygen only were present. The emission data from the AED were processed by the ChemStation software to give chromatograms for each element being investigated. From this data it is theoretically possible to determine the approximate ratios of carbon, oxygen and hydrogen and thus calculate the empirical formula for an individual compound within the mixture. The poor oxygen channel response precluded this being achieved on the desorbed headspace sample.

From the information available the three components of interest were tentatively identified as dipropylene glycol methyl ethers, and an authentic sample was obtained. A sample of the headspace vapours from product A was chromatographed using GC-MIP-AED and the carbon and oxygen channels monitored (Fig. 5(A)).

Subsequently, the sample of dipropylene glycol methyl ether was spiked onto the tobacco, allowed to equilibrate, sampled and the headspace analysed to give the chromatogram shown in Fig. 5(B). Clearly the responses are virtually identical. The oxygen response for the spiked sample matches that for the carbon channel, albeit with a much inferior signal to noise ratio. The relative responses for carbon and oxygen are such that the oxygen response is some two orders of magnitude lower than that for carbon. Hence the oxygen response for the unspiked samples is too low to detect. To confirm the identification, the mass spectra of the authentic sample were obtained and these are shown in Fig. 6. Comparison with the data in Fig. 3 reveals a strong similarity.

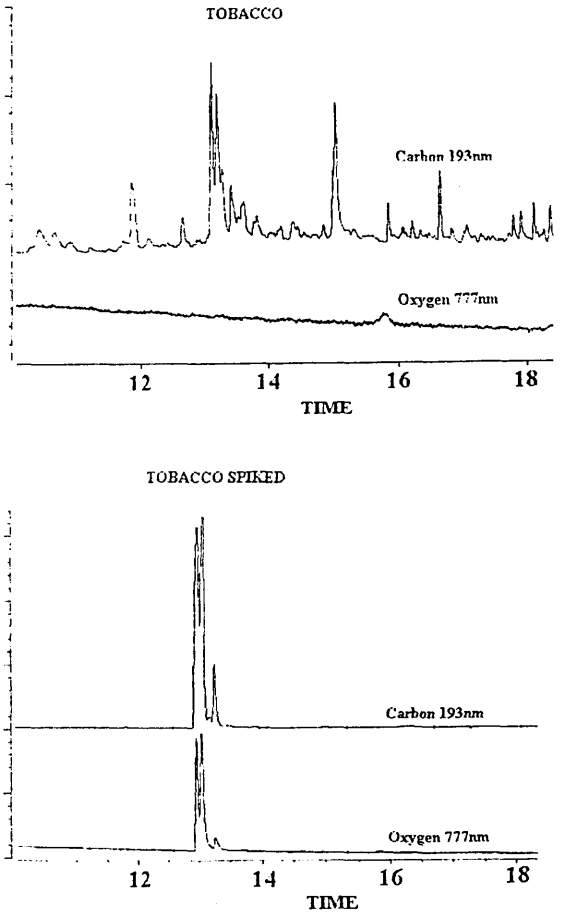

Fig. 5. Comparison of headspace vapours of sample A, and sample A spiked with propylene glycol methyl ether using atomic emission detection for carbon and oxygen.

4. Conclusion

The identification of unknown components of complex mixtures is often confounded by various factors such as poor matching with mass spectral library data, isomerisation and the absence of a parent ion. All three factors were observed for the three components found to be present in only one of the three tobacco products studied. By combining mass spectral information with data obtained from atomic emission however, unambiguous identification can be achieved. Mass fragmentograms provide evidence of the various sub-components present in the molecule whereas AED can yield evidence about the type and

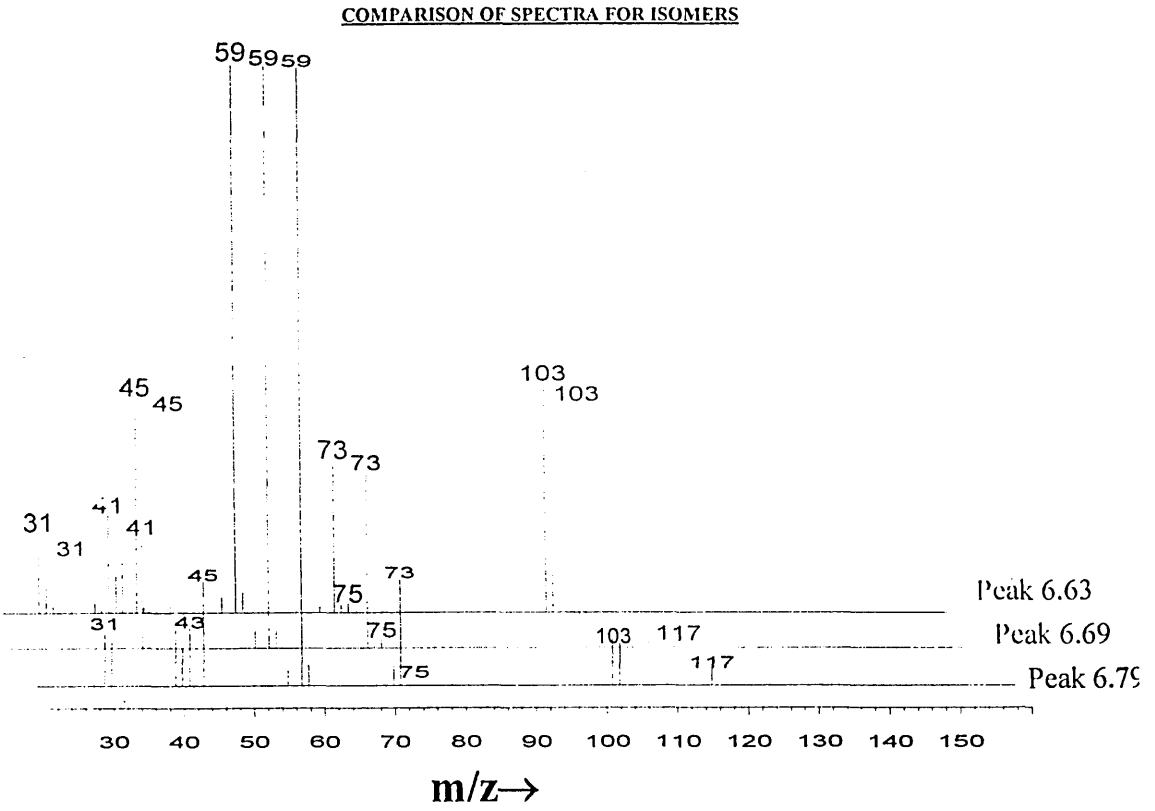

Fig. 6. Mass spectra of the three major components of a mixture of propylene glycol methyl ether for comparison with Fig. 3.

number of atoms present or absent. The final identification was thus of an isomeric mixture of three dipropyleneglycol methyl ethers.

The use of a multi-purpose injector system to facilitate the direct injection of ca 1 ml of headspace reduces sampling complexity and sampling time to a minimum and avoids the incomplete recovery of adsorbed species sometimes experienced with automatic thermal desorption (ATD) sample introduction techniques. Hence the results using direct headspace sampling (DHS)-GC-AED were obtained with a minimum of sampling time, and with increased sensitivity compared with ATD-GC-MS. A further disadvantage of the use of ATD-GC-MS is the relatively long sampling (and sampling device preparation) time which use of this technique necessitates.

The origin of the three components is unknown. However this ether is a commonly used industrial solvent and the most likely source therefore is the product packaging material from whence it has migrated to the product itself.

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