Odour Standards, Measurement and Characterisation

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Executive Summary

This report summarises the work that has been carried out on the measurement and characterisation of odorous species as part of the Valid Analytical Measurement (VAM) Programme's Odour and Indoor Air Project. The three main areas of research were (1) the development of gaseous odour standards to meet industrial requirements for odour monitoring; (2) an investigation of the validity and feasibility of using inelastic electron tunnelling spectroscopy (IETS) as an objective method for characterising odour; and (3) quantitative experimental studies to determine the limits of currently available techniques in measuring common odorous gases at ambient levels.

The principal deliverables and conclusions from the project are summarised below

- Traceable gas standards have been prepared to provide reference artefacts for the measurement of the main classes of odorous species, as well as targeting a number of specific industrial and environmental monitoring applications.

- The study into the relationship between IETS and odour revealed strong evidence that spectral features alone do not provide a good guide to the odour character of a molecule, though they may form part of a wider picture which includes the chemical environment of the receptors and the brain's processing of the signals. The complexity of the problem, together with the technical difficulty of single molecule spectroscopy, therefore make the prospect of an instrument based on these principles quite remote.

- Strong links have been made with UK and European users and manufacturers of "electronic noses" (arrays of sensors which use pattern recognition to match one volatile mixture with another), to the stage where NPL has a leading role in the formulation of an EC co-funded project on electronic nose standardisation.

- The experimental work demonstrated several alternative approaches which can be used to quantify the concentration of odorous species at ambient levels, and their areas of applicability. Gas chromatography with sulphur chemiluminescence detection gave good results for sulphur compounds such as hydrogen sulphide, carbonyl sulphide and thiols, which are common causes of complaints in industrial and agricultural areas. Gas chromatography with mass spectrometry provides a very versatile means of identifying unknown species, and quantifying a wide range of species down to parts-per-billion concentration levels.

CONTENTS

1 INTRODUCTION

This Report has been prepared for the National Measurement System Policy Unit of the Department of Trade and Industry as part of the Valid Analytical Measurement (VAM) Programme's Odour and Indoor Air Project (Project 1.4). The aim of this Report is to summarise the work that has taken place within this project on the measurement and characterisation of odorous species. The relevant milestones of the project are listed in the following table.

Table 1.1. Milestones of VAM Project 1.4 Related to Odour Measurement

Milestone	Definition
1.4.1	Complete report, taking account of requirements of UK and European standardisation and regulatory bodies, on the highest priority requirements for odour measurements.
1.4.2	Complete review and report on the availability of electron-tunnelling spectra of high priority odorous compounds.
1.4.4	Complete the preparation and validation of primary and traceable secondary binary calibration standards for at least four species required for calibrations in the chemical and aircraft industries.
1.4.5	Complete the preparation and validation of at least two sets of primary and traceable secondary multi-component standards for calibration of odour measurements
1.4.7	Define requirements for standardisation and traceability for multi-sensor (electronic nose) techniques through discussions with UK and European organisations, and participate in relevant activities of the European NOSE network.
1.4.8	Complete technical protocol to cover valid field sampling and measurements of odorous species
1.4.9	Complete experimental work to evaluate the capabilities of methods for the identification and quantification of odorous species including electron tunnelling spectroscopy and GC/MS
1.4.10	Complete technical report on the application of electron spectroscopy and related techniques to odour measurements

2 GENERAL BACKGROUND

2.1 DEFINITION OF ODOUR

Smell is the least well understood of our senses, and it should be emphasised that odour is defined on a subjective rather than objective basis. The ISO definition of odour [1] is:

'the organoleptic attribute perceptible by the olfactory organ on sniffing certain volatile substances.'

The attribute of a substance that makes it perceptible to the human nose is not yet, and perhaps cannot be, defined in terms of simple physico-chemical properties of the molecules concerned. For the time being, therefore, any true assessment of odour depends ultimately on the use of people and their subjective olfactory response.

2.2 THE DISTINCTION BETWEEN THE CONCENTRATION AND CHARACTER OF AN ODOUR

Even without any understanding of the olfactory mechanism, a quantitative measurement of the concentration or strength of an odour can be provided by the technique known as olfactometry. The current standard method of odour intensity measurement, as defined by CEN TC264 / WG2 'Odours', involves a panel of 'odour experts' being exposed to increasing dilution of the sample gas until the odour can no longer be detected. This is described in more detail in Section 4.2, and is purely concerned with the detectability of an odour by a "standard" human nose with no regard to the character or description of the odour. It is the concentration of odour which is most relevant in the area of complaints about industrial sources, and hence regulation.

In general, the character of an odour is at present defined on an ad-hoc basis, with different scales being employed for different particular uses. Standards do exist for the selection and training of people to identify specific odours, and individuals with a highly sensitive and highly trained olfactory sense are of great importance in various industries, notably perfumery. However, unlike in olfactometry, such experts are used in a qualitative rather than quantitative manner, to describe smells rather than to quantify them. The development of multi-sensor "electronic noses" represents an attempt to put such measurements on a more quantifiable basis (see Section 6)

2.3 INDUSTRIAL REQUIREMENTS FOR CALIBRATION AND STANDARDISATION

There a large number of industries which require on-line monitoring of odiferous species, where trace levels of certain compounds can have a significant detrimental effect on product quality. Examples include food production and packaging, the flavour and fragrance industry, the textile industry and the pharmaceutical industry.

There is also a strong requirement for odorous gas measurements for emission and environmental monitoring. This is particularly relevant to species with low odour thresholds, such as thiols, amines or ketones, which can have a significant malodour / nuisance impact at trace concentration levels. These levels cannot readily be measured in-situ, instead requiring sampling, pre-concentration then laboratory measurement.

3 REQUIREMENTS FOR AND REALISATION OF ODOROUS GAS STANDARDS

3.1 INDUSTRIAL PROCESSES THAT REQUIRE ODOUR MONITORING

The requirements for odour monitoring generally fall into two categories:

- Detection of malodorous species in product, plant emissions, or ambient air
- Monitoring of 'pleasant' odours in a product, a common requirement in the flavour and fragrance industries.

The work within this project has concentrated on the first of these areas, as this area of odour monitoring is a more general issue with wide applicability across a range of industrial sectors. Table 3.1 gives examples of the types of odorous species that can be produced during the manufacturing processes in different industries.

Table 3.1 - Examples of Odorous Pollutants in Various Industrial Areas

Industry	Sulphur Compounds	Nitrogen Compounds	Aldehydes and Ketones	Acids and alcohols	Hydrocarbons
Pharmaceutical	-	Acrylonitrile	-	Phenols Acrolene	Benzene Toluene
Insecticides	Hydrogen sulphide	-	-	Alcohols	Chlorobenzene Chlorine
Foundries		Ammonia Amines	Formaldehyde	Phenols	
Oil/asphalt plant	Thiols, Sulphides				Various
Aircraft industry			Formaldehyde Acetaldehyde Benzaldehyde		1-pentene 1-butene
Perfumes	-	-	Aldehydes Ketones	-	-
Textile	-	Amines	Formaldehyde	-	Solvents
Paper	Hydrogen sulphide Thiols Dimethylsulfide Dimethyldisulfide	-	-	-	-
Fish Processing	-	Trimethylamine Cadaverine Putrescine Ammonia	-	Fatty acids Butyric acid	-
Slaughter-houses	Hydrogen sulphide Thiols	Ammonia Amines	Aldehydes	Fatty acids	-
Pig farming	Hydrogen sulphide Thiols	Ammonia	Aldehydes	Fatty acids	
Manure Treatment	Disulfides	Trimethylamine	-	Propionic and Butyric acids	-

As indicated in the table above, the aircraft industry is one where odorous hydrocaron emissions are significant. Table 3.2 shows the range of volatile organic species that are emitted, and shows how the emitted concentrations level compare to the odour recognition thresholds for those species. All italicised entries are for species that are emitted at levels above their odour threshold. These data show that there are a number of species that could have a significant odour impact, with 1-pentene having the highest emission factor of 370 times the odour threshold.

Table 3.2 - Concentrations of Hydrocarbon Species Emitted by Model CFM-56 and TF-39 Jet Engines compared to the 100% Odour Recognition Thresholds for those Species

Species	Measured Engine Exhaust Concentrations		Odour Recognition Threshold (100%)	Odour factor for TF-39 emissions
	CFM-56 (ppm)	TF-39 (ppm)	(ppm)	(MEEC/ORT)
Ethylene	11.84	34.68	500	0.069
Propylene	2.66	9.90	50	0.20
Acetylene	2.15	9.16	1200	0.0076
1-butane	*0.76*	*2.80*	*0.07*	*40*
Methane	3.94	10.90	10000	0.0012
Formaldehyde	*9.30*	*15.20*	*1.0*	*15*
1-pentene	*0.20*	*0.74*	*0.002*	*370*
Propane	0.08	0.46	11000	4.2E-05
Ethane	0.41	1.35	1500	0.0009
1,3-butadiene	*0.53*	*1.57*	*1.5*	*1.05*
n-pentane	0.07	0.37	900	0.00041
n-hexane	0.17	1.26	245	0.0051
Benzene	0.33	1.30	300	0.0043
n-heptane	0.18	1.18	200	0.0059
Toluene	0.18	0.77	40	0.019
o-xylene	0.07	0.30	0.4	0.75
n-nonane	0.02	0.24	0.4	0.6
n-octane	0.07	0.55	2	0.28
Ethylbenzene	0.06	0.22	0.5	0.44
Styrene	*0.06*	*0.20*	*0.05*	*4*
Phenol	0.04	0.10	20	0.005
1-decane	*0.02*	*0.03*	*0.02*	*1.5*
Undecane	0.03	0.11	0.2	0.55
Naphthalene	*0.06*	*0.11*	*0.1*	*1.1*
Methyl styrene	*0.15*	*0.05*	*0.05*	*1*
Acetaldehyde	*1.10*	*4.60*	*0.3*	*15*
Acrolein	0.80	2.23	20	0.11
Propanol	0.36	0.83	45	0.018
Acetone	.022	0.50	300	0.0017
Crotonaldehyde	*0.35*	*0.98*	*0.2*	*4.9*
Benzaldehyde	*0.94*	*0.27*	*0.005*	*54*

Note : Emission values are for engines operating at idle power settings with JP-4 fuel.

Another major area of odour pollution is in the sewage and waste treatment industries. Table 3.3 lists the characteristics of some of the key odorous compounds found in these industries. It should be noted that these examples represent only a small sub-set of the total range of odorous species that can be present. As can be seen from the table, the majority of malodorous species are relatively short chain organic molecules with sulphur, nitrogen or oxygen functionality.

In all of the industries mentioned above there is an increasing requirement to measure emissions of odorous species in order to assess the occupational exposure and environmental impact of such emissions, and to monitor the effectiveness of any emission abatement techniques that are being employed. There is also a common requirement for the on-line monitoring of products for the presence of such malodorous species.

Table 3.3 - Characteristics of Odorous Compounds in Sewage / Waste Treatment Plants

Compound	Formula	Odour Characteristics	Odour Threshold (mg/ m^3 air)
Hydrogen Sulfide	H_2S	Rotten Egg	0.0001 -0.03
Methanethiol	CH_3SH	Cabbage, garlic	0.0005 -0.08
Ethanethiol	C_2H_5SH	Rotting Caggage	0.0001 -0.03
Dimethylsulfide	$(CH_3)_2S$	Rotting vegetables	0.0025 -0.65
Diethylsulfide	$(C_2H_5)_2S$	Ether	0.0045 -0.31
Dimethyl disulfide	$(CH_3)_2S_2$	Putrid	0.003 - 0.014
Ammonia	NH_3	Pungent, Irritating	0.5 –37
Methylamine	CH_3NH_2	Rotting fish	0.021
Ethylamine	$C_2H_5NH_2$	Pungent, ammoniacal	0.05 -0.83
Dimethylamine	$(CH_3)_2NH$	Rotting fish	0.047 -0.16
Indole	C_8H_7NH	Fecal, nauseating	0.0006
Scatole	C_9H_9NH	Fecal, nauseating	0.0008 -0.1
Cadaverine	$NH_2(CH_2)_5NH_2$	Rotting meat	
Acetic Acid	CH_3COOH	Vinegar	0.025 - 6.5
Butyric Acid	C_3H_7COOH	Rancid Butter	0.0004 – 3
Valeric Acid	C_4H_9COOH	Sweat, Perspiration	0.0008 - 1.3
Formaldehyde	HCHO	Acrid Suffocating	0.033-12
Acetaldehyde	CH_3CHO	Fruit, apple	0.04 - 1.8
Isovaleraldehyde	$(CH_3)_2CHCH_2CHO$	Fruit, apple	0.013 –15
Acetone	CH_3COCH_3	Sweet/Fruit	1.1 – 240

In addition to the direct industrial requirement for monitoring of odorous species there is also a strong requirement for the monitoring of odorous species in ambient air. Odorous emissions are the most common source of public complaints about industrial pollution. The Environment Agency is looking into requirements for odour measurements as part of regulatory monitoring, but has no priorities defined yet.

3.2 PRIORITY GAS STANDARDS OF ODOROUS SPECIES

The discussion in the previous section shows the wide range of different odour species of industrial importance. Since it would not be practical to prepare standards for all of these, a few key species were identified to provide a cross section of the types of chemicals, and which also targetted some specific industrial requirements.

The CEN standard on olfactometry[2] specifies n-butanol as a reference species for odour measurement – see Section 4.2. This was therefore identified as one of the key odour standards with concentration levels of around 60 ppm, matching that specified in the CEN standard. This is about 2000 times the odour threshold - a level which is suitable for the dilution systems commonly used for olfactometry. This standard would also be suitable for comparison with those produced by Nmi, in Holland.

Some other odorous mixtures with industrial relevance were already being addressed under specific milestones in the VAM programme, these included carbonyl sulphide, formaldehyde, ammonia, benzene, toluene and xylene.

Based on the industrial requirements outlined in Section 3.1 the most important class of species identified for study within the VAM odour project were volatile organic compounds with active sulphur groups. Therefore, a range of sulphurous VOC standards were developed including ethanethiol, 2,2-dimethyl ethanethiol, dimethyl sulphide, and hydrogen sulphide. Sec-butylamine was also included to cover the nitrogenous odour species. The final species covered was 1-pentene, which has been identified as a key odour component in aircraft emissions, as shown in Table 3.2. By analogy with the concentration of n-butanol, mixtures of these species were typically prepared at concentrations of around 2,000 times the odour threshold.

Table 3.4 shows the odour threshold (OT) data for the different species in the odour standards. Most of these data have been taken from a report prepared for the Department of the Environment by AEA Technology[3]. In addition to showing the wide range in threshold levels for different species, these data also show the variation in threshold that has been reported by different researchers, which can be up to three orders of magnitude (in concentration units). This highlights one of the problems in quantitative odour measurement, in that the relationship between concentration and odour intensity for a given species is often ill-defined, so high accuracy concentration measurements do not necessarily lead to an accurate measure of odour intensity.

Table 3.4 – Odour Threshold Data for Key Pollutant Species

Species	Reported Threshold Range	Best Estimate of Threshold	
	($\mu g/m^3$)	($\mu g/m^3$)	(ppb)
Benzene	1500 – 108000	32500	8650
Toluene	470 – 790	644	160
Xylene	62 – 97	78	16
Ammonia	100-11600	1000	1300
Formaldehyde		490	365
Hydrogen sulphide		0.76	0.5
1-butanol	20 – 550	90	30
Dimethyl sulphide	0.34 – 1.1	0.7	0.25
Ethanethiol		0.043	0.15
Carbonyl sulphide		27.5	10.2
2,2-dimethyl ethanethiol	0.02 – 0.09	0.05	0.01
Butylamine	261 – 136000	6000	2

3.2.1 Binary Standards

Table 3.5 gives information on the binary gas standards prepared as part of VAM project 1.4. In all cases the standard gas mixtures were prepared using an internationally-agreed gravimetric process based on the weighing of pure components into specially passivated cylinders. Rigorous QA/QC procedures were followed throughout the preparation process, including purity checks before and after the weighing process. Trace gas standards, such as those produced during this project, are prepared in multiple stages of dilution, in order to minimise weighing uncertainties – for example, see the three concentration levels of ethanethiol standards listed in Table 3.5. The final column in the table indicates the factor above the (best estimate of) odour threshold for each for the standards produced.

Table 3.5 Binary Odour Standards

Standard	Formula	Matrix Gas	Cylinder	Concentration (ppm)	Factor above OT
Hydrogen Sulphide	H_2S	Air	5600047	1.008	2,000
		Air	5600450	1.010	2,000
		N_2	H227	9.599	19,000
Pent-1-ene	C_5H_{10}	Air	5601833	93.77	47,000
		Air	5601588	4.993	2,500
		Air	5600722	4.971	2,500
n-Butanol	C_4H_9OH	Air	5600751	59.569	2,000
		Air	5601818	58.94	2,000
Ethanethiol	C_2H_5SH	Air	5601299	137.44	920,000
		Air	5600275	5.434	36,000
		Air	5601834	0.193	1,300
		Air	5601846	0.199	1,300
2,2-dimethyl ethanethiol	$(CH_3)_3CSH$	N_2	5600855	84.71	8,400,000
		N_2	5601144	4.97	500,000
Sec-butylamine	$C_4H_9NH_2$	N_2	5600732	91.17	46,000
		N_2	5600676	4.97	2,500

3.2.2 Multi-component Standards

One of the industrial sectors identified as requiring odorous gas standards was the waste management sector, and in particular the landfill management and solid waste incineration industries. As indicated in Section 3.1 there is a wide range of odorous gases emitted in these industries, however an earlier NPL Report on the 'Requirements for Gas Standards in the Waste Management Industry'[4] identified a sub-set of gases which provide a useful multi-component standard. Two standards were prepared based on these requirements, and the details of these are given in Table 3.6.

Table 3.6 Multi-component Odour Standards

Cylinder No.		5600479	5600088
Component Concentration	Ethanethiol	195.6 ppb	197.7 ppb
	Di-methyl sulphide	198.3 ppb	200.5 ppb
	Hydrogen sulphide	200.1 ppb	202.0 ppb
	Nitrogen	4.000 %	4.038 %
	Carbon dioxide	33.24 %	33.47 %
	Oxygen	0.192 %	-
	Methane	62.57 %	62.50 %

The major components in these standards have been selected to provide traceability for measurements of the calorific value of landfill gas. The minor odorous components provide reference levels in support of occupational exposure and environmental impact measurements.

4 STUDY OF POTENTIAL OBJECTIVE OLFACTOMETRY SCALES

4.1 CLASSIFICATION OF ODOURS

A fundamental question which arises when investigating odour character is whether human (mammalian) odour detection and classification is based on a set of primary odours and, by implication a set of primary odour receptors, or on a continuum of odour sensing. These two modes of sensing are best described by the two senses which use these modes (a) colour vision, where the eye responds to three primary colours (b) hearing, where the ear responds to a continuum of sound frequency. An alternative suggestion, that represents an intermediate situation between primary and continuum odour sensing, is that odour classification may be closer in nature to the mechanisms in the immune system, where there are a large number of different 'sensors' and the body builds up a 'library' of responses through inherited and learnt reaction to external stimuli.

Most odour models are based on the premise that primary odours do exist with respective primary odour receptors. A subsequent question which must be answered is the number of such primary receptors that exist.

One of the most influential classifications of primary odours was produced by Amoore[5] in the 1950s. The method used here was to rationalise the different descriptors of odour and class molecules accordingly. By so doing, a list of seven so-called primary odours was produced:

(a) Ethereal
(b) Camphoraceous
(c) Musky
(d) Floral
(e) Minty
(f) Pungent
(g) Putrid

Examples of chemicals in these categories are given in Table 4.1 below:

Table 4.1 - Examples of 'Primary' Odourants as Defined by Amoore

'Primary' Odour	Example Species
Ethereal	Acetonitrile, carbon tetrachloride, dimethyl ether, propyl alcohol, tetrahydrofuran
Camphoraceous	Borneol, chloretone, cyclohexanol, 2,2-dinitopentane, hexachloroethane
Musky	Cyclohexadecanone, ethylene undecanedioate, phenylacetic acid, tetradecanolactone, undecamethylene oxalate
Floral	Acetophenone, benzophenone, diphenyl ether, methyl benzoate, nonanol
Minty	Cyclohexanone, cycloheptanone, menthone, piperitol, tetraethulurea
Pungent	Acetic acid, sulphur dioxide, formaldehyde, cyclobutylamine, acetaldehyde
Putrid	Skatole, putrescine, hydrogen sulphide, hexylmercaptan, phosphine

Since the 50s there have been several other attempts to determine primary odours by grouping together semantic descriptions of odour quality. An example of a recent

determination based on the analysis of 126 odour descriptors relating to 1573 organic compounds, gives 19 categories or clusters of odour[6]. Overlap coefficients were calculated by the authors to express similarities between odour descriptors and the breadth and meaning of the terms used to describe them. Cluster analysis showed that there were 19 categories of odour. These categories are reported to agree with earlier proposals for classification of primary odours.

Reference Odours and 'Odour Space'

A model for referencing odour quality to specific odoriferous molecules based on a classification of odour descriptor and structure has been reported[7]. The approach was based on the analysis of 1,400 molecules from which 650 odour evocations were deduced, which were reduced to 135 basic odour evocations. A model of defining odour was then developed based on two approaches:

1. A double classification of the odourants by the structural data and descriptive data.
2. The classification of the 1,400 odourants based on the frequencies of associations encountered.

This analysis has lead the authors to conclude that 42 reference points (odours) are sufficient to define this structural olfactory relationship continuum (odorous space). See Annex A3 for more details.

Other methods of classifying odoriferous molecules have also been presented, including physicochemical parameters such as solubility, entropy or energy to classify odours[8,9]. Although parameters such as solubility can affect the ability of nose to detect an odour, it is generally considered that these sorts of parameter are not responsible for odour quality.

4.2 OLFACTOMETRIC ANALYSIS (HUMAN ODOUR PANELS)

Background to Olfactometric Analysis

The technique of olfactometry consists of presenting a panel of human assessors with an odorous gas which can be quantitatively diluted with neutral (odour-free) gas. The amount of dilution required for the odorous gas to reach its detection threshold for the panel yields a measurement of odour concentration.

One key problem with the technique is the large variability of olfactory sensitivity within the general population. To do a valid measurement with a random selection of people on the panel would require an impractically large panel. This problem is overcome by the careful selection of panel members. In the CEN draft standard[10], which is closely based on the Dutch approach developed over the last 10 years or so, it is proposed that the panel members are standardised by their sensitivity to one specific odourant: n-butanol. In this way the olfactometer expresses odour concentrations in terms of "n-butanol mass equivalents".

The accepted odour threshold for n-butanol is 30 ppb. In this system, then, an accurate concentration standard for n-butanol is required for the proper assessment of the panel on a particular dilution instrument. Typical olfactometers can dilute the odorous gas by factors of 100 to 250,000 , and the assessment of the panel uses a butanol standard at 60 ppm, which is

then diluted by a factor of around 2,000, ie mid-range for the instrument, to reach the odour threshold. At present it is understood that the only producer of primary standards for butanol is NMi in Delft, which provides traceability for a small number of accredited suppliers in Holland.

The dilution system of the olfactometer can of course be calibrated with non-odorous gas mixtures and standardized measurement techniques. Carbon monoxide mixtures are commonly used for this purpose.

The labour intensiveness of olfactometry means that it is not commonly practiced. Indeed the odour thresholds of only a very few compounds have been determined reliably by this technique.

4.2.2 Odour Panel Measurements

Odour panels can assess three characteristics of odour: threshold, intensity and quality.

Threshold Measurement

This is a measurement of the lowest stimulus intensity (odour concentration) that the subject can distinguish from an odour free situation (performed by dynamic dilution of known gas concentrations). The odour threshold for a species is generally defined as the concentration at which there is a 50% probability of the odour being detected, ie the concentration at which half the members of an odour panel can detect the odour.

Intensity Measurement

The odour intensity, I, is a measure of how strong a particular odour is. Odour intensity can in general only be defined in relative, subjective terms, by comparing one odour to another. Steven's law (1957) is usually quoted when referring to odour intensity, where the relationship between odour intensity and odourant concentration follows the general power law:

$$I = kc^n$$

or

$$\log I = \log k + n \log c$$

Both n and k are constants for a given odourant, where :

> n gives an indication of how quickly odour intensity rises with concentration. An exponent equal to 1 indicates that an odourant's perceived intensity increases at the same rate as the change in concentration. A value of n greater than (less than) one indicates that the relative odour intensity rises faster (slower) than the relative change in concentration.

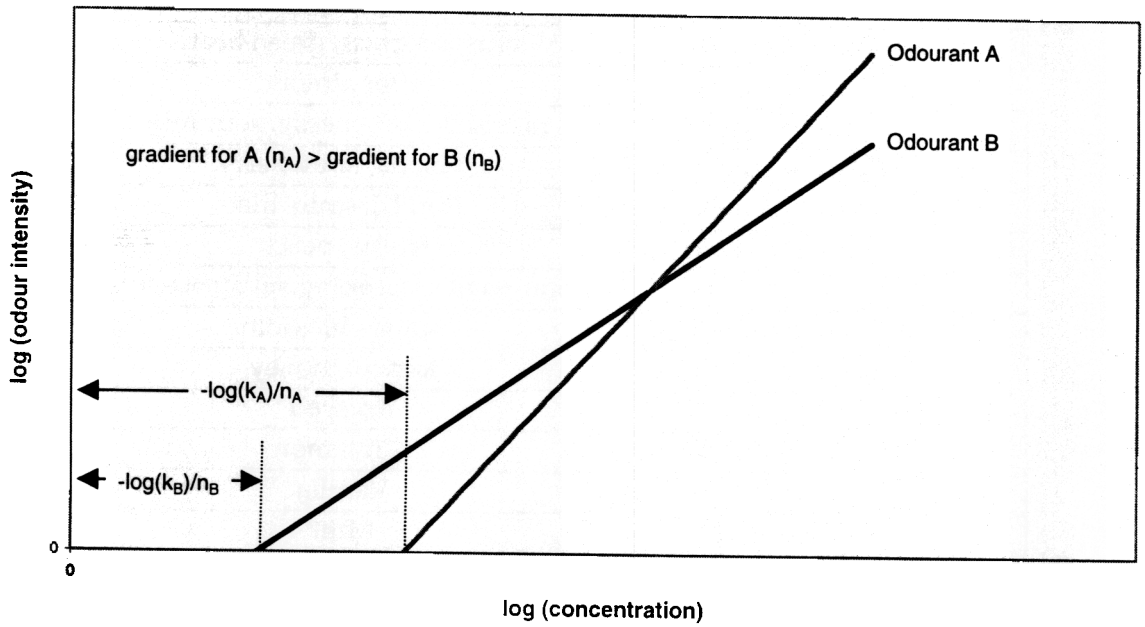
- k is related to the odourant's threshold concentration.

The increase in perceived intensity with concentration can therefore be represented by a straight line for two odourants, A and B on log/log co-ordinates, as shown in Figure 4.1.

It should be noted that, depending on the values of n and k, the rank order of the perceived intensity of two odourants can change according to the specific concentration level (as

demonstrated in the diagram above where the odour intensity of A becomes stronger than B at higher concentration levels).

Figure 4.1 - Diagram of the Perceived Intensity vs. Concentration Relationships between two Odourants A and B



Empirical measurements have shown that the values of n vary for different odourants, ranging from 0.1 to >1, with typical values between 0.2 and 0.7[11,12,13]. The value of k is known to vary over six orders of magnitude for different chemicals.

The relationship between odour intensity and concentration in mixtures is of special interest. There is little evidence to suggest that the odour quality of a mixture differs significantly from that of the individual components[14]. However, with regard to odour intensity, all sorts of interactive effects, such as additivity, synergism, suppression, together with their dependence on several factors including type of molecule, concentration and mixing ratio have been reported. Several models have been proposed to predict odour intensities of multi-component mixtures, and these have been reviewed[15]. However, as with other areas of olfaction research, there is as yet no generally accepted model.

Quality Measurement

Odour quality is the term for what a particular species (or mixture) actually smells like. Generally an odour profile is used to define odour quality, where the odour of interest is compared against a standard set of odour references and hence classified. An ISO standard[16] exists for the initiation and training of assessors for the detection and recognition of odours. Twenty four separate odoriferous chemicals, analogous to primary odours, are required for this odour quality training, and these are listed in Table 4.2.

Table 4.2 – List of Chemicals used for Odour Recognition Training

No.	Chemical Name	Descriptor of Odour
1	d-Limonene	lemon, orange zest
2	Citral	fresh, lemon
3	Geraniol	Rose
4	cis-3-Hexen-1-ol	crushed grass, green beans
5	Benzaldehyde	bitter almond
6	Butyric acid	rancid butter, cheesy, sour milk
7	Ethyl butanoate	banana, strawberry
8	Benzyl acetate	floral, jasmin, lilac
9	g-Undecalactone	fruity , peach
10	2-Phenylethanol	floral-scented cleaning substance, rose
11	methyl anthranilate	orange blossom
12	ethyl phenyl acetate	apricot, honey
13	anethole	Aniseed
14	Cinnamaldehyde	Cinnamon
15	Vanillin	Vanilla
16	l-Menthol	Mint
17	Terpinyl acetate	spicy, pine
18	Thymol	Spicy, fresh thyme, grass
19	b-Caryophyllene	carrot, woody
20	a-Satalol	woody, sandalwood
21	Eugenol	Cloves
22	1-Octen-3-ol	Mushroom
23	2-Methylisoborneol	Musty
24	Methional	mashed potato, grilled onion, grilled meat

4.2.3 Olfactometers

An olfactometer is an instrument for the preparation and delivery of an odour stimulus to a chemoreception system – usually an human assessment panel. Various reviews[17,18] have been published on the instrumental design of such olfactometers. The olfactometer is designed to generate an odorous air sample, dilute it with odourless air, and present the diluted air samples under controlled conditions to a panellist whose response with regard to odour intensity perception is recorded. The standardisation of olfactometric equipment and procedures[19,20] owes much to the air pollution control community. The olfactometer is largely used for the determination of odour thresholds, which are defined as the concentration at which a panellist perceives an odour in 50% of the trials. However, as indicated previously (see Table 3.4), the literature contains large variations in threshold values. Probable reasons for this are:

odourant purity;
loss of odourant due to adsorption within the olfactometer;

- variability of panellists;
- flow rate of air reaching the panellist;
- descending or ascending concentrations presented to the panellist ('memory effects').

Gas Chromatograph (GC) Sniffing

Human sniffing at the exit ports of GC-columns is a well established technique[21] which is still in use. The GC is used to separate the various components in a mixture; the human nose is then used as the detection method because of its higher sensitivity to odorous species compared to conventional GC detectors. However, as with odour panel measurements, the method suffers from the subjectivity of the individual assessor, who may or may not be representative of the population as a whole. Despite this limitation, GC sniffing is still used as a screening procedure to determine the importance of individual compounds for the odour and flavour of a given sample mixture.

In the analysis of odorous mixtures GC sniffing is a complementary method to standard olfactometry. With standard olfactometry, olfactometric data for the mixture as a whole can be obtained, whereas with the GC sniffing technique the individual components of the mixture can be assessed, but cannot be simply summed to give the mixture's integral odour intensity. It should also be noted that the application of this technique is limited to thermally stable compounds.

Odour Values

The odour value for a particular odourant gives a measure related to its odour intensity[22]. The odour value (OV) of a substance, is defined as the quotient of its actual concentration and its threshold concentration (usually in air):

Odour Value = (actual concentration of odourant)/ (threshold concentration of odourant)

Originally odour values were intended to be used for assessing the relative importance of single components that contribute to the total odour of a mixture[23]. However, later they have been applied as a quantitative measure to specify an odourant's intensity[24], and to calculate the odour intensity of mixtures.

The odour values cannot be regarded as an absolute scale of odour intensity, at best only a relative one. This is because :

- There is a non linear relationship between concentration and odour intensity, in most cases following the power law described in Section 4.2.2.
  Odour values of single components of a mixture do not account for the possible interactions within that mixture which may result in the odour quality and/or the intensity of a component being altered.

4.3 THEORIES OF ODOUR PERCEPTION

Theories on the way in which the nose differentiates odours have existed for many centuries. Although many theories have been proposed, there are two main explanations for the odour sensing ability of the nose. One of these is based on a recognition model, where the shape of the odorous molecule is recognised, generally referred to as structure-odour

relationships. The second model is a vibrational one, where the nose senses a set of vibrations of the molecule. Both of these theories will be reviewed in the following sections.

A great deal of research into odour perception has been carried out by the biological research community[25-31]. They emphasise that however the sensor within the nose is triggered, this information must subsequently be processed into a perceived odour by the brain, and this processing may well be the dominant part of the perception mechanism.

Biological Models of Odour Detection

It is estimated[32] that the human nose can recognise approximately 10,000 different odours. This raises a number of obvious questions :

- How is this range of specification achieved?
- Does each different odour type require a different receptor (sensor)?
- If there are a limited number of sensors, how does the brain perceive an odour?

Despite much effort in this area, the final answers to these questions remain undetermined, and the research continues.

The basic anatomy of the nose and olfactory system have been understood for some time. In humans the initial detection of odours takes place at the posterior of the nose in the region known as the olfactory epithelium. This area contains millions of neurons, which extend out at one end into the nasal cavity and hence the air being sampled. The other end of the cells are connected via axons to the olfactory bulb in the brain. In the bulb the axons converge at sites called glomeruli. By examining the DNA of humans it has been estimated that approximately 1000 genes encode 1000 different odour receptors. From this the authors conclude[33] that due to the large number of odours that can be detected each of the 1000 different receptors must respond to several different odour molecules. Further experiments have shown that each sensory neuron expresses only one receptor type. It appears that there is a random distribution of receptors within the olfactory epithelium. However, there is strong evidence[34] to suggest that receptors of one type connect to each individual glomerulus. As the glomeruli in the brain are differentially sensitive to specific odours, and the positions of the individual glomeruli are topologically defined, the olfactory bulb provides a two-dimensional map that identifies which of the numerous receptors have been activated in the nose. The odour is then perceived in the olfactory cortex.

There are two other areas in the nasal cavity which respond to odour / chemicals. The first is the trigeminal nerve which is associated with the detection of irritants (acidic gases for example) the second is the vomeronasal organ, which may be vestigial in humans.

Quantitative Structure-Activity Relationships (QSARS)

A 'stereochemical theory' of odour was postulated by Amoore[5] in the early 50's, which related odour quality to molecular shape. Furthermore, Amoore considered that all odours were based on various combinations of a limited number of primary odours[35]. Initially, he postulated that there were seven Primary Odours. Further, by listing molecules with similar odours and analysing these molecules, he concluded that the most important factor which appeared to govern the odour of a particular chemical was its overall size.

Molecules could also be classified on the degree to which a single spatial configuration could be assigned to it. Three types of molecule were classified:

- **Invariant** - most rigid molecules (shape due to covalent bonding)
- **Determinate** - shape determined by steric hindrance, dipole interaction or hydrogen bonding
- **Articulate** - single bonds with free rotation

It was postulated that by assuming only a small number of primary odours, and assuming that the receptor sites for different primary odours were perfectly distinct, all odours could be described. Such a model also predicted that by considering probability, rigid molecules would be able to fit only one site at a time, and thus have less complex smells than articulate ones.

With subsequent work Amoore tried to investigate whether further primary odours existed[36]. By choosing human subjects with specific anosmias (inability to smell a particular odour), attempts to identify further primary odours were made. For example, the butyric group of compounds were identified as primary. It was concluded that there may be as many as 20 to 30 primary odours, while some previously-defined primary odours such as 'musky' would need to be subdivided.

Since the work of Amoore, many publications have been produced citing structure - odour relationships. These publications have been recently reviewed[37]. With the onset of powerful computing techniques, mathematical relationships between biological activity and structure have been sought, leading to models that describe these relationships, which are formally known as Quantitative Structure-Activity Relationships (QSAR). Such relationships are well known in pharmacochemistry and have been used to design and predict the activity of new drugs.

Several QSARs relating to odour have been published. The three characteristics of odour that have been described by these relationships are quality, intensity and threshold. For example, Amoore[38] assessed the benzaldehyde-likeness of the odour of 25 alkyl-substituted benzaldehydes and nitrobenzenes, and benzonitrile, and correlated this with molecular shape. A significant number of QSARs have been published and recently reviewed[39].

4.3.3 Molecular Vibration – Odour Relationships

Originally postulated in 1937 by Dyson[40], Wright[41] developed a vibrational theory of odour in the 50s-60s. The theory was based on a correlation between odour and infrared spectra, but no mechanism on how the vibrations were detected was presented.

Dyson concluded that odour is related to a characteristic molecular vibration pattern rather than a characteristic structure or reactivity, and assigned certain odours to Raman frequencies in the range 1500-3000 cm^{-1}.

However, Wright has argued that this assignment of frequencies is questionable, because:

- If odour is correlated to this range of frequencies, it could equally well be correlated with the corresponding functional groups, and there would be no need for a vibrational theory. This observation seems to be corroborated by the observation[42]

that butyl alcohol has an indistinguishable odour whether the OH functional group is hydrogen or deuterium terminated.
At the temperature in the nose, 37°C, vibrational states above 1000 cm^{-1} will not be significantly populated, and so any correlation between odour and molecular vibration must be looked for at frequencies below about 700 cm^{-1}. This range of the spectrum is more characteristic of the molecule of interest as a whole, and less that of any functional group, so that this region is of special interest in any relationship to odour.

In further work[43] the following conclusions were reached :

Some degree of relationship exists between odour and molecular vibration characteristics under 700 cm^{-1}.

- The spectrum between 100 and 700 cm^{-1} appeared to be arranged along an effective continuum, with lower frequencies characterised by pleasant odorous sensations and the higher frequencies characterised by unpleasant sensations. However, later work indicates that a rather more complex relationship exists[44] .
- Trigeminal or pungent sensations appeared to be associated with a sparse spectrum or single vibration in the region, and with an intense line around 900 cm^{-1}.

Recent work by Turin[45] has again postulated that the vibrational properties of molecules dictate their odour characteristics. The novel approach in this work is that a mechanism by which the nose can sense the vibrations has been proposed, and is based on Inelastic Electron Tunnelling Spectroscopy (IETS)[46]. A description of conventional IETS can be found elsewhere[47]. The proposed biological tunneling mechanism is composed of a soluble electron donor level and an empty zinc level, spanning the binding site for an odourant molecule. When the molecule occupies the binding site, electrons can tunnel, and can by so doing lose energy by exciting the vibrational modes of the molecule. Turin has postulated that unlike conventional IETS, biological IETS will not involve scanning an energy range, but that the range of vibrational energies will be covered by a series of receptors each responding to a different vibrational energy. The reducing power of electrons within a biological system has been estimated at 500 mV, which is sufficient to excite frequencies up to 4000 cm^{-1}. As the biological system is working at body temperature, Turin postulates that the donor and acceptor levels across the tunnelling gap will have a minimum gap of 2kT (400 cm^{-1}), allowing the range 0-4000 cm^{-1} to be covered by 10 or so receptors. Furthermore, Turin expects that vibrational modes below kT will not be detected by the biological system because:

these modes will already be thermally excited, therefore electrons will be as likely to gain energy from them as to excite them to a higher vibrational level;
if the difference in energy between donor and acceptor levels is of the order of kT, thermal broadening of the levels will mean that electrons will flow whether or not an odourant is present.

Isotopically different molecules are expected by this theory to possess different odours. Turin attempts to show this with the example of acetophenone and acetophenone-d8. The results reported are that although both odourants have similar odour profiles, the difference between them is striking: acetophenone-d8 is fruitier and has less toluene-like character than acetophenone, and also has a much stronger bitter almonds character.

Although the situation is far from fully resolved, the evidence that tunnelling spectroscopy may play a central role in the detection of odour is persuasive. Moreover, as a relatively

simple physical property is involved, there exists the possibility of developing an instrument which can at least increase the objectivity of odour measurements. One of the aims of this project was to investigate this possibility, and this is discussed in the following section.

4.4 INELASTIC ELECTRON TUNNELLING SPECTROSCOPY

Planar Tunnelling Spectroscopy

There were extensive studies of the vibrational modes of molecules by tunnelling spectroscopy in the 1970s and early 1980s. The technique, known as Inelastic Electron Tunnelling Spectroscopy, looked at the quantum tunnelling of electrons through single molecular layers of the species of interest, adsorbed onto oxide surfaces, which were in turn grown on top of a planar metal electrode. The upper electrode was formed by a metal layer deposited over the adsorbate. Vibrational features contribute to the tunnelling current above characteristic voltages, and are best observed in the second derivative of the current-voltage curve. To obtain well resolved spectra, the measurements were carried out at very low temperatures (2K). Because the bonding between the molecules and the oxide layer changes the symmetry of the molecule and hence its vibrational modes, the spectrum actually describes the combination of the monolayer and the oxide layer.

Many tunnelling spectra were obtained by this technique, and they have been collated in a review publication[48]. It reprints 156 spectra of monolayers on aluminium oxide, including several odorous species such as thiols and pyridine. There are also 15 spectra of absorbates on magnesium oxide.

There are, however, several reasons why spectra obtained in this way may not directly mimic the postulated nasal mechanism, and why it is a limited technique for further work. A key requirement for the technique is that the test molecule adsorbs chemically (chemisorbs) as a near-monolayer to the oxide layer. There are many odorous molecules which would not do this on convenient materials, and for those that do, the surface bond may remove or shift the vibrational feature of most interest for its odorous properties. Moreover, the IETS spectrum will be influenced by the electric properties of the surrounding material, in this case metal, which is likely to produce a significantly different spectrum from that observed by any nasal receptor.

Despite these reservations, the possibility of developing a quantitative relationship between a physical parameter of a molecule and its odour, meant that it was considered worthwhile to conduct a preliminary investigation of the correspondence between IETS spectra and odour characteristics using the available sources of data. The results of this investigation are presented in Section 4.4.4.

Scanning Tunnelling Microscope Techniques

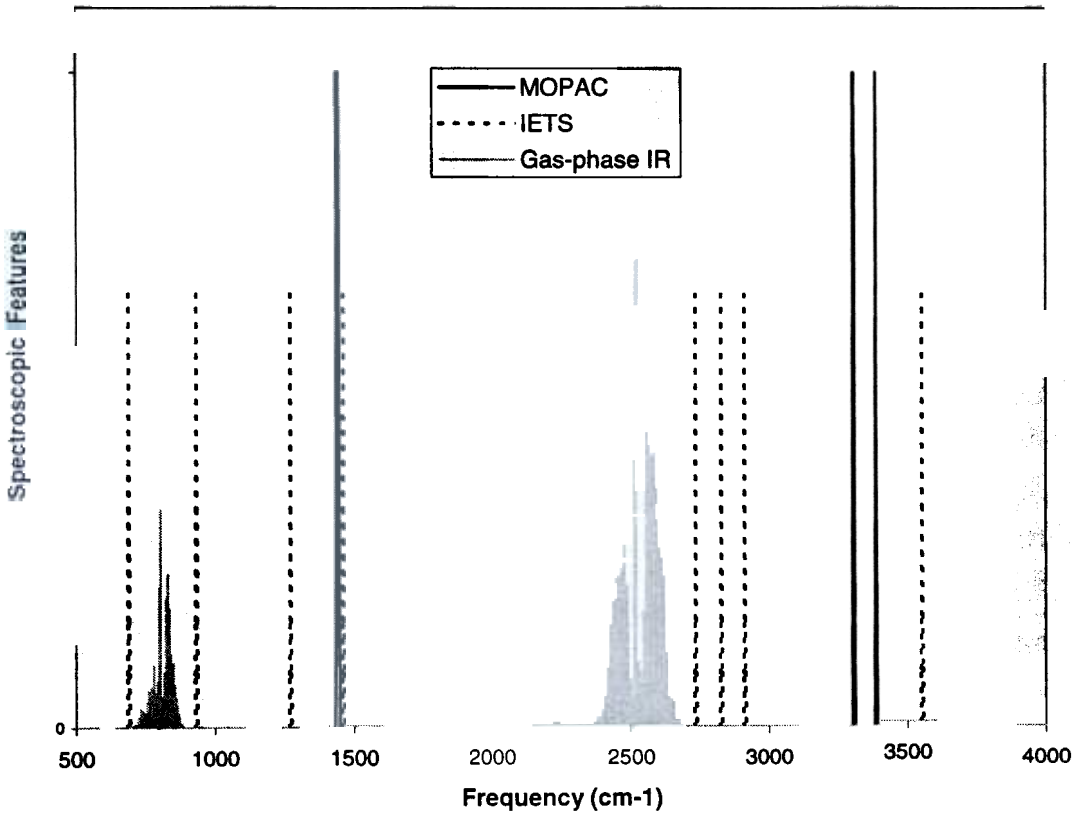
The use of a scanning probe rather than an upper electrode is superficially a very attractive improvement over the planar technique, as it holds the promise of spectral measurements of single molecules. Preliminary work with sorbic acid on graphite[49] and 1-octadecanethiol on gold[50] have demonstrated some of the techniques, but cannot yet be said to have produced useful spectra. It should be emphasised that the tunnelling mechanism in the STM technique is significantly different to the planar situation, but may be more analogous to the postulated nasal receptor.

With the atomically smooth electrode surfaces and large ordered monolayers commonly used in STM, it may be feasible for the molecules to be physisorbed (rather than chemisorbed) to the lower electrode, enlarging the range of molecules that could be investigated. The use of a metal substrate will alter the spectrum in the same way as for the planar technique, but as zinc is thought to play a key role in the nasal receptor this may make the alterations more appropriate.

The geometry of the STM technique is also likely to affect the tunnelling characteristics, such as the ratio of tunnelling by elastic and inelastic processes, and hence the spectrum. It may be possible to observe the tunnelling spectrum using only the first derivative of the current-voltage curve, but the intrinsically low currents may make signal-to-noise a problem.

The technique has not been extensively tried for the purpose of tunnelling spectroscopy, and although there are significant technical obstacles there are interesting possibilities worthy of further investigation. However, due to the complexity and cost of such experimental work it was decided that such research should not be undertaken until the results of the preliminary investigation of the relationship between IETS and odour had been assessed.

Figure 4.2 – Main Spectroscopic Features of Methane – Comparison of MOPAC Prediction, IETS Spectrum and IR Gas- phase Spectrum



4.4.3 Model Calculation of Tunnelling Spectra

As part of his investigation of the tunnelling spectroscopy theory of odour, Turin[45] adopted the approach of calculating the expected tunnelling spectra for a particular molecule in a biological environment, using an algorithm called CHYPRE. This used software to calculate

the theoretical mode frequencies and partial charges, and to produce spectra modified to take into account local effects and thermal broadening. Calculation of spectra is undoubtedly the most practical method for investigating the plausibility of the theory, although it does not in itself help in the development of relevant instrumentation.

The details of this algorithm are commercially sensitive and, together with the lack of suitable measured spectra, it is therefore difficult to judge the effectiveness of this method. However, it is known that the heart of the CHYPRE algorithm is a publicly available package called MOPAC. Therefore, a short study was carried out to assess the potential of MOPAC in the accurate prediction of infrared and IETS spectra.

Figure 4.2 shows a comparison of the frequencies of the main infrared absorption features of methane for gas-phase optical absorption[51], the IETS absorption features[48] and the absorptions predicted by MOPAC. There is a clear correspondence between the gas-phase IR data and the MOPAC prediction, although there is a large frequency shift and the MOPAC simulation vastly over-simplifies the absorption spectrum. However, the relationship with the IETS spectrum is not at all clear.

Figure 4.3 – Main Spectroscopic Features of Benzene –
Comparison of MOPAC Prediction, IETS Spectrum and IR Gas- phase Spectrum

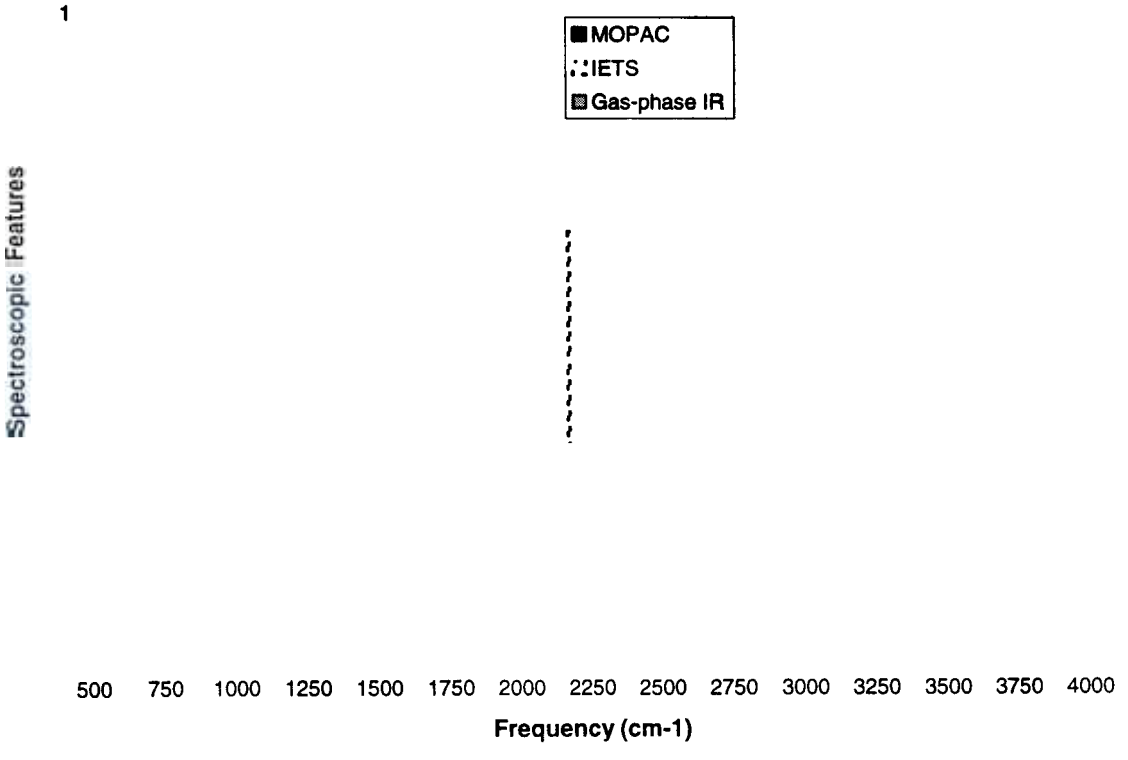


Figure 4.3 shows a similar comparison for the IR absorption spectrum of benzene. In this case there is no obvious relationship between any of the three data sets. In both cases these comparisons have been carried out for relatively simple molecules, and the lack of agreement for these simple cases suggests it is unlikely that MOPAC would be a suitable tool for accurately predicting the IETS spectra of complex odorous molecules. The study of

the relationship between IETS and odour therefore concentrated on using available sources of measured IETS data.

4.4.4 Relationship Between IETS and Odour

In order to investigate whether there was a direct link between the IETS spectrum of a given species and its smell, the frequency of the measured IETS absorption features for a wide range of species was recorded. All of these measurements have been made using planar tunnelling techniques at cryogenic temperatures[48]. The species were then grouped according to their known odour characteristics, and the results of these groupings are summarised in the following figures (Figures 4.4 – 4.9). A complete summary of the complete IETS absorption dataset is given in Annex A4. In these figures each IETS feature is assumed to have a width of 200 cm^{-1}. This width was selected arbitrarily to be of the same order, but less than, the expected frequency resolution of the tunnelling sensors in the nose. Turin's paper [45] suggests that, due to thermal broadening of the IETS lines, the frequency resolution of the sensors would be approximately 400 cm^{-1}.

Figure 4.4 - IETS Absorption Features of Odourless Species

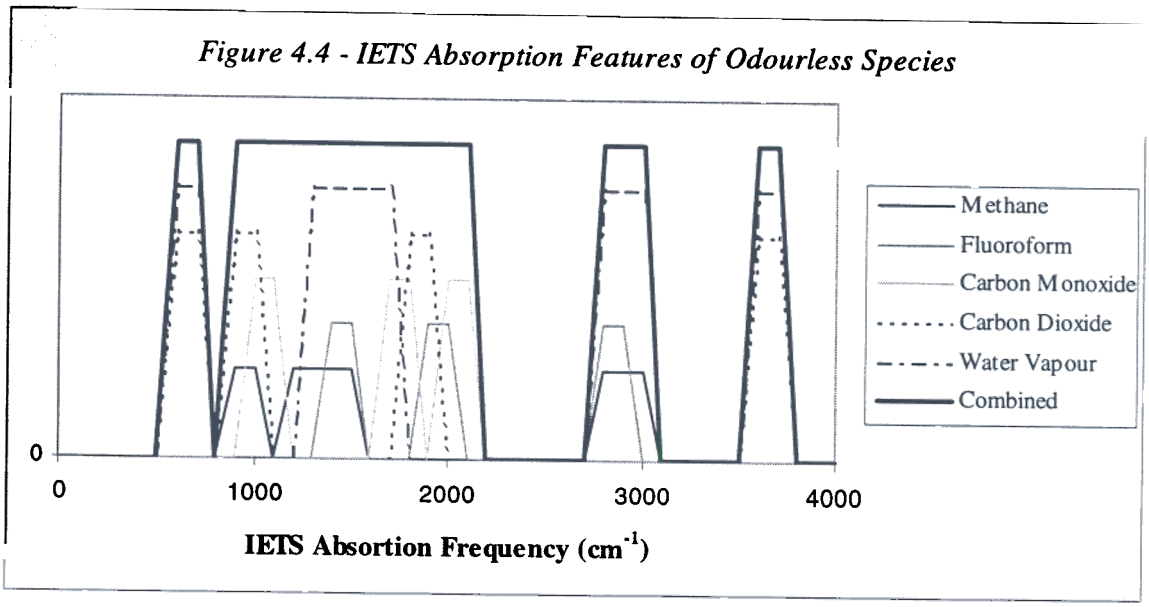


Figure 4.4 shows the IETS absorption features of five odourless species. Under the hypothesis that the odour of a given species is determined purely by its tunnelling spectra, then the frequencies of the features in this figure should correspond to 'dead' regions in the odour sensing spectrum, and that any absorption in these regions would not contribute to the smell of a particular species.

Figure 4.5 - IETS Absorption Features of Species with an Ammonia-like Odour

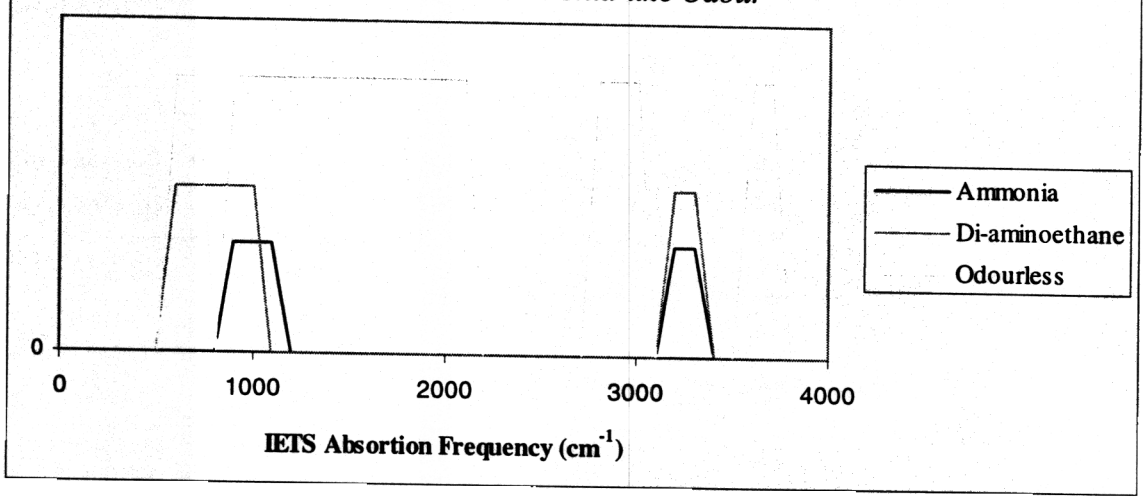


Figure 4.5 shows the IETS feature for two species with an ammonia-like smell. In this case, both species have features around 3200 cm^{-1}, which do not appear in any of the odourless examples, possibly supporting the IETS-Odour hypothesis. However, biological evidence suggests that the pungent 'smell' of ammonia is actually due to a different process to the normal odour perception mechanism – triggered by the trigeminal nerve (see Section 4.3.2). Figure 4.6 shows a more typical example, in this case four species with an aromatic benzol-like odour. All of these species have absorptions around 1000 cm^{-1}, and three of the four have features somewhere in the 'clear' region between 2100 cm^{-1} and 2800 cm^{-1}, but there is no obvious overall pattern.

Figure 4.6 - IETS Absorption Features of Species with an Aromatic (benzol-like) Odour

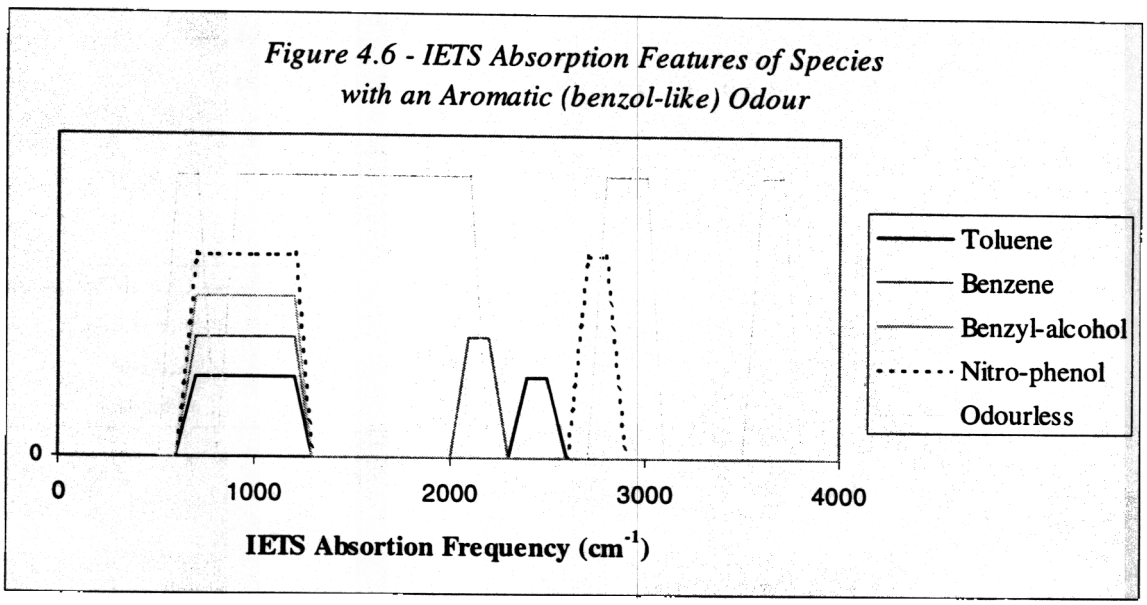


Figure 4.7 - IETS Absorption Features of Species with a Bitter Almond Odour

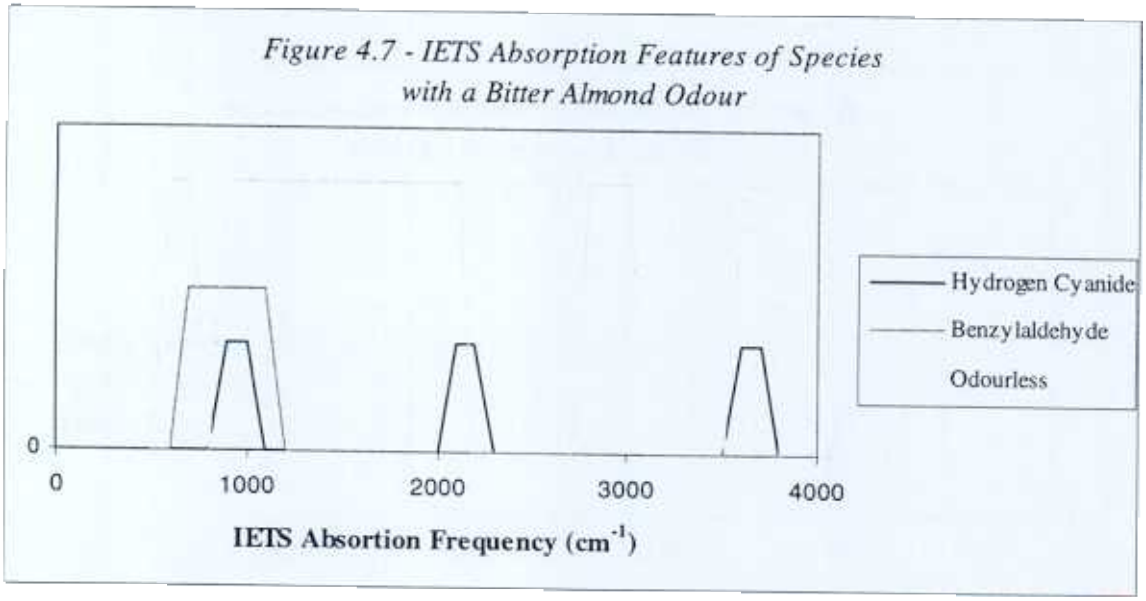
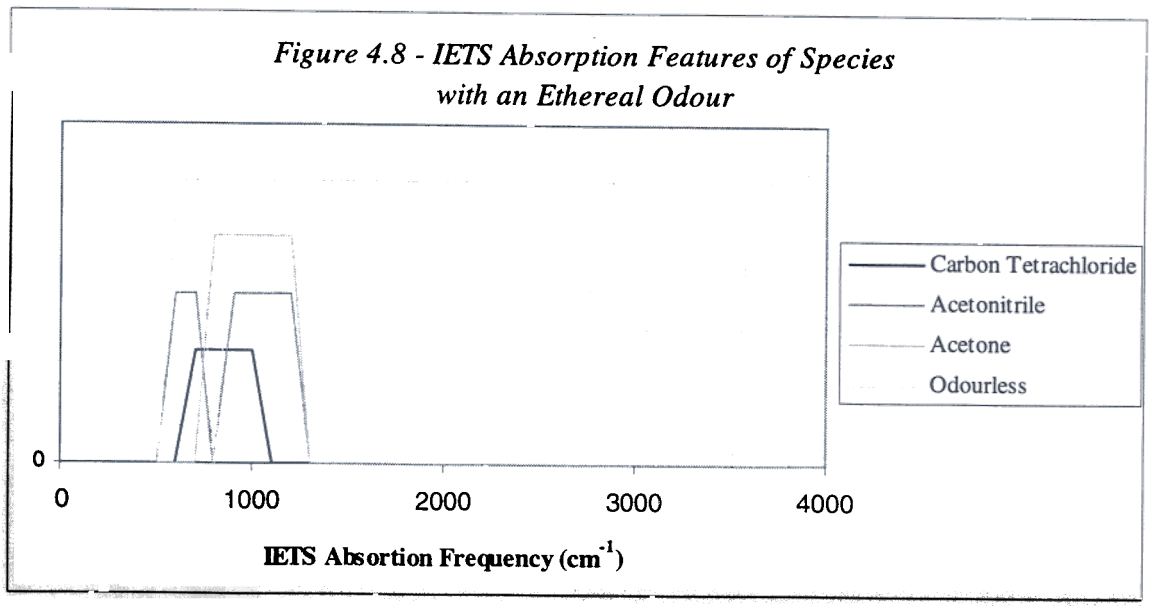


Figure 4.7 shows the IETS absorption frequencies for hydrogen cyanide and benzaldehyde, which both smell of bitter almonds. Apart from feature around 900 cm^{-1}, which occurs for many other species there is no obvious link between the two spectra. The similar smell of these two species remains one of the classic puzzles of odour research, and an examination of the IETS spectra does not appear to offer any new insights into this particular issue (see Section 7.3 for a further discussion of these two species).

The IETS characteristics of three species with an 'ethereal' odour are shown in Figure 4.8. All three species only show IETS features between 500 cm^{-1} and 1200 cm^{-1}. However, most of these features lie within the 'odourless' region, and as in previous examples, there is little evidence for a common pattern in these spectra.

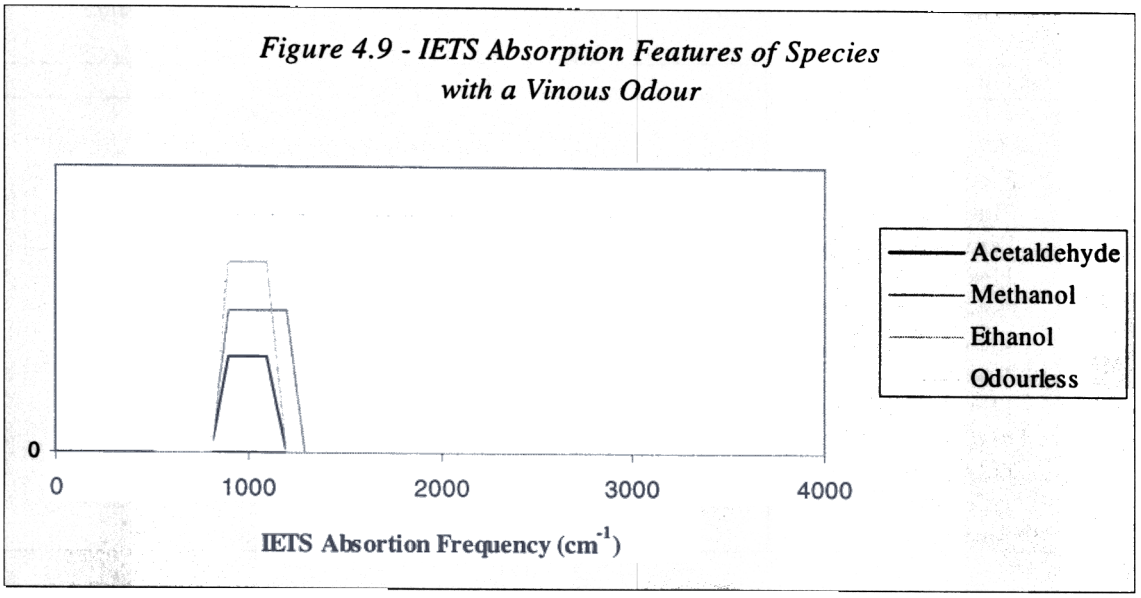
Figure 4.8 - IETS Absorption Features of Species with an Ethereal Odour



The final example is shown in Figure 4.9, and this gives perhaps the clearest example of the lack of an obvious direct link between IETS spectra and odour. All three of these species have fairly complex odours which include a 'vinous' component. The odour of acetadehyde is described as 'pungent, choking, vinous and fruity', methanol as 'vinous and harsh' and

ethanol as 'vinous and sweet'. However, all three species have very similar, and very simple, IETS spectra which all lie within the odourless region.

Figure 4.9 - IETS Absorption Features of Species with a Vinous Odour



4.4.5 Infrared Absorption

A molecule's infrared absorption spectrum is closely related to its electron tunnelling spectrum, but specific features have different strengths in the two cases because of different selection rules, and the effects of the molecule being adsorbed onto a surface. Despite these differences, information on the infrared absorption spectra of different species is much more readily available than measurements of the IETS spectra. The main infrared absorption features for a range of key odour species was obtained from various sources[51, 52], and the combined results of this study are presented in Annex A4.

One of the reasons for undertaking this particular study was to look at the change in infrared spectra for functionally related compounds with increasing carbon number, and compare this to the changing odour characteristics. Three different classes of species were investigated : aldehydes, ketones and alcohols. Tables 4.3 to 4.5 below indicate how the odour character of these species changes with increasing carbon number.

Table 4.6 shows how the gaseous infrared absorption spectra changes in three key regions of the spectrum – 700 cm^{-1} to 800 cm^{-1}, 2690 cm^{-1} to 3020 cm^{-1}, and 3435 cm^{-1} to 3500 cm^{-1} (the complete IR spectra are given in Annex A4). In this table the black areas indicate the frequency of the main absorption peaks, while the grey areas indicate regions of above-background absorption. The frequency resolution in these tables is approximately 5 cm^{-1}, and it should be noted that this is much higher than the predicted 400 cm^{-1} resolution of the biological odour sensor.

The results show that while there are clear trends in the absorption spectra with increasing carbon number - as would be expected from the effects of increasing molecular mass on the vibrational frequencies – the maximum size of the shift from lightest to heaviest species is less than 100 cm^{-1} which would not be resolved by the proposed sensor. In addition, there is

often minimal spectral change between one species and the next, despite significant changes in the odour character.

Table 4.3 - Odour Characters of Functionally Related Compounds : Aldehydes

Name of Aldehyde	Odour description
Methanal (Formaldehyde)	Choking, lachrymatory
Ethanal (Acetaldehyde)	Chocking, vinous, fruity
Propanal	Choking, suffocating, fruity
Butanal	Chocking, pungent, fruity
Pentanal	Choking, pungent, fruity, oily
Hexanal	Very powerful, fruity-green
Heptanal	very powerful, coarse, vinous-fruity
Octanal	Very powerful, fatty, orange-peel
Nonanal	very powerful, fatty
Decanal	very powerful, waxy, orange eel
Undecanal	moderately powerful, waxy, floral
Dodecanal	Moderately powerful, fresh, with a violet like tonality
Tridecanal	Moderately powerful, fresh
Tetradecanal	Very weak, dry citrus, warm

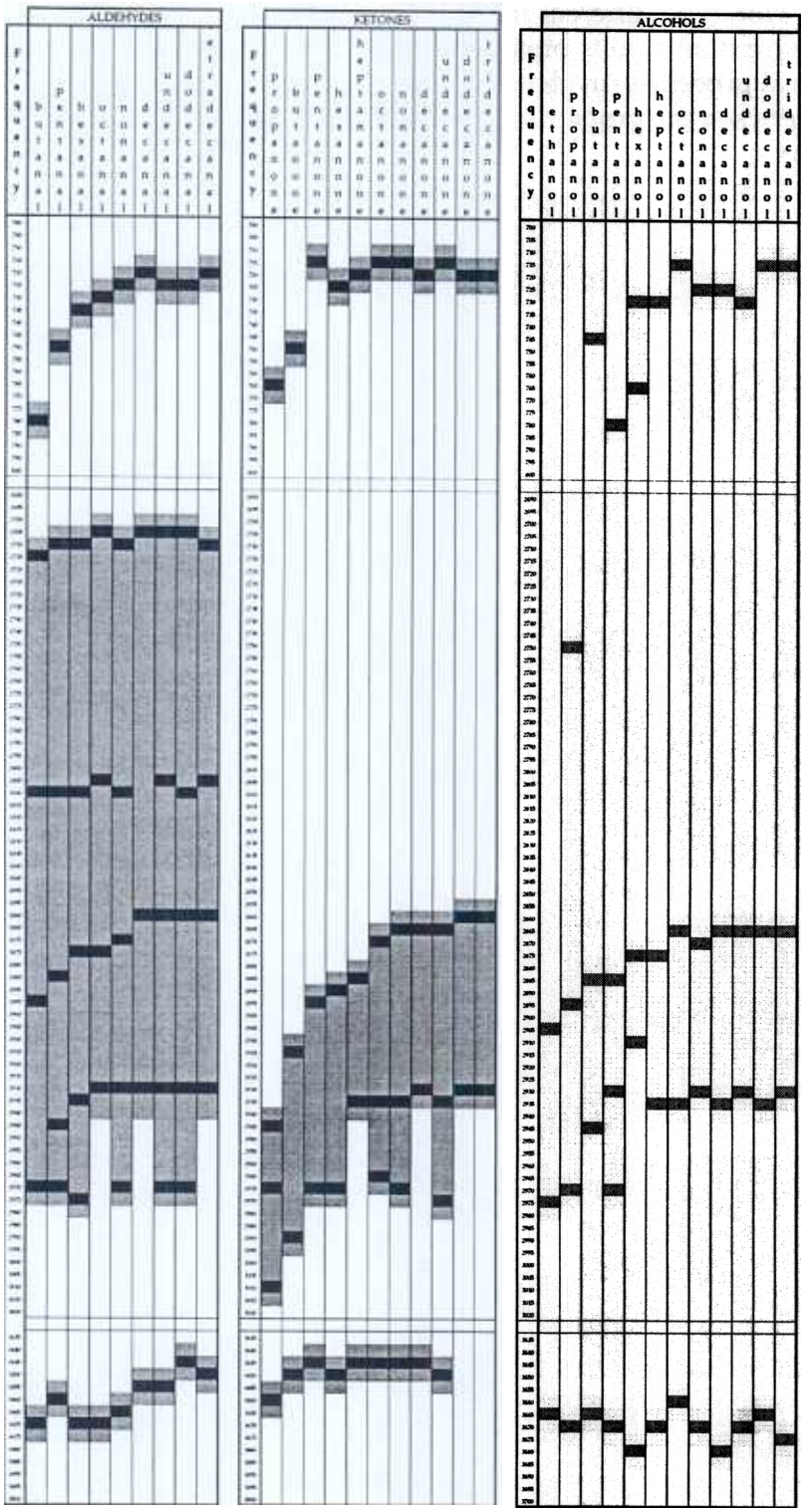
Table 4.4 - Odour Characters of Functionally Related Compounds : Ketones

Name of Ketone	Odour Description
Propanone	Harsh, ethereal
Butanone	Ethereal, not unpleasant
Pentan-2-one	Ethereal, not unpleasant
Hexan-2-one	Ethereal, fruity
Heptan-2-one	Sweet, fruity, spearmint
Octan-2-one	Floral, green-fruity, herbaceous
Nonan-2-one	Fruity, floral, herbaceous
Decan-2-one	Fruity, orange-like, floral
Undecan-2-one	Fruity, orange-like, waxy, floral
Dodecan-2-one	Orange-like, waxy, floral
Tridecanol-2-one	Herbaceous, oily

Table 4.5 - Odour Characters of Functionally Related Compounds : Alcohols (Straight Chain Aliphatic Alcohols)

Name of Alcohol	Odour Description
Methanol	Vinous, harsh
Ethanol	Vinous, sweet
Propan-1-ol	Vinous, harsh
Butan-1-ol	Choking, harsh, vinous
Pentan-1-ol	Choking, harsh, vinous
Hexan-1-ol	Vinous, fruity, harsh
Heptan-1-ol	Light, fresh, vinous, fatty, green
Octan-1-ol	Strong, fatty, orange-like, balsamic
Nonan-1-ol	Powerful, fresh, oily with a suggestion of rose
Decan-1-ol	Waxy-floral, fresh, rose like
Undecan-1-ol	Fresh, oily, floral, fruity
Dodecan-1-ol	Rather weak, waxy, green
Tridecanol-1-ol	Very weak, waxy, woolly
Tertadecan-1-ol	Extremely faint, waxy
Pentadecan-1-ol	Almost odourless

'able nfrar Absorptio F equencies of Gaseous Aldehyd Ket nd A hols



The conclusion of these basic studies of the relationships between IETS and infrared spectra of a species and its associated odour is that there is no obvious relationship between odour and absorption frequency, particularly given the predicted low resolution of the odour sensor. Some questions remain about the effects of molecular orientation within the sensor, and how this would be different for a biological sensor compared to the planar tunnelling (gas phase absorption) results presented here. However, without more detailed knowledge of the biological processes involved in odour sensing it seems unlikely that a deterministic relationship between the properties of a molecule and its perceived odour will be realised in the near future.

5 VALID FIELD SAMPLING AND MEASUREMENT METHODS

5.1 REQUIREMENTS FOR AMBIENT ODOUR DETECTION

As has been indicated previously, there is a strong requirement for monitoring trace levels of odorous species in ambient air. Such measurements are needed to assess the environmental impact of industrial and waste emissions, provide source attribution for pollution events, and to assess the effectiveness of abatement techniques. The sensitivity and accuracy of such measurements are dependent upon both the method used to sample the ambient air and the analysis technique applied to that sample. The following sections discuss the main sampling and analysis methods that can be used for the monitoring of ambient odour concentrations.

5.2 SAMPLING METHODS

5.2.1 Canister Sampling

Canister sampling is generally used where pre-concentration of the species of interest is not required. The method typically used is to draw the samples into previously-evacuated gas cylinders which have specially-passivated internal walls (eg electro-polished) to ensure that their interiors are inert to the species being sampled. The cylinder preparation procedure involves evacuation, heating and rolling; filling with zero air or nitrogen; and preliminary (zero) measurement to ensure that the background readings are well below the required measurement levels (typically less than one ppb) before the final evacuation stage. The typical sampling procedure involves opening the valve of the cylinder so that the flow rate into the cylinder is about one litre per minute. Cylinder volume are generally between five and ten litres.

The major concerns with this type of sampling are losses, chemical or physical in nature, either by adsorption to the container walls or reaction in the gaseous state. This is particularly relevant for more reactive species, and compounds with sulphur-groups (which are often the major sources of ambient odour pollution). In general, metal containers cannot be used to sample these types of species, and alternative vessels have to be used. Glass vials with teflon stoppers are one option. However, sample bags are more commonly used for environmental applications. These bags are formed from either plastic or rubber and covered with specific polymers such as Teflon, Mylar or Tedlar. These coatings are chosen to minimise loss of sample by adsorption. Studies of the adsorption of ethylbenzene on different coatings have demonstrated the suitability of Tedlar as a low adsorption coating, with Teflon also exhibiting good qualities, whereas Polyethylene would be a poor choice of coating. However, even with a coating such as Tedlar a maximum of 2 hours is recommended between sampling and analysis.

A recent development in cylinder passivation technology opens up new possibilities in ambient sampling of odorous species. In this technique the surfaces of the canister and sample line are passivated by coating them with a Si-based compound similar to silica. This process produces an inert surface that is suitable for the sampling of various reactive species including hydrogen sulphide, thiols and alcohols. This treatment is not however suitable for the handling of hydrogen fluoride or caustic chemicals.

It is as important to use suitably inert materials in the sample and analysis lines as in the sample canister itself. The use of inappropriate materials can significantly reduce both the sensitivity and accuracy of any measurement technique. For example, sulphur compounds have a strong tendency to stick to stainless steel, therefore the use of any stainless steel pipework, values and/or regulators can have a major effect in the analysis of sulphur compounds, particularly at trace levels where sample line absorption and memory effects can have a more significant impact.

5.2.2 Sampling onto Sorbent Material

Sampling onto sorbent materials is generally used where pre-concentration of the species of interest is required. This type of sampling can either be performed passively using diffusive samplers, or actively using pumped sampling.

A diffusive sampler can be defined as ' a device which is capable of taking samples of gases or vapours from the atmosphere at a rate controlled by a physical process such as gaseous diffusion through a static air layer or a porous material and/or permeation through a membrane, but which does not involve the active movement of air through the device'. This type of sampling is cheap and simple to perform, but the results are dependent on the location of the sampler and the ambient conditions during the sampling period.

Pumped sampling involves the similar types of sampler to the diffusive case, but with the addition of a pump to draw a controlled flow of air through the sample volume. Although this adds to the complexity and cost of the sample system, the results are generally more sensitive and accurate as they involve a larger, known volume of air, and are less dependent on ambient conditions.

The general procedures for the sampling and analysis of VOCs in ambient, indoor and workplace environments using pumped samplers are set out in the International Standard ISO 16017-1 'Indoor, ambient and workplace air – Sampling and analysis of volatile organic compounds by sorbent tube/thermal desorption/capillary gas chromatography. Part 1 : Pumped sampling'. The specified concentration range over which these procedures are applicable is approximately 0.5 $\mu g/m^3$ to 100 mg/m^3 (equivalent to a range of 0.15 ppb to 30 ppm for butanol). This range is limited at the upper concentration by the sorptive capacity of the sampler and/or the linear dynamic range of the measuring GC. The lower limit of detection is defined by the noise level of the detector, and the purity of the sample blanks used to define the zero concentration levels (both in terms of the analyte and any possible interfering substances).

The standard sets out the requirements for suitable reagents, materials and apparatus; and the appropriate methods to be applied to sampling, measurement and calibration. The standard also includes information on the retention volumes, safe sampling volumes and desorption temperatures of a range of important VOCs when sampled using some of the main sorbent tube materials. Guidance on the appropriate sorbent material for different types of target species is also provided.

The equivalent information for diffusive sampling is set out in a related ISO standard[53].

Various absorbing material can be used for either process. Commonly used materials are: Carbotrap (activated carbon), Tenax, Porapack, Chromosorb and macroreticulated resins,

such as XADs. Table 5.1 gives examples of the sorbents that can be used for various classes of odorous molecules:

Table 5.1 - Sorbent Materials Suitable for Sampling Key Types of Odorous Compounds

Family of Compounds	Adsorbant
Mineral Acids	Na_2CO_3 5% on Chromosorb
Organic Acids	Carbotrap or XAD or Tenax
Organic Compounds	Activated Carbon
Thiols	Activated Carbon or Tenax
Amines	Activated Silica Gel
Alcohols	Activated Silica Gel

There are certain restrictions on the use of sorbents : the materials are generally not selective to families of odorous molecules, and quantification of compounds may be hampered by competitive adsorption. However, the adsorption efficiency, and therefore sensitivity, can be increased by using several different adsorbing materials, with or without the use of cryogenics, followed by back flushing or desorption.

Table 5.2 gives some of the key characteristics of commonly-used synthetic adsorbants:

Table 5.2 - Basic Properties of some Common Adsorbants

Adsorbant	Specific Surface Area (m^2/g)	Max Temperature (°C)	Polymer Type
Carbonax	14	500	DPPPO
Tenax	19	375	STY-DVB
Chromosorb			
101	<50	275	STY-DVB
102	300-400	250	STY-DVB
103	15-25	275	STY
104	100-200	250	Acrylate
105	600-700	250	Aromatic
106	700-800	225	STY
107	400-500	225	Acrylate
108	100-200	225	Acrylate
Porapak			
P	50-100	250	STY-EVB
Q	500-600	250	EVB-DVB
R	550-750	250	NVP
T	250-350	190	EGDMA
N	225-350	190	CVP
Amberlite			
XAD1	700-400	250	STY-DVB
XAD4	498		STY-DVB
XAD7	326		Acrylate

Desorption of the compounds of interest is performed thermally. This is usually achieved by heating in a flow of inert gas to the point where total desorption occurs, followed by separation of the compounds by gas chromatography. Care has to be taken not to exceed the maximum operating temperature of the adsorbent or to exceed the temperature where the

compounds of interest decompose or react. This may be a considerable problem in the analysis of complex mixtures.

An alternative to using thermal desorption is to use solvent extraction. This technique has been successfully used for the trapping and desorption of sulphurous compounds[54,55].

The use of sorbents specifically targeted on odorous species was considered. One possible material is zinc ricinoleate, which is used in a wide range of deodorizing products due to its effectiveness in binding species with unpleasant odours. It has long been known within the cosmetics industry that this chemical (and similar metal salts) binds strongly to amines, thiols and short-chain fatty acids making it ideal as the base for many commercial deodourants. Theoretically, this behaviour would also make it a useful material for absorption sampling of a range of key odorous species. However, at the current time a suitable desorption mechanism is not known, and useful measurements cannot be made until a suitable mechanism is identified.

5.3 MEASUREMENT METHODS

5.3.1 Gas Chromatography (GC)

The volatility of most odorous compounds means that they can be separated and quantified by gas chromatography and this is therefore the most generally applicable measurement method. Gas chromatography is a technique used to separate mixtures of gases and volatile liquids. The separation is achieved by the differential distribution of the individual components between the mobile and stationary phase. The stationary phase (usually an inert material covered with a non volatile liquid) has a large surface area and interacts to different degrees with the sample molecules, whilst the mobile phase (usually helium, nitrogen or argon) carries the sample species through the stationary phase. The speed of migration of the sample molecules through the stationary phase depends on properties like boiling point, polarity, solubility and adsorption. The individual components comprising the mixture elute from the column individually and can then be quantified by a range of detectors. The type of detector used after the GC separation phase needs to be matched to the types of species present in the sample. Three different options for odour analysis were investigated – Flame Ionisation Detection, Sulphur Chemi-luminescence Detection and Mass Spectrometric Detection. The results of these investigations are discussed in the following sections.

All of the above GC detectors have limits to their sensitivity for particular chemical species. The basic sensitivity of the GC method can be enhanced with a cryogenic pre-concentration step. The cryogenic pre-concentration method uses liquid nitrogen to cool an area of the sampling apparatus in the GC. This 'trap' is typically cooled to -100°C and held at this temperature as the gas is sampled, allowing the species of interest to condense out in the trap, while the matrix gas, usually nitrogen, passes straight through the system. The trap is then rapidly heated to thermally desorb the trapped sample. The evaporated sample then passes into the main GC. By measuring the volume of air that passed over the cryogenic trap and the volume sampled by the GC a sample concentration factor can be determined and then used to back-calculate the original sample concentration. The cryogenic sample concentration step can effectively increase the sample volume, and therefore the detection sensitivity, by factors of 1000 or more. However, cryogenic sample concentration is not suitable for all species and matrix gases. In the case of many sulphurous compounds the use of a cryogenic trap can caused significant repeatability problems due to various effects including variable surface absorption/desorption in the trap, thermal decomposition during

the trap heating phase, and chemical conversion in the trapping line. For these reasons, cryogenic pre-concentration was not used for the sulphur chemi-luminescence GC measurements.

5.3.2 GC with Flame Ionisation Detection (FID)

The flame ionisation detector (FID) is one of the most commonly used detectors in gas chromatography because it is a sensitive general-purpose instrument for the analysis of organic compounds. The basic principle involves burning organic molecules in a hydrogen flame. The resulting ions are accelerated towards a cathode by means of a potential difference across the flame. A current flows at the cathode and is proportional to the amount of organic material ionised by the flame.

Table 5.3 – GC-FID Measurements of Multi-component Hydrocarbon Standard

Species	Concentration (ppb)	Uncertainty (ppb)	Odour Threshold (ppb)
Ethane	21.4	0.9	
Ethene	14.9	0.6	
Ethyne	31.4	1.3	800,000
Propane	16.7	0.7	
Propene	27.6	1.1	22,400
n-butane	6.6	0.3	800,000
i-butane	15.5	0.6	800,000
Trans-2-butene	11.4	0.5	
Cis-2-butene	18.9	0.8	
1-butene	22.7	0.9	6,000
1,3-butadiene	19.3	0.8	455
n-pentane	17.2	0.3	
i-pentane	48.8	1.0	
Trans-2-pentene	46.5	0.9	
Cis-2-pentene	25.4	0.5	
n-hexane	19.9	0.4	
2-methylpentane	10.0	0.2	
3-methylpentane	24.5	0.5	
Isoprene	40.2	0.8	
n-heptane	32.1	0.6	220,000
Benzene	13.1	0.3	8650
Toluene	30.7	0.6	160
Ethylbenzene	21.8	0.4	
m-xylene	16.8	0.3	16
o-xylene	7.5	0.2	16
1,3,5-trimethyl benzene	3.6	0.1	
1,2,4-trimethyl benzene	6.0	0.1	

FID detection is suitable for a wide range of volatile organic compounds. Table 5.3 shows the measurement uncertainty associated with the GC-FID analysis of a multi-component standard containing trace levels of a range of hydrocarbons. The odour thresholds for these

species (where known) are also indicated. In general, the odour thresholds for these simple hydrocarbons are relatively high and FID detection is therefore a suitable method for odour measurements of these species.

5.3.3 Sulphur Chemiluminescence

A GC detector option of particular relevance to measurements of odiferous species is the use of a sulphur chemi-luminescence detector (SCD). The SCD is extremely sensitive to the presence of sulphur containing compounds. The detection process has two stages. The first stage is the formation of sulphur monoxide in the presence of a hydrogen flame (much like the FID), however the second stage is based on the chemiluminescent reaction of sulphur monoxide with ozone to form sulphur dioxide and a photon. The photons are detected by a blue-sensitive photomultiplier tube.

A series of measurements of the sulphurous odour standards (described in Section 3.2) were performed to assess the applicability and sensitivity of this technique to some of the key odour species.

The first measurements were made using one of the multi-component odour standards containing approximately 200 ppb of hydrogen sulphide, dimethyl sulphide and ethanethiol in a balance gas mixture of methane and carbon dioxide (Cylinder 5600088 - see Section 3.2.2). A low volume regulator was used to flow the sample gas rapidly into a Tedlar bag (flow rate ~500 ml/sec). A 0.15 ml sample from the Tedlar bag was then injected directly into the SCD/GC through all-fluorinated pipework to minimise wall-losses. The estimated detection limits for the 0.15 ml sample volume was 50 ppb for hydrogen sulphide, 16 ppb for dimethyl sulphide and 5 ppb for ethanethiol. It should be noted that the sensitivity of the measurements would be expected to improve if the balance gas was nitrogen rather than methane and carbon dioxide. This is because of the effect of large quantities of methane on the flame ionisation stage, which reduces the efficiency of sulphur dioxide production

The level of improvement achievable in a nitrogen matrix was demonstrated in the second experiment. In this case Tedlar bag sampling was used in the analysis of a 100 ppb hydrogen sulphide standard (binary standard with nitrogen as the matrix gas), and the detection limit for a 1 ml sample was 1 ppb. This represents an eight-fold improvement in the detection sensitivity over the measurements made in methane/carbon dioxide described above.

Measurements of a 60 ppb carbonyl sulphide standard (binary standard in nitrogen) were made by direct sampling through a low-volume regulator. The detection limit for a 1 ml sample volume was 0.5 ppb.

Direct sampling was also used for the measurement of carbon disulphide and sulphur dioxide (both in nitrogen). In both cases the concentration of the standard was 100 ppm, much higher than for the previous standards. The relatively high concentrations meant that the SCD has to be run in low sensitivity mode with a sample volume of only 0.04 ml. Even under these conditions a detection sensitivity of approximately 125 ppb was demonstrated for both species.

Table 5.4 summarises the result of the GC-SCD measurements, with the detection sensitivities normalised to a sample volume of 1 ml. It should be noted that, in all of the results discussed here and in following sections, the detection limit is defined as the concentration required to give a signal three times the measured signal-to-noise ratio (where

the noise level is defined as the peak-to-peak variation in the background signal close to the relevant peak). This therefore represents a fairly conservative estimate of the achievable detection limit.

Table 5.4 Estimated Detection Sensitivities for a Range of Odorous Species using GC-SCD Detection and a 1 ml Sample Volume

Species	Matrix Gas(es)	GC-SCD Sensitivity (ppb)	Odour Threshold (ppb)
Hydrogen Sulphide	CH_4/CO_2	8	0.5
Dimethyl Sulphide	CH_4/CO_2	2	0.25
Ethanethiol	CH_4/CO_2	1	0.15
Hydrogen Sulphide	N_2	1	0.5
Carbonyl Sulphide	N_2	0.5	10
Carbon Disulphide	N_2	<5	30
Sulphur Dioxide	N_2	<5	470

As can be seen from the results table all the sensitivities for measurements in nitrogen are close to or below the odour threshold, and even the sensitivities with the less suitable methane/carbon dioxide matrix are within a order of magnitude of the threshold. Significantly higher sensitivities could be achieved if a larger sample volume was used. However, this would require the use of a pre-concentration stage and lead to the increased repeatability uncertainties discussed in Section 5.3.1.

5.3.4 GC-Mass Spectrometry (GC-MS)

The mass selective detector (MSD) is a general purpose detector, unlike the SCD which is specific to sulphur containing compounds. The detection method is based around a low resolution quadrupole mass spectrometer. After eluting from the GC column the sample is ionised using electron impact. The resulting ions are accelerated into an area of the spectrometer where they are sorted into order of increasing mass by the use of a quadrupole magnetic field. The ions are then sequentially accelerated in order of mass towards an electron multiplier and are quantified as a measured current. The resulting measurement of the ion fragmentation pattern made up from different masses of varying intensities can be used to positively identify chemical species.

The GC-MS can be run in two different modes. In Total Ion Counting (TIC) mode the abundance of all the ions (within specified mass limits) exiting the GC column are measured. This mode allows the ion fragmentation pattern to be monitored for different retention times, and is ideally suited to the measurement of multiple species, and the identification of unknown components. The alternative operating mode is Single Ion Monitoring (SIM), where the abundance of a specific ion mass is measured against GC retention time. This mode gives higher sensitivity than the TIC mode, but each measurement can only be targeted on a single species (or, more accurately, a single ion).

General Measurements of Odorous Species

A series of GC-MS measurements were made of various odour standards. Tables 5.5 and 5.6 summarise the results of these measurements for both TIC and SIM modes. The sensitivities in these tables have been normalised to a one litre sample volume. It should be noted that

this is 1000 times the sample volume used for the GC-SCD sensitivities given in Table 5.4. The TIC results show ppb sensitivity for a wide range of species, while switching to SIM mode results gives, on average, an eight-fold improvement in the detection sensitivity of the GC-MS technique.

Table 5.5 Summary of GC-MS Sensitivities when Operating in TIC Mode

Species	Concentration of Standard (ppb)	Sample Volume (ml)	Signal-to-Noise Ratio	GC-MS Sensitivity (ppb)	Odour Threshold (ppb)
Hydrogen sulphide	9600	100	59.5	48	0.5
Carbonyl sulphide	63.6	300	11.4	5.0	10.2
Pent-1-ene	4990	100	392	3.8	2
di-methyl sulphide	200	100	22.0	2.7	0.25
1-butanol	59600	20	880	4.1	30
Benzene	63.1	300	151	0.38	8650
Toluene	107.1	300	532	0.18	160
Ethylbenzene	51.9	300	450	0.10	500
m- & p-xylene	63.1	300	495	0.11	16
o-xylene	33.1	300	324	0.09	16

Table 5.6 Summary of GC-MS Sensitivities when Operating in SIM Mode

Species	Concentration of Standard (ppb)	Sample Volume (ml)	Signal-to-Noise Ratio	GC-MS Sensitivity (ppb)	Odour Threshold (ppb)
Hydrogen sulphide	9600	100	392	7.3	0.5
Carbonyl sulphide	63.6	300	171	0.33	10.2
Pent-1-ene	4990	100	1134	1.3	2
di-methyl sulphide	200	100	164	0.37	0.25
1-butanol	59600	20	6128	0.58	30
Benzene	63.1	300	1334	0.042	8650
Toluene	107.1	300	4304	0.022	160
Ethylbenzene	51.9	300	3650	0.013	500
m- & p-xylene	63.1	300	3119	0.018	16
o-xylene	33.1	300	2106	0.014	16

Thiol Measurements

The potential of the GC-MS technique for the measurement of trace thiol concentrations was investigated. Initial measurements of the ethanethiol standard showed complete conversion of the ethanethiol into diethyl disulphide. This highlights the problems of using cryogenic pre-concentration in the measurement of sulphurous species (see section 5.3.1). This is particularly the case for primary thiols, such as methanethiol and ethanethiol, which are easily oxidised into the disulphide form[56]. This result suggests that, while GC-MS measurements of primary thiols are particularly difficult, the presence of disulphide in an analysis could imply the presence of the primary thiol in the original sample gas.

Thiol measurements continued with a 4.97 ppm binary standard of 2,2-dimethyl ethanethiol. This species is one of the tertiary thiols, which are generally more stable than the primaries, and which are some of the most odorous species known. The presence of unconverted thiol was observed by the MS detector, with an average detection sensitivity of 0.851 ppb in TIC

mode and 0.357 ppb in SIM mode. This compares to an odour threshold of 0.01 ppb. It should also be pointed out that there was considerable scatter in the results of repeated measurements, particularly in the SIM measurements. Some conversion of the 2,2-dimethyl ethanethiol to tert-butyly disulphide was observed. The level of conversion was found to be influenced by the sorbent material used, with 10% to 18% conversion on Tenax TA, and 8% to 10% on glass beads (when in TIC mode).

The results of the thiol measurements show that sub-ppb sensitivity is achievable with the GC-MS. However, this is typically well above the odour threshold for this class of species and significant problems remain with the accuracy and repeatability of the technique. The majority of these problems are likely to be due to the cryogenic pre-concentration stage, and further work would be required to identify the best materials and conditions in order to optimise the performance and repeatability of the GC-MS method in this application.

Amine Measurements

In order to test the sensitivity of the GC-MS technique for measurements of amines a series of measurements were made of the sec-butylamine binary standard (4.97 ppm in nitrogen). Three measurements were made of a 600 ml sample using basic glass traps. This experiment gave rise to considerable scatter in the measured peak areas. However, the best run of the three gave a minimum detectable concentration of 7.8 ppb in TIC mode, and 3.0 ppb in SIM mode (in both cases assuming a one litre sample). These results indicated that, with a little additional work on sample line passivation, and optimal GC-MS operating conditions, measurements at or below the odour threshold of 2 ppb should be feasible.

Chiral Stationary Phase GC

One of the unusual properties of odorous species is that optically active stereoisomers or enantiomers (chiral compounds) are known to be able to posses different odour qualities. The most illustrative examples of this phenomenon are the enantiomers of carvone and menthol[45].

The increasing interest in the odour qualities of these materials was initiated by the development of new chromatographic separation techniques on optically active stationary phases, or chiral stationary phases (CSP)[57]. A recent review[58] has shown that at present more than 230 different CSPs for GC have been described in the literature, with more than 40 of these being now commercially available. Recently, isotope dilution techniques have also been applied in the study of enantiomeric odorous compounds as a test of authenticity of product[59]. Several reviews have been published the odour qualities of chiral compounds[60-62], including the role of chirality in structure-odour relationships[63]. See Annex A3 for a further discussion of the relationship between chirality and odour.

Proposed Methodology for Ambient Odour Analysis

As can been seen from the results presented in the previous sections, the GC-SCD measurement method is, in general, more sensitive than the GC-MS for concentration determination of specific sulphur-bearing species. However, the results can be difficult to interpret if a totally unknown sample is introduced into the system. The results from the GC-MS in TIC mode show the capability to make simultaneous measurements of a wide range of odorous species at ppb sensitivity levels, and the ability to identify unknown

components from their ion fragmentation patterns. It is therefore proposed that the measurement method for an ambient sample containing unknown odiferous species should use the following basic procedure :

1. Screening measurement by GC-MS in total ion counting mode with cryogenic pre-concentration. This preliminary measurement would enable the assessment of the general composition of the sample, the types of species present, and the general concentration levels of the pollutants. This can be followed by one or more of the following three options, depending on the results of the initial screening.

2. If the screening indicates the presence (or likely presence) of important sulphur-bearing compounds, then GC-SCD measurements should be performed to evaluate the concentration levels present with the best sensitivity and accuracy.

3. If the screening indicates the presence of important hydrocarbon species (including oxygenated and/or halogenated hydrocarbons), then GC-FID measurements should be performed to evaluate the relevant concentration levels.

4. If species are identified that are not suitable for standard or sulphur-GC analysis, then Single Ion Measurements should be made with a GC-MS system targeted on those specific species.

Such an analysis would require only a few litres of ambient air.

The technical possibilities and understanding of ambient odour measurements are developing rapidly, and the procedure given above should be seen as a preliminary conclusion, rather than the final solution to the problem of ambient odour measurement.

6 STANDARDISATION AND CALIBRATION OF ARTIFICIAL OLFACTOMETERS (ELECTRONIC NOSES)

6.1 BACKGROUND TO ELECTRONIC NOSE MEASUREMENTS

An electronic nose can be defined as 'an instrument which comprises an array of electronic chemical sensors with partial specificity and an appropriate pattern recognition system, capable of recognising simple or complex odours (and other gaseous mixtures)'[64]. The ability of an electronic nose to rapidly discriminate between slight variations in complex mixtures makes the techniques ideal for on-line process diagnostics and screening across a wide range of application areas. A recent international symposium on Olfaction and Electronic Noses[65] highlighted the variety of monitoring applications currently being researched. Examples included :

- Detection and identification of micro-organisms in headspace samples
- Qualitative and quantitative analysis in the petroleum industry
- Detection of amniotic fluid in vaginal smears
- Detection of TNT
  Development of a field odour detector for environmental applications
- Quality control applications in the automotive industry
- Discrimination between clean and contaminated cows teats in a milking system
  Analysis of cosmetic raw materials
  Differentiation of wine aromas
- Classification and degradation studies of olive oils
- Flavour analysis in foods

The sensors involved are based on a large number of physico-chemical principles, none of which is claimed to directly mimic the human nose. These include :

> electrochemical sensors - usually conducting polymers, semiconductors or metal oxides whose electrical conductivity changes as volatile molecules are absorbed;
> coated optical fibres, whose fluorescence changes in wavelength and intensity when gases are absorbed in the coating;
> piezoelectric elements whose properties change as material is absorbed;
> quartz microbalances which directly measure the mass absorbed onto a polymer coating.

The affinity of the volatile molecules for the surface of the sensor is a key factor in the suitability and selectivity of the different sensors.

An array of sensors (typically 10 to 20) with differing responsivity is used. The complex response to a particular sample is compared with the response from control samples using sophisticated pattern matching techniques such as those based on neural networks, which reduce the multi-parameter signal to perhaps two critical parameters that can be plotted simply. The sensor arrays are usually selected specifically for the application, and the instrument is trained for a given application using real samples.

It is important to note that electronic noses are not directly measuring the odour of the sample, as the sensors do not specifically respond to the odour of the sampled chemicals. A recent comparison of an electronic nose with a human panel has shown that the human nose

was more sensitive than its electronic counterpart. Also the electronic nose showed a linear response with change in odourant concentration, whereas the human nose exhibits logarithmic behaviour. However, in most of the application areas, the chemical changes measured by an electronic nose are indicative of a change in the odour, and this type of system may represent the first step in the development of automated, non-subjective odour measurement techniques.

6.2 EUROPEAN NETWORK ON ARTIFICIAL OLFACTORY SENSING (NOSE)

The majority of the work on electronic nose development is being performed by SMEs and University research groups, and it was recognised by the research community that many aspects of the developments, particularly those associated with calibration and standardisation required collaboration and knowledge transfer between the different groups. Therefore, the European NOSE network formed at the beginning of 1999 to provide "a forum for information exchange between users, researchers, developers and producers of devices and systems" with the overall aim of improving the "effectiveness of European R&D in artificial olfaction technologies"[66]. The Network currently has 92 members covering instrument manufacturers, industrial users, University research groups, and Government Laboratories including NPL.

6.3 REQUIREMENTS FOR STANDARDISATION

It has been recognised by the electronic nose R&D community that widespread uptake of the technology has been severely restricted by the lack of standardisation in this area[67]. Therefore, one of the Special Interest Groups of the NOSE network is concerned with 'Standards and Definitions of Terms'. The aims of this group are to:

- Develop and define terms necessary within the field of electronic noses in order to quantify more objectively instrumental performance characteristics;
  Develop and define acceptable objective instrumental performance characteristics and the associated test procedures;
- Seek to develop an internationally acceptable methodology for harmonisation of performance tests;
  Seek to define calibrations and tests to disseminate harmonised test procedures to the user community.

NPL have been closely involved in the activities of this group, building on our experience in the development of calibration and standardisation procedures for analytical measurement techniques. A number of knowledge transfer activities have taken place, the main one of which was Workshop at NPL on 17th March 2000. The 24 attendees represented a cross-section of the industrial companies developing and/or exploiting electronic nose technology, academic and government research groups, and National Metrological Institutes. The purpose of this workshop was to review the current status of standardisation within the Electronic Nose Community, and to develop an action plan for further developments in this area. A summary of the resulting discussions is included as Annex A5.

The conclusions from the workshop were that there was a clear requirement within the field of electronic nose measurement for the development of a traceability framework. All areas of the community recognised this and were keen for such a framework to be put in place.

However, a significant amount of work needs to be done before an acceptable International Standard could be written. The proposed mechanism to achieve this was for a core group of partners to prepare and submit an Expression of Interest to the European Commission. If acceptable this would be followed by a Dedicated Call for a two to three year collaborative project into the feasibility of using a limited number of reference artefacts to provide calibration and traceability for the use of electronic noses in the food industry. This project would involve input from manufacturers, users, research organisations, and National Measurement Institutes.

Following the workshop, NPL coordinated the preparation of the Expression of Interest, and this was submitted to the EC in June 2000. A copy of submitted document is included as Annex A6.

7 CONCLUSIONS

7.1 ODOUR STANDARDS

Traceable gas standards of key odorous species have been prepared gravimetrically and made available for dissemination. Binary standards, with trace levels of a single odorous gas in a matrix of nitrogen or air, have been developed to provide reference artefacts for the main types of odorous species, as well as targeting a number of specific industrial and environmental monitoring applications. The concentration levels in these standards has been set to follow the guidelines established by the CEN olfactometry standard (~2000 times the odour threshold). Multi-component odour standards, with trace levels of three odorous species in matrix of methane, carbon dioxide, (oxygen) and nitrogen, have been prepared to meet the odour monitoring requirements of the landfill and waste treatment industries.

7.2 MEASUREMENT OF ODOROUS GASES

An investigation took place into the best available techniques for the measurement of trace levels of odorous gases, such as might be found in ambient air samples. The study covered sampling and analysis methods, with gas chromatography identified as the principal analysis tool. Experimental research was carried out into the suitability of three GC-detection methods for odour applications. The odour standards described above were used as reference samples to determine the sensitivity of the different detectors.

The results of the study showed that flame ionisation detection was suitable for trace level measurements of basic volatile hydrocarbons, while mass spectrometric detection (in total ion counting mode) provided ppb-level sensitivities for a wide range of odorous species, as well as identifying unknown components in a mixture. The GC-MS sensitivity could be approved by an order of magnitude by switching to Single Ion Mode, but with measurements restricted to a single species at a time. The highest sensitivity for odorous species was given by sulphur chemi-luminensence detection, but limited to sulphurous species and requiring prior knowledge of the likely components in the sample. The accuracy of the measurements was generally limited by the repeatability of the sampling efficiency, particularly in the case of 'sticky' species. The use of suitably passivated components throughout the entire sample and analysis process represents a major element in making accurate odour measurements.

7.3 ODOUR CHARACTERSATION

The investigation of the relationship between inelastic tunnelling (and gaseous infrared absorption) spectra and perceived odour character did not provide any clear evidence of a link between the two. Basic models of odour perception probably over-simplify the actual mechanism for the detection and identification of different odours. In general these models attempt to relate the perception of a particular odour simply to the receptor response to that chemical. Other, perhaps critical, factors include the local chemistry and environment at the receptor, which may enhance or inhibit a receptors response to a particular molecule, and the way in which the brain interprets the signals from the odour receptors. One of the arguments presented for the latter view [68] is the similar bitter almond smell of benzaldehyde and hydrogen cyanide. These two species have very different physical and chemical characteristics and it is difficult to explain how they could trigger the same odour

detector response. However, when it is realised that both are volatile species produced by the breakdown of amygdalin – a flavour precursor found in natural almonds – then it seems feasible that the brain could associate the odour responses to either of these species with the same almond 'smell'. If this argument is correct, it would probably preclude the establishment of a deterministic odour scale, where the perceived smell could be directly related to the chemo-physical properties of the sampled molecules. However, improved knowledge of the sensing mechanism, and the properties of the odorous molecules that trigger the odour response, would provide important details in the study of olfaction, including information on the vast range of odour thresholds for different species, and possibly provide the ability to predict the likely smell of unknown chemicals.

Electronic noses, even if they do not employ the same sensors as the human nose, may have a significant role to play in the monitoring and characterisation of odours in the future.

8 ACKNOWLEDGEMENTS

The contributions of Luca Turin and George Walmsley to the discussions associated with this work are gratefully acknowledged. Other parties consulted include Barry Jones (Brunel University), Mike Woodfield and Nigel Gibson (AEA Technology), Ormonde Joel (Environment Agency) and Anton Alink (NMi, Delft).

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10 ANNEXES

Supporting documentation and additional information is contained in the following annexes.

A1 Preliminary Odour Report - This report was submitted to the NMSPU in March 1998, and summarises the work carried out on the odour project up to that point. (NB the original version of this report contained an Annex produced by Queens University, Belfast that is not included here)

A2 Example Results of GC-MS Measurements of Odiferous Species - Annex A2 contains example chromatograms of the GC-MS measurements made of the various odour standards. The results of these measurements are summarised in Section 5.3.4.

A3 Additional Information on Odour Characteristics – This annex contains three sections with additional background information on odour characteristics. Section 1 describes the 19 point 'primary' odour categorisation developed by Abbe. Section 2 outlines a model that defines 'odour space' with respect to 42 reference odours in terms of the odour descriptor and molecular structure. The final section reviews the odour characteristics of a range of chiral compounds.

A4 Data Summary from the Study of Inelastic Electron Tunnelling Spectroscopy and Infrared Absorption Spectroscopy - The complete results of the IETS and Infrared Absorption studies discussed in Sections 4.4.4 and 4.4.5 are presented in this Annex.

A5 Electronic-Nose Workshop Summary - Annex A6 contains the summary of the discussions at the Electronic Nose Workshop held at NPL in March 2000, organised on behalf of the European NOSE Network, Special Interest Group II – Standards and Definition of Terms (see Section 6.3).

A6 'Development of Standard Procedures and Protocols for the Characterisation of Electronic Noses' - Expression of Interest Submitted to the EC Growth Programme - Annex A7 contains the EC Expression of Interest prepared as a result of the Electronic Nose Workshop.

A7 Glossary of Odour Descriptive Terms - The final Annex provides a glossary and definition of some of the key terms used in the description of odours.

ANNEX A1 –

PRELIMINARY REPORT ON ODOUR MEASUREMENTS AND STANDARDS

REQUIREMENTS FOR GAS CONCENTRATION STANDARDS FOR ODOUR MEASUREMENTS, AND AVAILABILITY OF ELECTRON TUNNELLING SPECTRA OF ODOROUS COMPOUNDS

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March 1998

1 INTRODUCTION

This Report has been prepared for the National Measurement System Policy Unit of the DTI as part of the Valid Analytical Measurement Programme's Odour and Indoor Air Project (milestones 1 and 2).

2 BACKGROUND

2.1 DEFINITION OF ODOUR

Smell is the least well understood of our senses, and it should be emphasised that odour is defined on a subjective rather than objective basis. The ISO definition of odour is:

> *the organoleptic attribute perceptible by the olfactory organ on sniffing certain volatile substances. (ISO 5492)*

The attribute of a substance that makes it perceptible to the human nose is not yet, and perhaps cannot be, defined in terms of simple physico-chemical properties of the molecules concerned. For the time being, therefore, any true assessment of odour depends ultimately on the use of people and their subjective olfactory response.

2.2 THE DISTINCTION BETWEEN THE CONCENTRATION AND CHARACTER OF AN ODOUR

Even without any understanding of the olfactory mechanism, a quantitative measurement of the concentration or strength of an odour can be provided by the

technique known as olfactometry. This is purely concerned with the detectability of an odour by a "standard" human nose, and has no regard to the character or description of the odour. It is described in more detail in Section 2.3. It is the concentration of odour which is most relevant in the area of complaints about industrial sources, and hence regulation.

The character of an odour is at present defined on an ad hoc basis, with different scales being employed for different particular uses. Individuals with a highly sensitive and highly trained olfactory sense are of great importance in the food and drink industry, and most particularly in the perfumery industry. Unlike in olfactometry, they are used generally in a qualitative rather than quantitative manner, to describe smells rather than to quantify them. Their role can to some extent be mimicked by "electronic noses", described in Section 2.4.

2.3 ODOUR CONCENTRATION MEASUREMENT - OLFACTOMETRY

The technique of olfactometry consists of presenting a panel of human assessors with an odorous gas which can be quantitatively diluted with neutral (odour-free) gas. The amount of dilution required for the odorous gas to reach its detection threshold for the panel yields a measurement of odour concentration.

One key problem with the technique is the large variability of olfactory sensitivity within the general population. To do a valid measurement with a random selection of people on the panel would require an impractically large panel. This problem is overcome by the careful selection of panel members. In the CEN TC264 WG2 draft standard, which is closely based on the Dutch approach developed over the last 10 years or so, it is proposed that the panel members are standardised by their sensitivity to one specific odorant: n-butanol. In this way the olfactometer expresses odour concentrations in terms of "n-butanol mass equivalents".

The accepted odour threshold for n-butanol is 40 ppb. In this system, then, an accurate concentration standard for n-butanol is required for the proper assessment of the panel on a particular dilution instrument. Typical olfactometers can dilute the odorous gas by 100x to 250,000x , and the assessment of the panel uses a butanol standard at 60 ppm, which is then diluted by around 2,000x, ie mid-range for the instrument, to reach the odour threshold.

At present it is understood that the only producer of primary standards for butanol is NMi in Delft, which provides traceability for a small number of accredited suppliers in Holland.

The dilution system of the olfactometer can of course be calibrated with non-odorous gas mixtures, and carbon monoxide mixtures are commonly used for this purpose.

The labour intensiveness of olfactometry means that it is not commonly practiced. Indeed the odour thresholds of only a very few compounds have been determined reliably by this technique.

2.4 ODOUR CHARACTER MATCHING TECHNIQUES - ELECTRONIC NOSES

There are a number of commercial and research-based instruments which perform analyses of certain volatile substances using an array of sensors, and these are often referred to as "electronic noses". Trade names include Alphamos, AromaScan and Neotronics. It should be emphasised that they do not measure odour, and hence do not strictly fall within the field of odour measurements, but they are worth describing here briefly.

The sensors involved are based on a large number of physico-chemical principles, none of which is claimed to mimic the human nose. These include electrochemical sensors - usually conducting polymers, semiconductors or metal oxides whose electrical conductivity changes as volatile molecules are absorbed; coated optical fibres, whose fluorescence changes in wavelength and intensity; piezoelectric elements whose properties change as material is absorbed; and quartz microbalances directly measuring the mass absorbed onto a polymer coating. The affinity of the volatile molecules for the surface of the sensor is a key factor in the suitability and selectivity of the different sensors.

An array of up to around 12 sensors with differing responsivity is used. The complex response to a particular sample is generally compared with the response from control samples using sophisticated pattern matching techniques such as those based on neural networks, which reduce the multi-parameter signal to perhaps two critical parameters that can be plotted simply.

These systems are used in the food and drink industry to monitor, for example, whether a brewing process is proceeding normally. The sensor arrays are usually selected specifically for the application, and "calibrations" performed with real samples. In practice they are used to match some particular properties of volatile molecules, and this may fortuitously match their odour character at the same time.

There might be value in well-characterised gas mixtures being used by the sensor manufacturer when assessing sensors. However, an accurate measurement of response would not be needed. It may also be useful to observe the performance of the pattern recognition software when challenged with a series of known gas mixtures. The field of electronic noses will be investigated more fully later in the project.

2.5 POSSIBLE OBJECTIVE ODOUR CHARACTERISATION - THE ELECTRON TUNNELLING THEORY

In an ideal world, odour measurement would be performed using an instrument which responded to the same physico-chemical properties as the nose, analogously to the spectral composition of light and sound being used for sight and hearing. This should provide objective measures of both the concentration and character of an odour.

It needs to be emphasised at this point that even a "nasal receptor with readout" would not necessarily be capable of providing the means to measure odour adequately. The sampling of the volatile molecules, in particular their transport to the receptors across a mucous layer and their binding to the receptor, will be a crucial part of the smelling process - biology and biochemistry will clearly play a far larger role for smell than for sight and hearing. Also, there may well be a significant role for the brain in interpreting the receptor signals as odour sensations, so that data processing becomes as important as data collection.

There is not yet a consensus on the physico-chemical attributes of volatile molecules which are detected by the nasal receptors. In general, theories fall into two groups. Firstly, those which postulate receptors based on properties related to the physical structure of the molecule, such as its shape or the geometric arrangement of electric charge. The second group postulates receptors which respond to features in the infrared spectra of the molecules.

The spectral postulate has been around for many years, as correlations between spectral features and odours have been apparent. Until recently, however, there was no plausible mechanism for the receptor to detect spectral features. A mechanism has recently been postulated by Luca Turin of University College, London who proposed that the features are observed by the effect of the molecule's presence on tunnelling currents between closely spaced (organic) electrodes - a distinct and far more plausible mechanism than any detection of features by absorption of photons.

Infrared features in the range 0 - 4000 cm^{-1} translate into tunnelling features at potential differences of 0 - 480 mV.

A molecule's infrared absorption spectrum is closely related to its electron tunnelling spectrum, but specific features have different strengths in the two cases because of different selection rules, and the effects of the molecule being adsorbed onto a surface.

Although the situation is far from fully resolved, the evidence that tunnelling spectroscopy plays a central role in the detection of odour is persuasive. Moreover, as a relatively simple physical property is involved, there exists the possibility of developing an instrument which can at least increase the objectivity of odour measurements. One of the aims of this project is to investigate this possibility.

3 INDUSTRIAL PROCESSES WHICH MAY REQUIRE MONITORING

Public complaints about odour tend to be caused by the following industrial sectors:

rendering plants, producing complex mixtures of mercaptans and amines;

solvent based plant, producing hydrocarbons;

foundries, which can produce amines, phenols, formaldehyde and ammonia;

sewage works, producing hydrogen sulphide, ammonia, skatoles, mercaptans, amines and indoles;

landfill sites, producing mercaptans

oil/asphalt plant, producing hydrocarbons, sulphides and mercaptans;

agriculture eg chicken farms.

Combustion sources are not normally a problem, though carbonyl sulphide (OCS) is thought to be a problem from some cement kilns.

The Environment Agency is looking into requirements for odour measurements as part of regulatory monitoring, but has no priorities defined yet.

The aircraft industry is concerned about odorous hydrocarbon emissions from jet engines, the most likely problems being from 1-pentene, 1-butene, formaldehyde, acetaldehyde, and benzaldehyde.

The specific requirements for industrial monitoring are therefore not clear, but are likely to involve the species mentioned above.

4 PRIORITY GAS MIXTURES REQUIRED

The CEN standard's emphasis on n-butanol provides good grounds for primary mixtures at around 60 ppm to be produced, for comparison with those of NMi.

Some other odorous mixtures with industrial relevance are already being addressed under specific milestones in the VAM programme: carbonyl sulphide, formaldehyde and ammonia. The species considered most useful to add to the VAM odour project are 1-pentene, ethyl mercaptan, and hydrogen sulphide.

By analogy with the concentration of n-butanol, it is proposed to prepare mixtures of these species at concentrations of about 2,000 times the odour threshold, ie

n-butanol	60 ppm
1-pentene	4 ppm
ethyl mercaptan	200 ppb
hydrogen sulphide	1 ppm

5 DETERMINATION OF TUNNELLING SPECTRA

5.1 PLANAR TUNNELLING SPECTROSCOPY

There were extensive studies of the vibrational modes of molecules by tunnelling spectroscopy in the 1970s and early 1980s. The technique, known as Inelastic Electron Tunnelling Spectroscopy, looked at tunnelling through single molecular layers of the species of interest, adsorbed onto oxide surfaces, which were in turn grown on top of a planar metal electrode. The upper electrode was formed by a metal layer deposited over the adsorbate. Vibrational features contribute to the tunnelling current above characteristic voltages, and are best observed in the second derivative of the current-voltage curve. To obtain well resolved spectra, the measurements were carried out at very low temperatures (2K). Because the bonding between the molecules and the oxide layer changes the symmetry of the molecule

and hence its vibrational modes, the spectrum actually describes the combination of the monolayer and the oxide layer.

Many tunnelling spectra were obtained by this technique, and they have been collated in the reference given below (Walmsley and Tomlin 1985). It reprints 156 spectra of monolayers on aluminium oxide, include several odorous species such as thiols and pyridine. There are also 15 spectra of absorbates on magnesium oxide.

There are, however, several reasons why spectra obtained in this way may not mimic the postulated nasal mechanism, and why it is a limited technique for further work. A key requirement for the technique is that the test molecule adsorbs chemically (chemisorbs) as a near-monolayer to the oxide layer. There are many odorous molecules which would not do this on convenient materials, and for those that do, the surface bond may remove or shift the vibrational feature of most interest for its odorous properties.

Moreover, the IETS spectrum will be influenced by the electric properties of the surrounding material, in this case metal, which is likely to produce a significantly different spectrum from that observed by any nasal receptor.

According to Walmsley very little work of note has taken place in this area since 1985.

5.2 SCANNING TUNNELLING MICROSCOPE TECHNIQUES

The use of a scanning probe rather than an upper electrode is superficially a very attractive improvement over the planar technique, as it holds the promise of spectral measurements of single molecules. Preliminary work with sorbic acid on graphite (Smith et al 1987) and 1-octadecanethiol on gold (NPL investigation at Queen's University, Belfast) has demonstrated some of the techniques, but cannot yet be said to have produced useful spectra. It should be emphasised that the tunnelling mechanism in the STM technique is significantly different to the planar situation, but may be more analagous to the postulated nasal receptor.

With the atomically smooth electrode surfaces and large ordered monolayers commonly used in STM, it may be feasible for the molecules to be physisorbed (rather than chemisorbed) to the lower electrode, enlarging the range of molecules that could be investigated. The use of a metal substrate will alter the spectrum in the same way as for the planar technique, but as zinc is thought to play a key role in the nasal receptor this may make the alterations more appropriate.

The geometry of the STM technique is also likely to affect the tunnelling characteristics, such as the ratio of tunnelling by elastic and inelastic processes, and hence the spectrum. It may be possible to observe the tunnelling spectrum using only the first derivative of the current-voltage curve, but the intrinsically low currents may make signal-to-noise a problem.

The technique has not been extensively tried for the purpose of tunnelling spectroscopy, and although there are significant technical obstacles there are interesting possibilities to be explored.

5.3 CALCULATION OF TUNNELLING SPECTRA

As part of his investigation of the tunnelling spectroscopy theory of odour, Turin (1996) adopted the approach of calculating the expected tunnelling spectra for a particular molecule in a biological environment, using an algorithm called CHYPRE. This used software to calculate the theoretical mode frequencies and partial charges, and to produce spectra modified to take into account local effects and thermal broadening.

The details of this algorithm are commercially sensitive and, together with the lack of suitable measured spectra, it is therefore difficult to judge the effectiveness of this method.

Calculation of spectra is undoubtedly the most practical method for investigating the plausibility of the theory, although it does not in itself help in the development of relevant instrumentation.

6 SUMMARY

The field of odour measurement has been briefly summarised. Priority gas concentration standards have been identified as n-butanol at 60 ppm, 1-pentene at 4 ppm, ethyl mercaptan at 200 ppb, and hydrogen sulphide at 1 ppm.

There is a very interesting possible relationship between a molecule's tunnelling spectrum and its odour character. The spectrum in question, however, will depend on how the molecule is bonded to the surface, and on the local environment. A nasal receptor would probably involve the odorous molecule binding to a protein molecule in a protein/water environment at room temperature.

Many measured spectra of odorous molecules adsorbed onto metal oxide layers at low temperatures have been published. Techniques for obtaining spectra using Scanning Tunnelling Microscopy probes are showing promising results. However, further research is needed to investigate the relevance of such results to the situation in a postulated nasal receptor, and to determine the means by which spectra most closely related to the odour characteristics of a molecule can be determined. Methods for theoretical derivation of the relevant tunnelling spectra are also important.

It should also be noted that a working description of the sensation of smell is likely to involve other complex factors as well as the receptor itself.

7 ACKNOWLEDGEMENTS

The contributions of Luca Turin and George Walmsley to the discussions associated with this work are gratefully acknowledged. Other parties consulted include Mike Woodfield and Nigel Gibson (AEA Technology), Ormonde Joel (Environment Agency) and Anton Alink (NMi, Delft).

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ANNEX A2 –

EXAMPLE RESULTS OF GC-MS MEASUREMENTS OF ODIFEROUS SPECIES

This annex contains example chromatograms of the GC-MS measurements made as part of the VAM Odour project. A summary of the measurements is given in the following table.

Figure	Species	Conc. (ppb)	Ret. Time (mins)	Comments
A2.1	pent-1-ene	5,000	3.41	
A2.2	***BTEX***			
	Benzene	63	2.17	
	Toluene	107	3.51	
	ethylbenzene	52	6.11	
	o-xylene	63	6.34	
	m- & p-xylene	33	6.96	
A2.3	***30 comp nat gas.***			
	2-Me-pentane	4.8	3.80	
	3-Me-pentane	7.4	3.96	
	n-hexane	8.4	4.30	
	Benzene	14.4	5.29	
	cylcohexane	12.7	5.31	
	n-heptane	6.4	6.59	Other species unresolvable
	Toluene	11.1	8.93	
	ethylbenzene	4.6	12.79	
	o-xylene	3.7	13.00	
	m-xylene	5.64	13.51	
	1,2,4-tri-Me-benzene	2.84	14.93	
	1,3,5-tri-Me-benzene	3.34	15.28	
A2.4	Me2S	200	3.07	Part of multicomponent mixture 5600088
A2.5	OCS	10,000	2.48	
A2.6	EtSH	199	N/A	100% converstion to (EtS)2 (rt = 14.02min)
A2.7	1-butanol	59,000	5.18	
A2.8	H2S	10,000	2.40	
A2.9	t-butylmercaptan	5,000	4.09	~10% conversion to (Me3S)2 (rt = 10.01 min)
A2.10	sec-butylamine	5,000	3.99	

Figure A2.1 GC-MS Chromatogram of Pent-1-ene Binary Standard

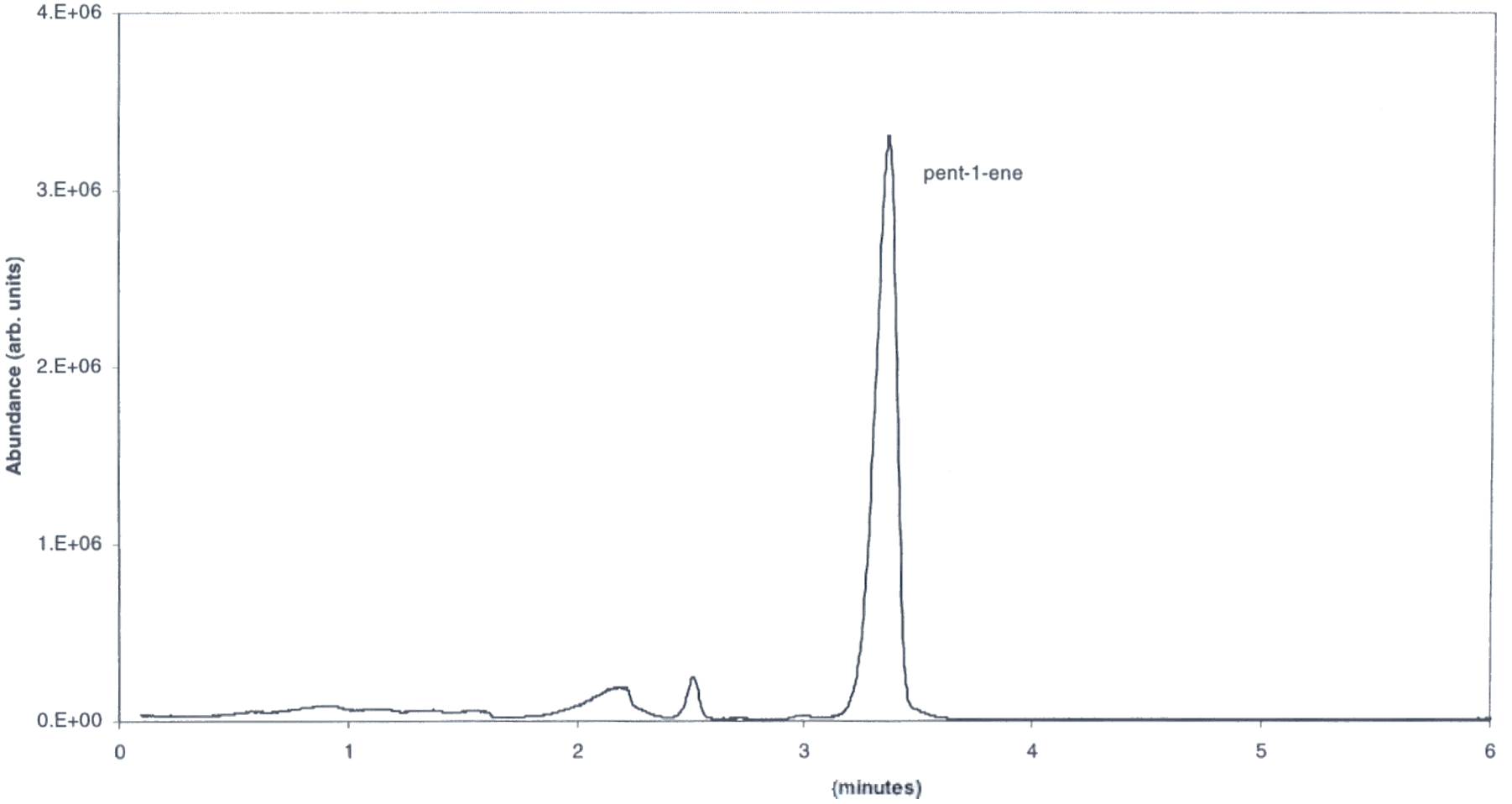


Figure A2.2 GC-MS Chromatogram of Multi-component BTEX Standard

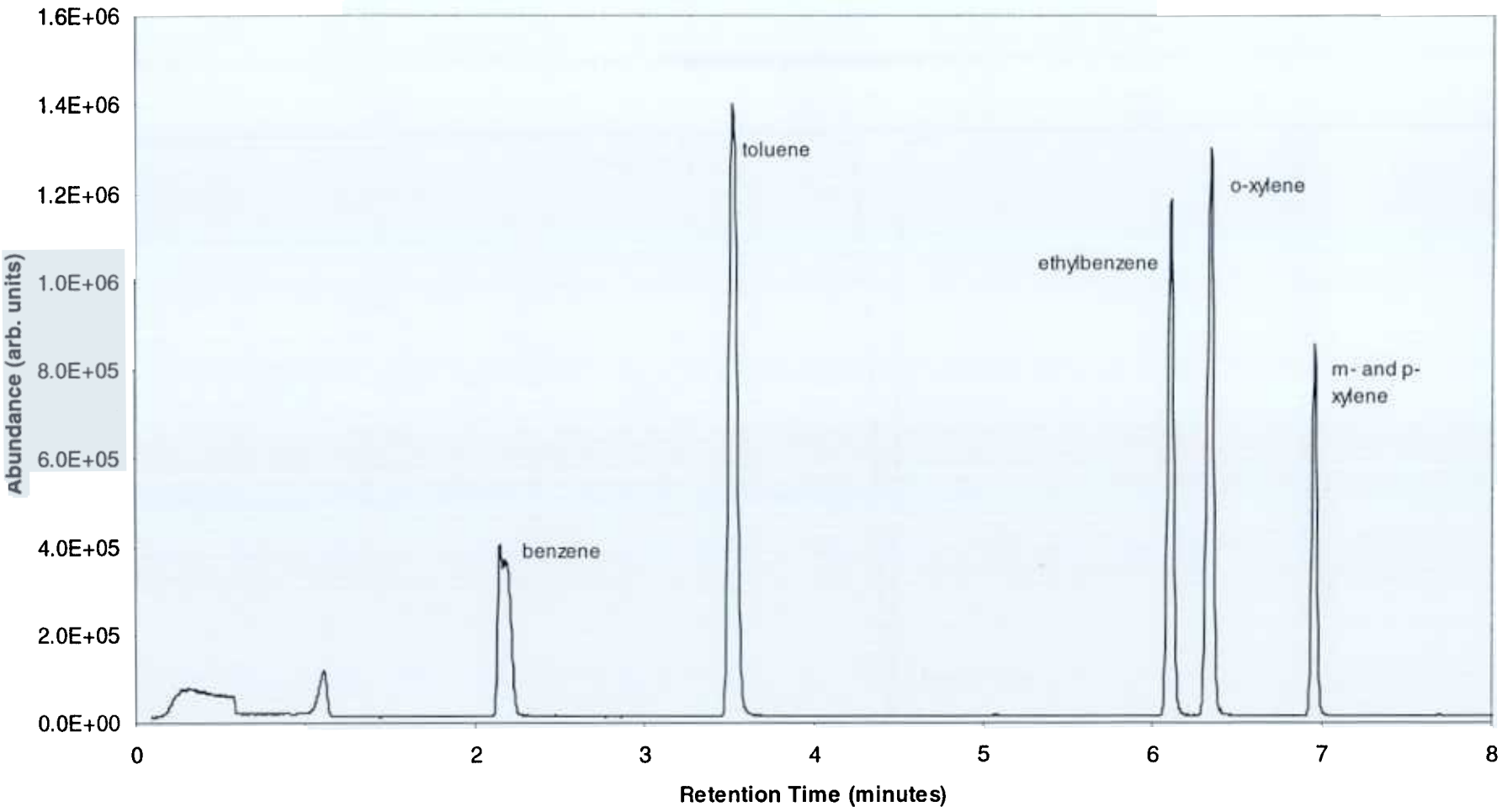


Figure A2.3 GC-MS Chromatogram of Multi-componenet Natural Gas Standard

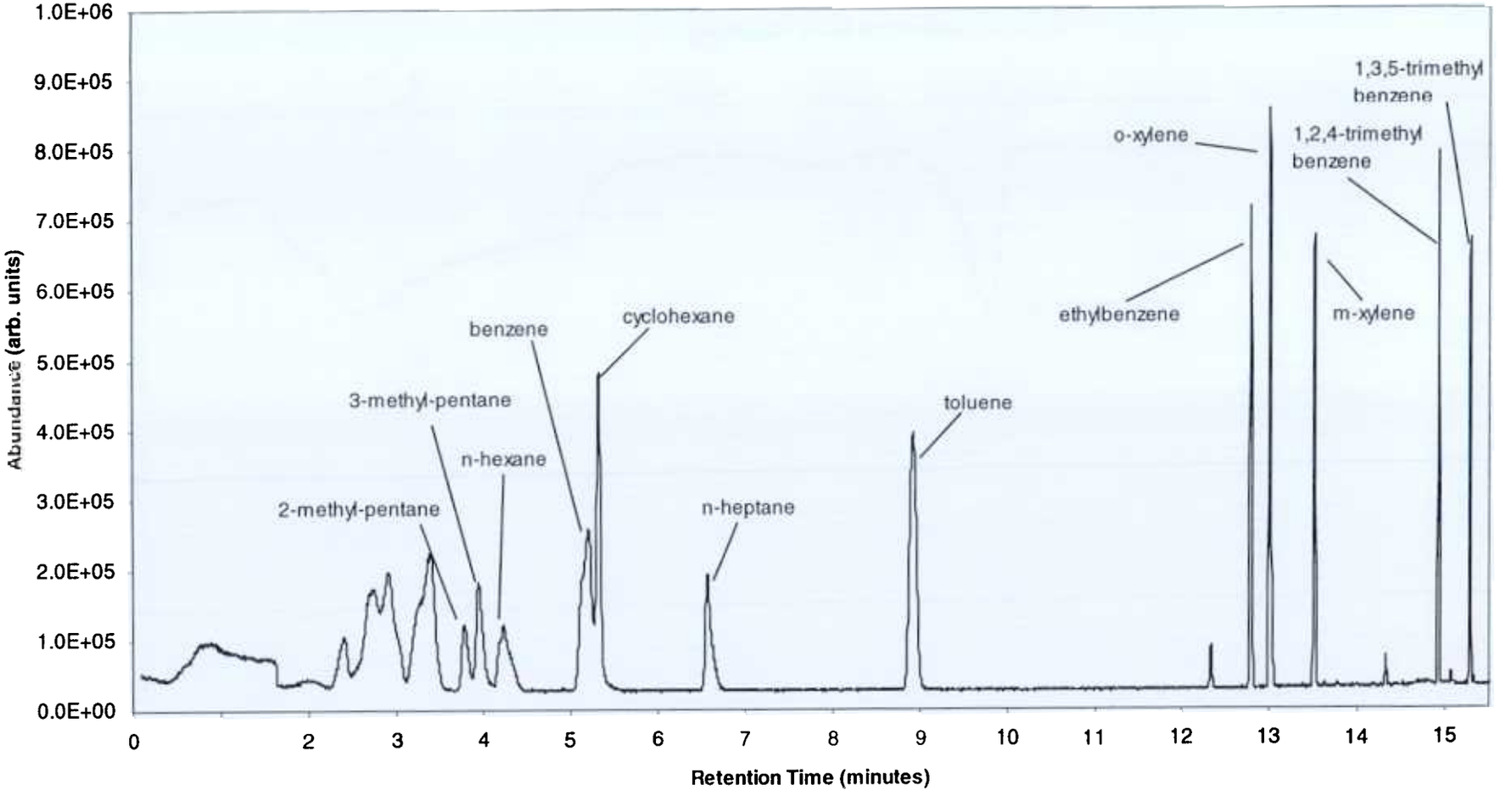


Figure A2.4 GC-MS Chromatogram of Multi-component Standard containing Dimethylsulphide

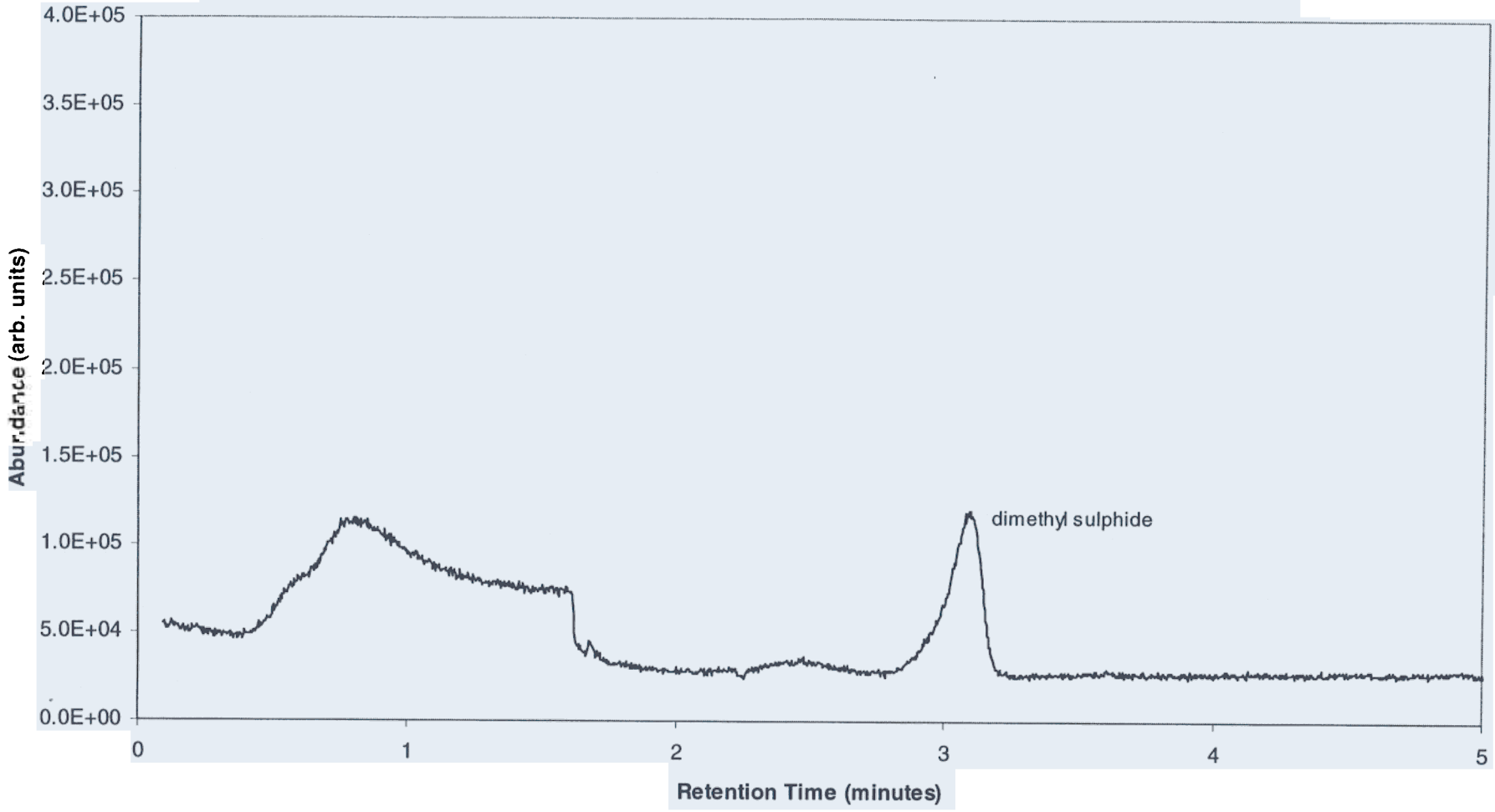


Figure A2.5 GC-MS Chromatogram of Binary Carbonyl Sulphide Standard

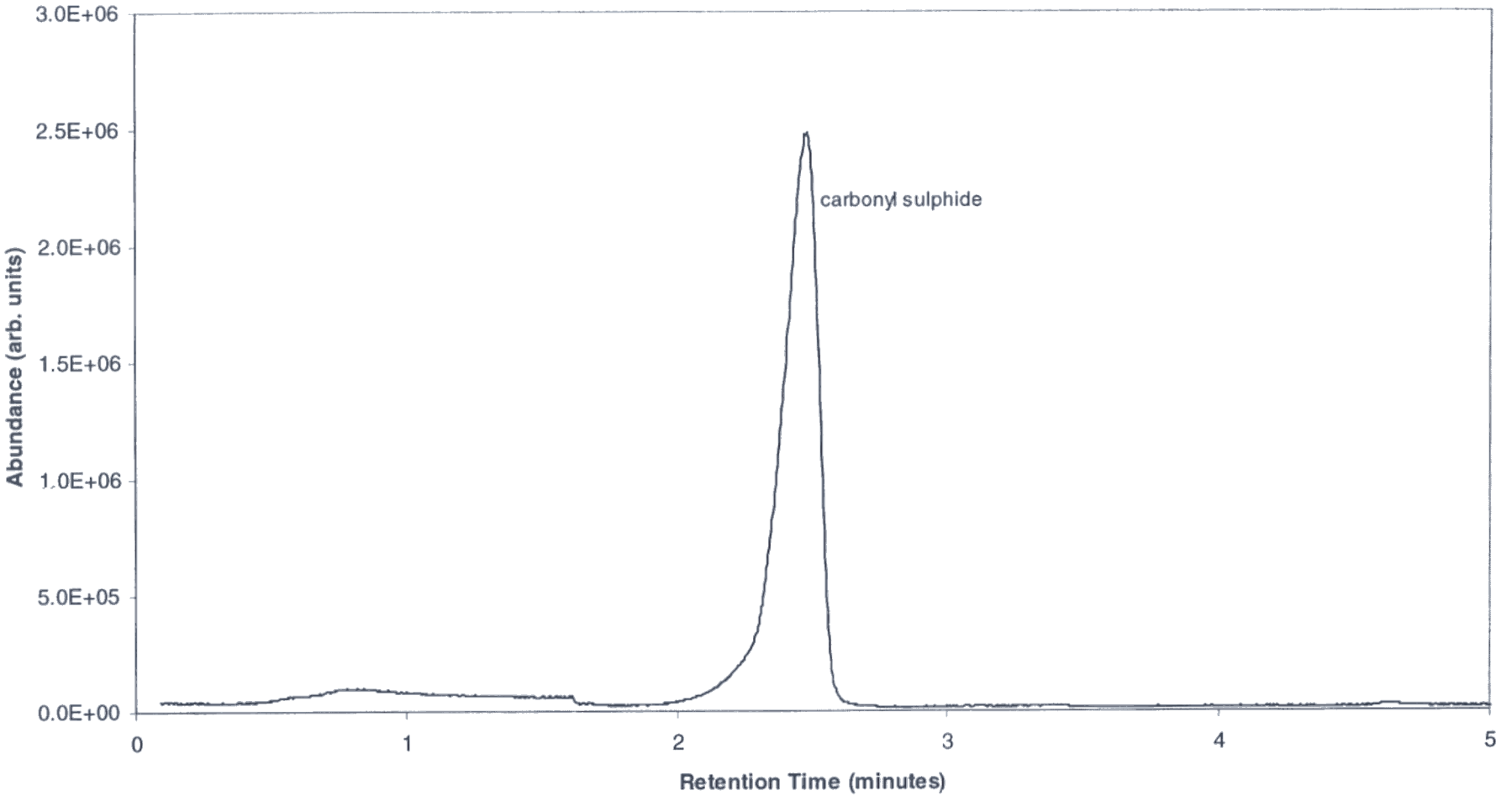


Figure A2.6 GC-MS Chromatogram of Binary Ethylmercaptan Standard

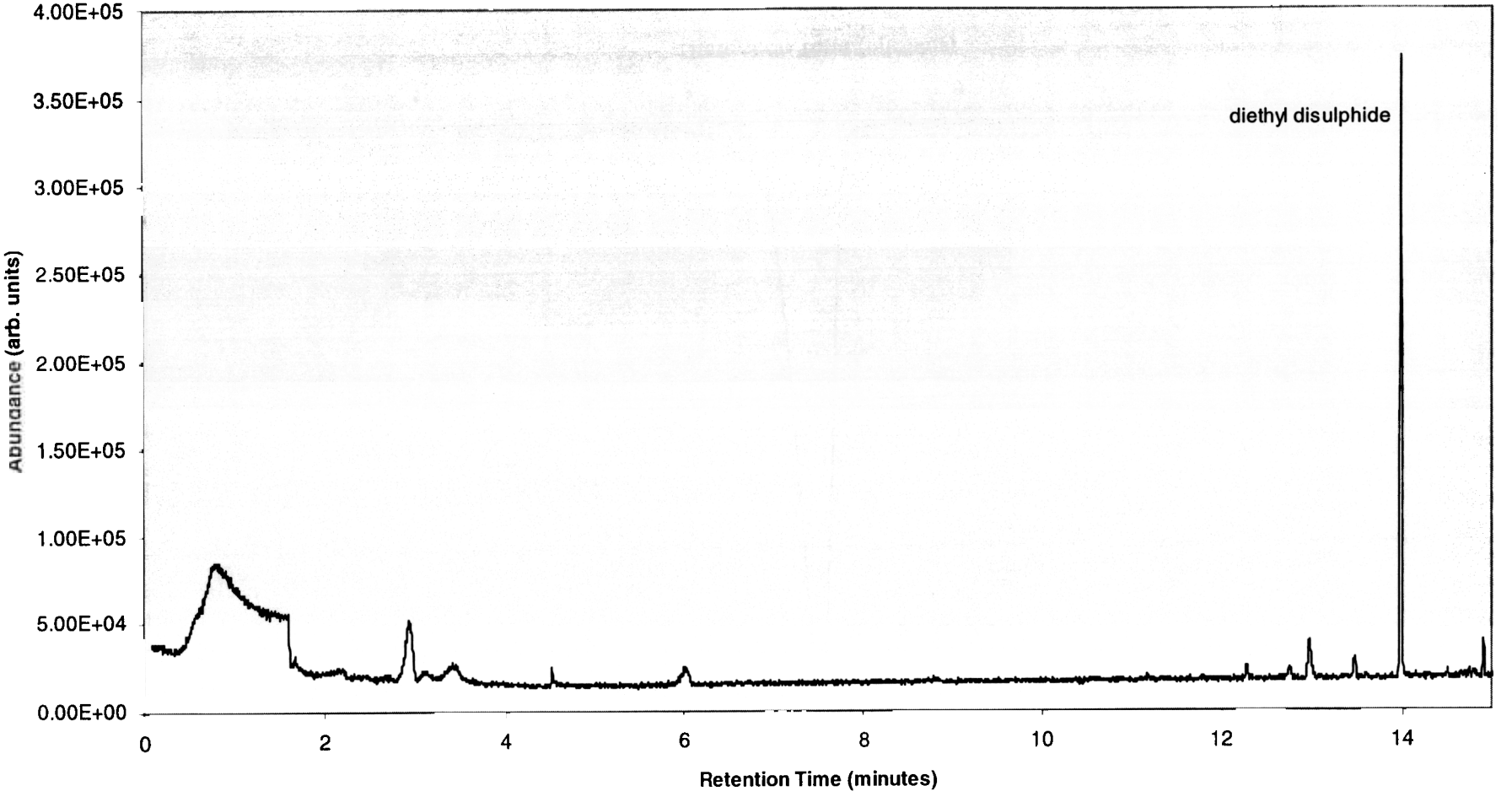


Figure A2.7 GC-MS Chromatogram of Binary 1-Butanol Standard

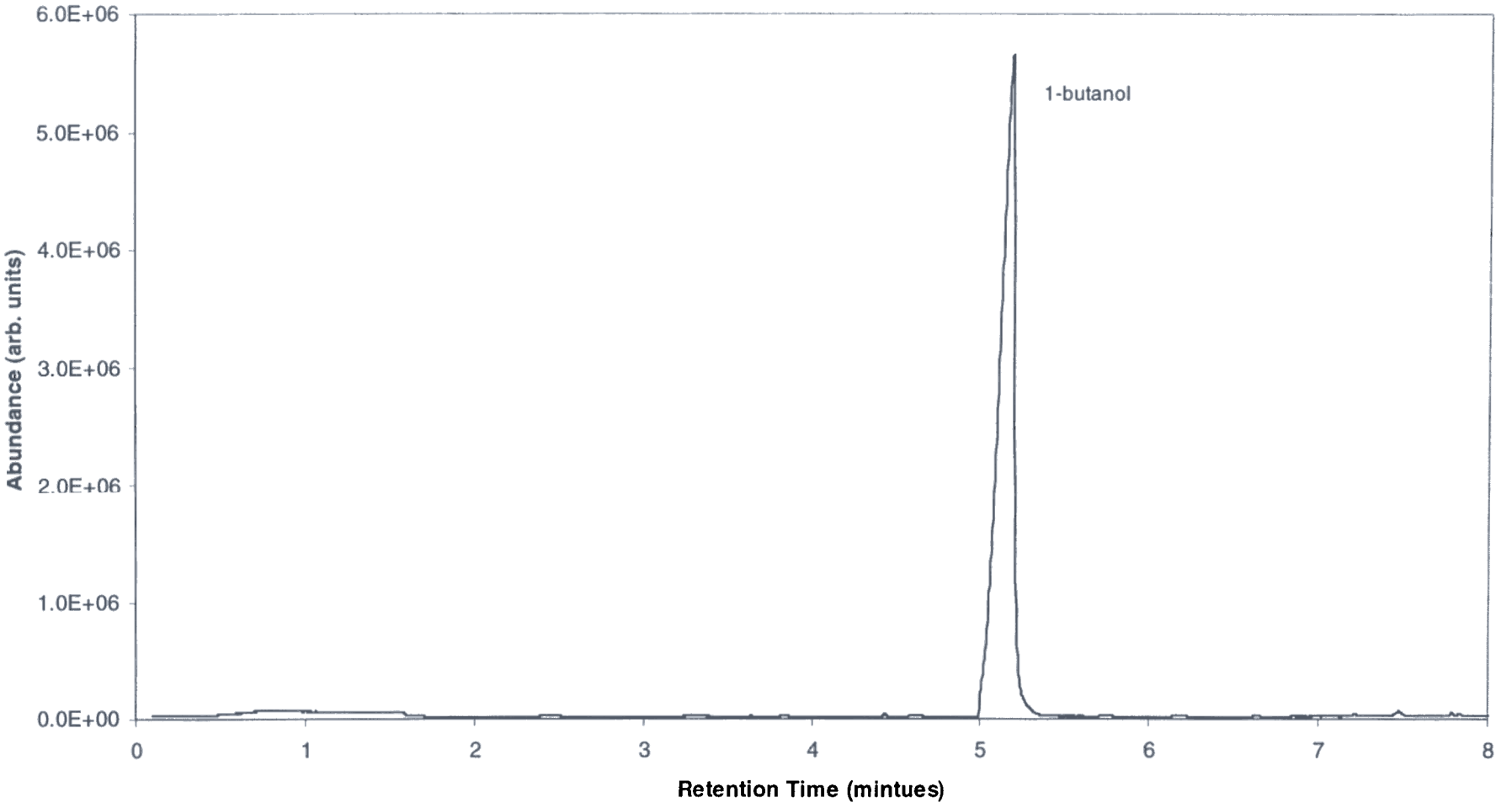


Figure A2.8 GC-MS Chromatogram of Binary Hydrogen Sulphide Standard

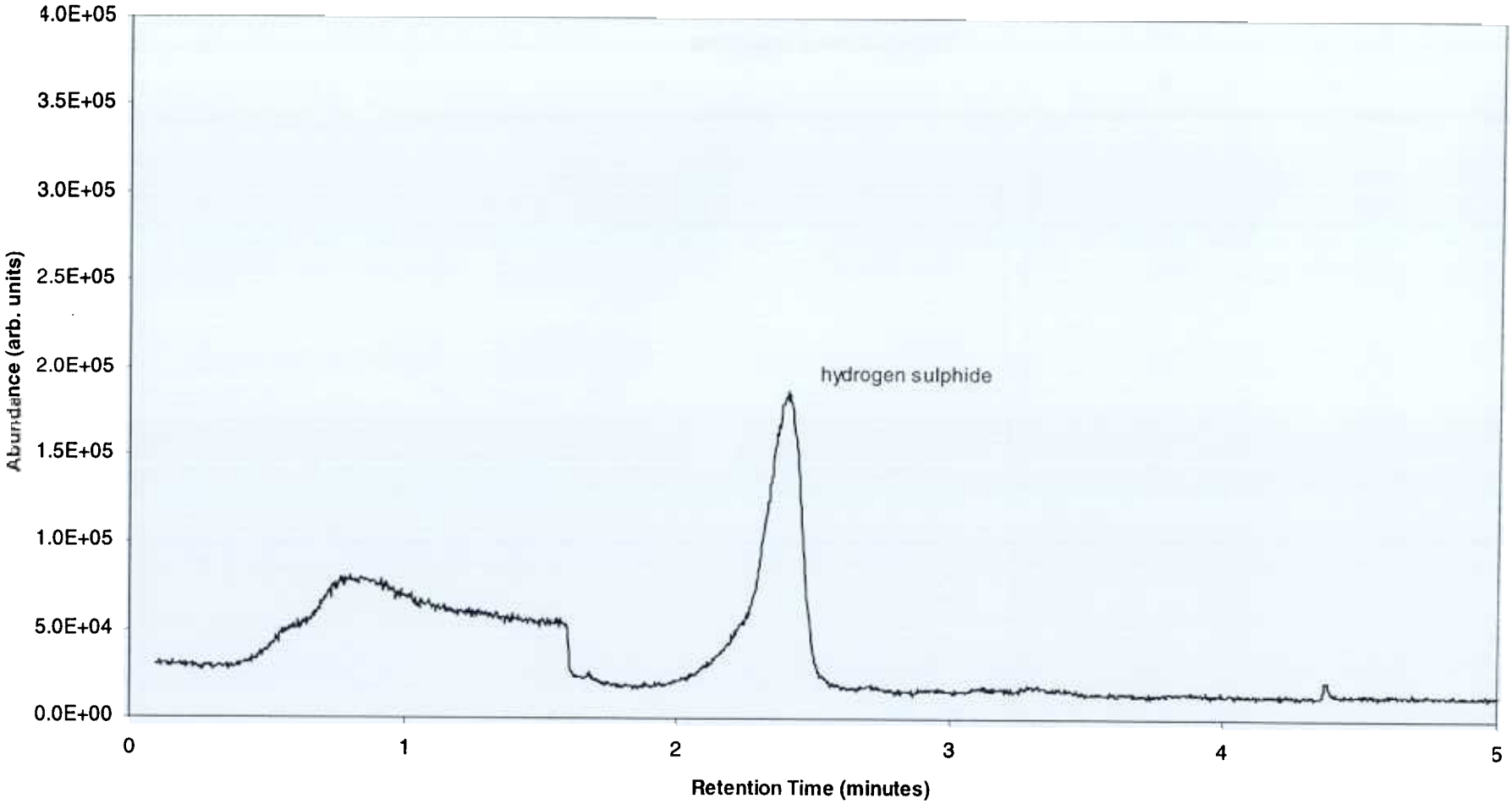


Figure A2.9 GC-MS Chromatogram of Binary tert-Butylmercaptan Standard

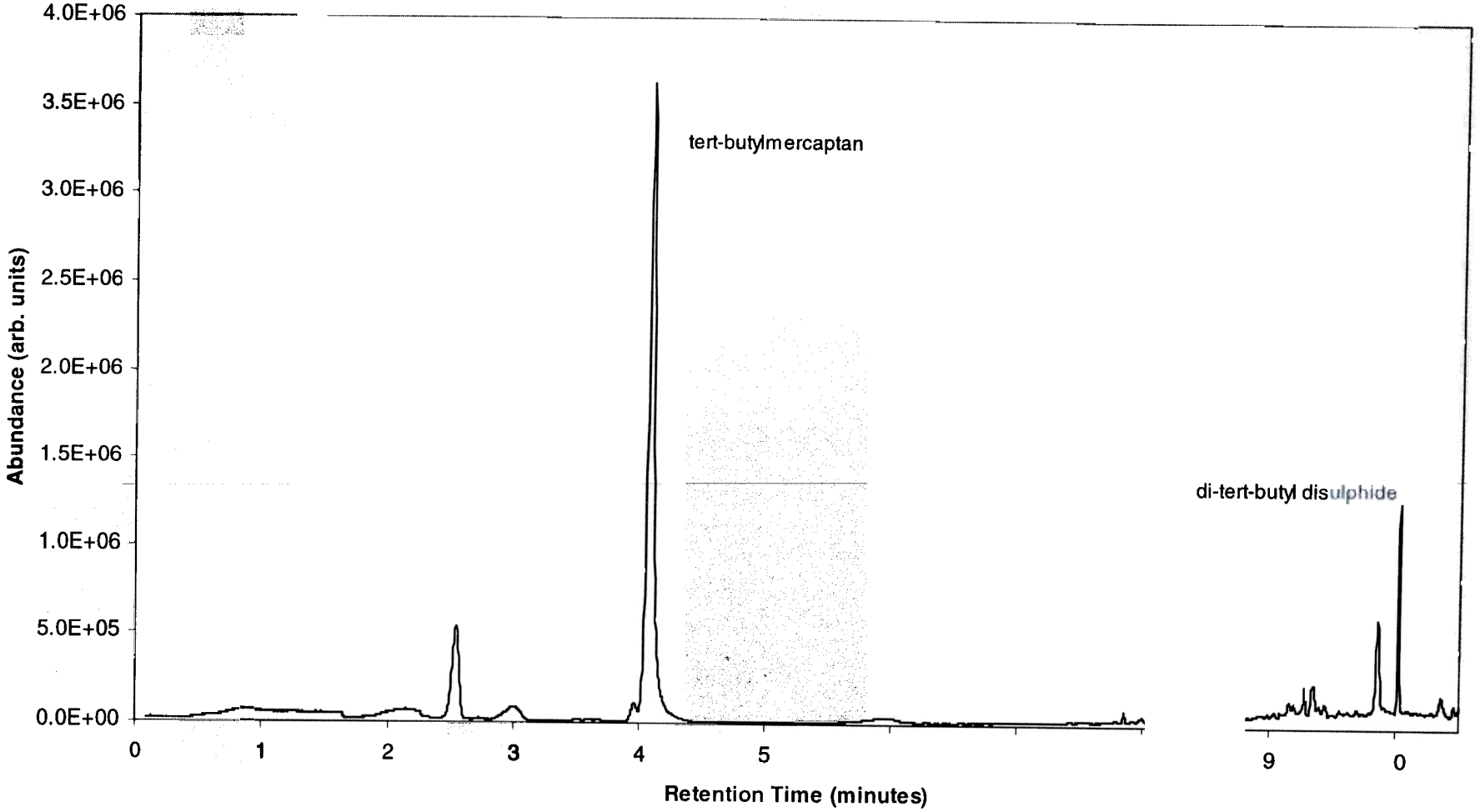
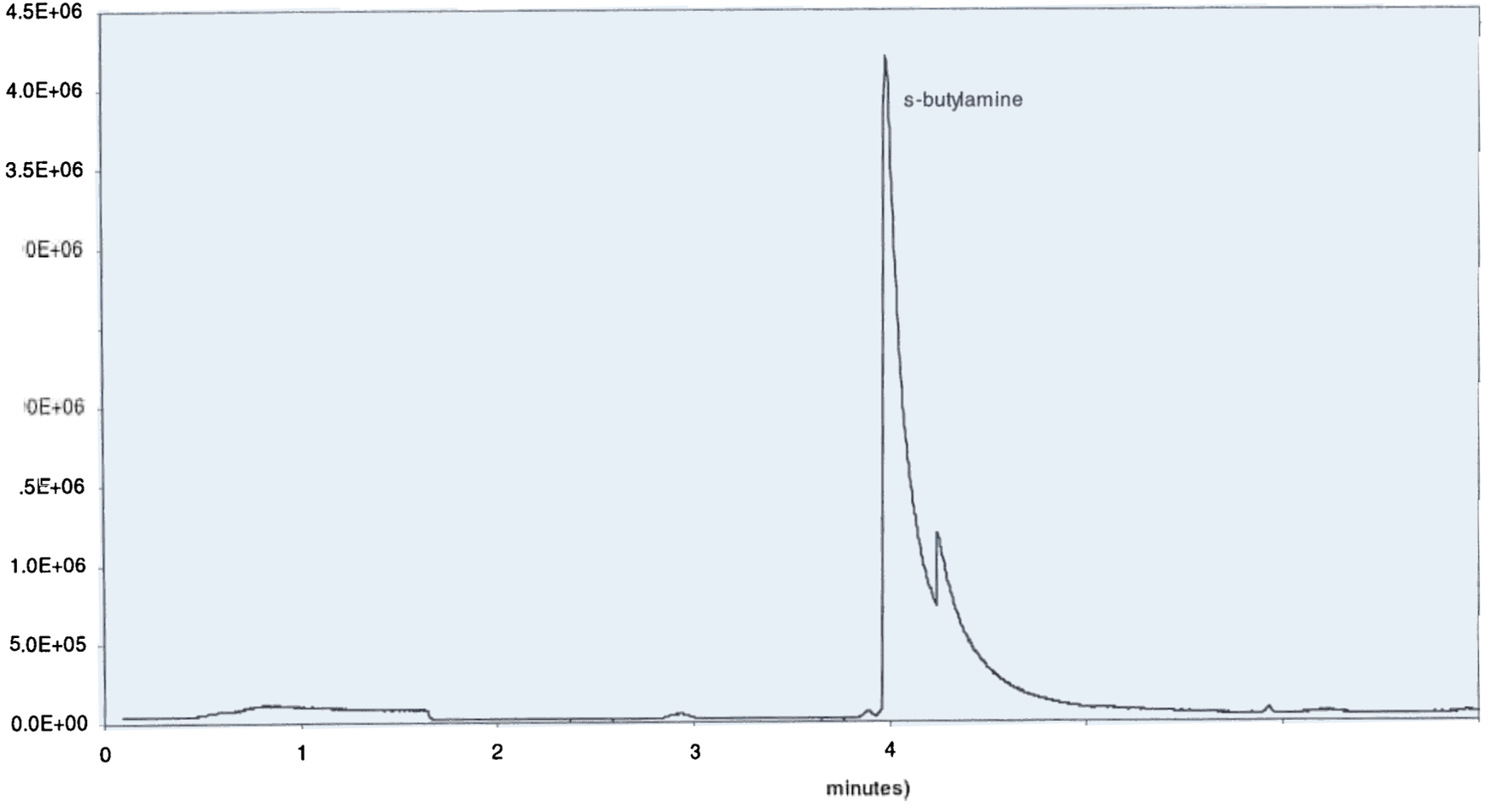


Figure A2.10 GC-MS Chromatogram of Binary sec-Butylamine Standard



ANNEX A3

ADDITIONAL INFORMATION ON ODOUR CHARACTERISTICS

A3.1 DEFINITION OF PRIMARY ODOURS

Since the 50s there have been several other attempts to determine primary odours by grouping together semantic descriptions of odour quality. An example of a recent determination is surmised in Table A3.1 below; the results below have been reported[1] from the analysis of 126 odour descriptors relating to 1573 organic compounds, to give 19 categories or clusters of odour. Overlap coefficients were calculated by the authors to express similarities between odour descriptors and the breadth and meaning of the terms used to describe them. Cluster analysis showed that there were 19 categories of odour. These categories are reported to agree with earlier proposals for classification of primary odours.

Table A3.1 - Categories of Odour defined by Abbe

Cluster	Comprehensive Descriptor	Individual Descriptor
1	Balsamic	Amber, oriental
	Spicy	Cinnamic
2	Floral	Hyancinth, hliotrope, narcissus, lily, mimosa, lilac
	Pungent	Exotic-flower
	Rosy	Tuberose
3	Herbaceous	Wintergreen
	Anise	Fennel
	-	Chemical
4	Herbaceous	Tobacco, hay, coumarin, fungus, tea, lavender
	-	Mushroom
5	-	Bread, Almond
6	Fruity	Apple, pineapple, banana, jasmine apricot, plum, pear, peach, rum, apple-peel, strawberry, raspberry, gardenia
	Ethereal	(Ethereal)
7	Oily	Coconut, cheesy, quinone, cognac
	Vinous	Brandy, fermented, cognac,
	-	Buttery, creamy, berry
8	Fruity	Grape, mandarin, petitgrain, orange
	Floral	Grape, mandarin, petitgrain, orange blossom
9	Citrusy	Lemony
	-	Bergamot
10	-	Acid
11	Fatty	Rancid
	-	Waxy, violet, weedy
12	Green	Leafy, vegetable, metallic, foliage, violet-leaf, cabbage, cucumber
		Gassy, geranium, radish
13	Animal	Civet
	Honey	(Honey)
14	Musky	Ambrette
	-	Aldehyde
15	Woody	Peppery, sap, bark
	Camphoraceous	(Camphoraceous)
	Minty	(Minty)
16	Earthy	Mossy, root, walnut
	Musty	(Musty)
	Nutty	(Nutty), Oakmoss, hazelnut
17	Medicinal	Phenolic
	-	Tar, leather, smoky
18	-	Bitter-almond
19	Caramellic	Burnt , coffee
	-	Onion, sulfureous, garlic

H. Abe, S. Kanaya, T. Komukai, Y. Takahashi and S. Sasaki, Anal. Chim. Acta 239 (1990) 73

A3.2 REFERENCE ODOURS AND 'ODOUR SPACE'

A model for referencing odour quality to specific odoriferous molecules based on a classification of odour descriptor and structure has been reported[2]. The approach was based on the analysis of 1,400 molecules from which 650 odour evocations were deduced, which were reduced to 135 basic odour evocations. A model of defining odour was then developed based on two approaches:

1 A double classification of the odorants by the structural data and descriptive data.

2. The classification of the 1,400 odorants based on the frequencies of associations encountered.

This analysis has lead the authors to conclude that 42 reference points (odours) are sufficient to define this structural olfactory relationship continuum (odorous space). These reference odours are given in Table A3.2.

Table A3.2 – The 42 Reference Odours required to define the 'Odour Space' developed by Jaubert

	Reference Odour		Reference Odour
1	d-limonene	22	α-pinene
2	Citral	23	terpinyl acetate
3	Linalool	24	methyl salicylate
4	Calone	25	d-camphor
5	cis-3-hexanol	26	thymol
6	Nonanal	27	b-caryophyllene
7	2,3-butanedione, butyric acid and 1-octen-3-ol	28	cinnamaldehyde
8	Isobutylamine	29	eugenol
9	Cyclopentanone	30	8-, 12-oxido-13,14,15,16-tetranorlabdane
10	ethyl isobutyrate	31	vetiveryl acetate
11	γ-undecalactone	32	evernyl
12	p-hydroxyphenyl butanone	33	methyl isoborneol
13	benzyl acetate	34	isobutylquinoleine
14	2-phenylethyl alcohol	35	ambrettolide
15	methyl anthranilate	36	skatole
16	ethyl phenylacetate	37	ethylmaltol
17	(E)-anethole	38	methional
18	Hydroxycoumarin	39	2,5-dimethylpyrazine
19	benzaldehyde and cinnamic alcohol	40	phenol
20	Vanillin	41	diallyl disulfide
21	I-menthol	42	dimethyl disulfide

[2] J.-N. Jaubert, C. Tapiero, J.-C. Dore, Perfumer & Flavorist 20 (1995) 1

A3.3 CHIRAL COMPOUNDS AND ODOUR

Optically active stereoisomers or enantiomers (chiral compounds) are known to be able to posses different odour qualities. The most illustrative example of this phenomenon are the enantiomers of carvone and menthol.

The increasing interest in the odour qualities of these materials was initiated by the development of new chromatographic separation techniques[3] on optically active stationary phases, or chiral stationary phases (CSP). A recent review[4] has shown that at present more than 230 different CSPs for GC have been described in the literature, with more than 40 of these being now commercially available. Recently, isotope dilution techniques[5] have also been applied in the study of enantiomeric odorous compounds as a test of authenticity of product. Several reviews have been published[6,7,8] the odour qualities of chiral compounds, including the role of chirality in structure-odour relationships[9].

In nature, compounds generally occur in either mostly the left- or right- handed forms. The occurrence of an excess of one of the enantiomers in a mixture is defined by the percentage of the enantiomeric excess. The enantiomeric excess concentration is the absolute value of the difference of the percentages of the two enatiomers.

R- (rectus) and S- (sinster) are symbols for the absolute configuration of the enantiomers. The R-enantiomer ia a clockwise system and the S-enantiomer a counterclockwise system for the four different substituents attached to the asymmetric carbon atom. The addition of (+) or (-) indicates the real rotation of polarised light by the enantiomer. The (+)-enantiomer, formerly called (d), is dextrorotatory and the (-)-enantiomer, formerly called (l), is levorotatry.

Examples of the odour quality and odour thresholds are given Tables A3.3 and A3.4 respectively.

Table A3.3 - Examples of the Different Odour Qualities of Aliphatic Enantiomers

Odour descriptions of aliphatic enantiomers	
Compound	Odour
(S)-(-)-2-methylbutanol	etheral, fresh
(R)-(+)-2-methylbutanol	fermented, fatty
(S)-(+)-2-methylbutanal	pungent, fresh, fruity
(R)-(-)-2-methylbutanal	pungent, caprylic
(S)-(+)-2-heptyl acetate	Fruity
(R)-(-)-2-heptyl acetate	penetrating, sweaty
(S)-(+)-1-octene-3-ol	moldy, grassy, artificial
(R)-(-)-1-octene-3-ol	fruity, genuine mushroom-like

[3] A. Mosandl, Food Reviews International 4 (1988) 1
[4] B. Koppenhoefer, R. Graf, H. Holzscuh, A. Nothdurft, U. Trettin, P. Piras and C. Roussel, J. Chromatogr. 666 (1994) 557
[5] A. Mosandl, J. Chromatography, 624 (1992) 267
[6] M.G.J. Beets, Structure-Activity Relationships in Human Chemoreception, London: Applied Science Publishers, (1978) pp 127-148
[7] W. Pickenhagen, in Flavour Chemistry: Trends and developments, ACS Symp Series 388, Washington, DC:ACS (1989) pp 151-157
[8] M. H. Boelens, H. Boelens and L.J. van Gemert, Perfumer & Flavorist, 18 (1993) 1
[9] M. Chastrette et al., Chem. Senses, 17 (1992) 555

Table A3.4 - Examples of the Different Odour Thresholds of Aliphatic Enantiomers

Odour Threshold of aliphatic enantiomers / mg m^{-3} of air	
Compound	Odour Threshold (mg m^{-3} of air)
(S)-(+)-2-butanol	23
(R)-(-)-2-butanol	17
(S)-(+)-2-octanol	0.024
(R)-(-)-2-octanol	0.022
(S)-(-)-limonene	0.0084
(R)-(+)-limonene	0.0059
(S)-(+)-linalool	0.035 - 0.040
(R)-(-)-linalool	0.009 - 0.011
(S)-(+)-carvone	0.30 - 0.40
(R)-(-)-carvone	0.10-0.12
(R)-(+)-(E)-α-ionone	0.002 - 0.008
(S)-(-)-(E)-α-ionone	0.002 - 0.008

In a review of the odour characteristics of over 50 pairs of enatiomers, the following observations have been made[8]:

- There is a tendency for nonpolar (hydrocarbons) and slightly polar compounds to show no difference or moderately significant differences in their odour qualities and threshold values.
- Strongly polar and bipolar compounds show signifcant differences in their sensory properties.

Further, it has been reported that three categories of pairs of enantiomers can be distinguished

- The sensory properties of the two enantiomers differ slightly in intensity or in quality (e.g. terpenoid hydrocarbons and spherical camphoraceous compounds)
- The enatiomers have the same main character but differ in secondary notes and intensity (e.g. aliphatic and monoterpenoid alcohols and some esters)
- The odours of the two enantiomers differ both in quality and in intensity (carvone, nootkatone, androstenone, bifunctional compounds)

ANNEX A4 –

DATA SUMMARY FROM THE STUDY OF INELASTIC ELECTRON TUNNELLING SPECTROSCOPY AND INFRARED ABSORPTION SPECTROSCOPY

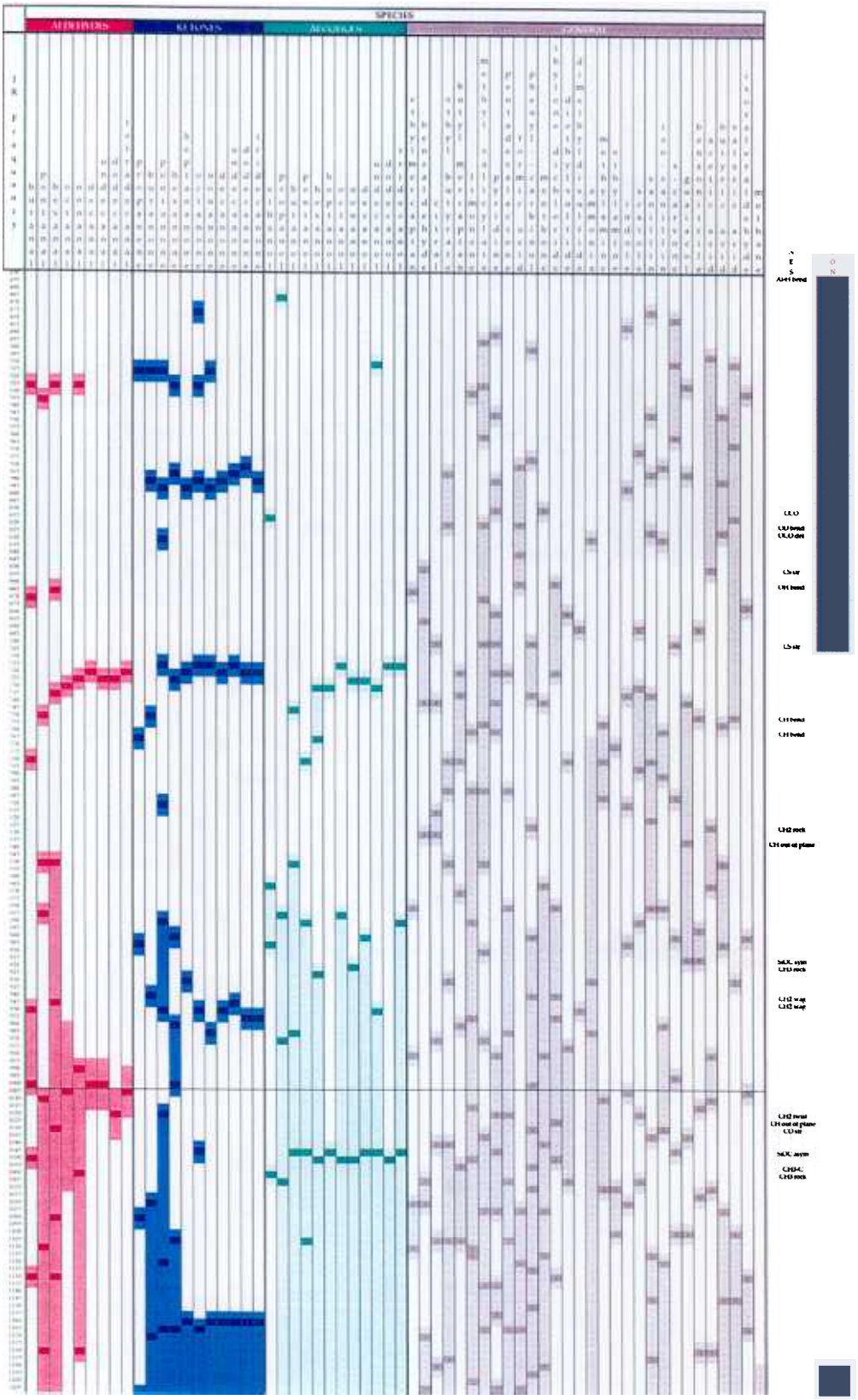
Table A4.1 IETS Absorption Frequencies for a Range of Species (and Odour Descriptions where Available)

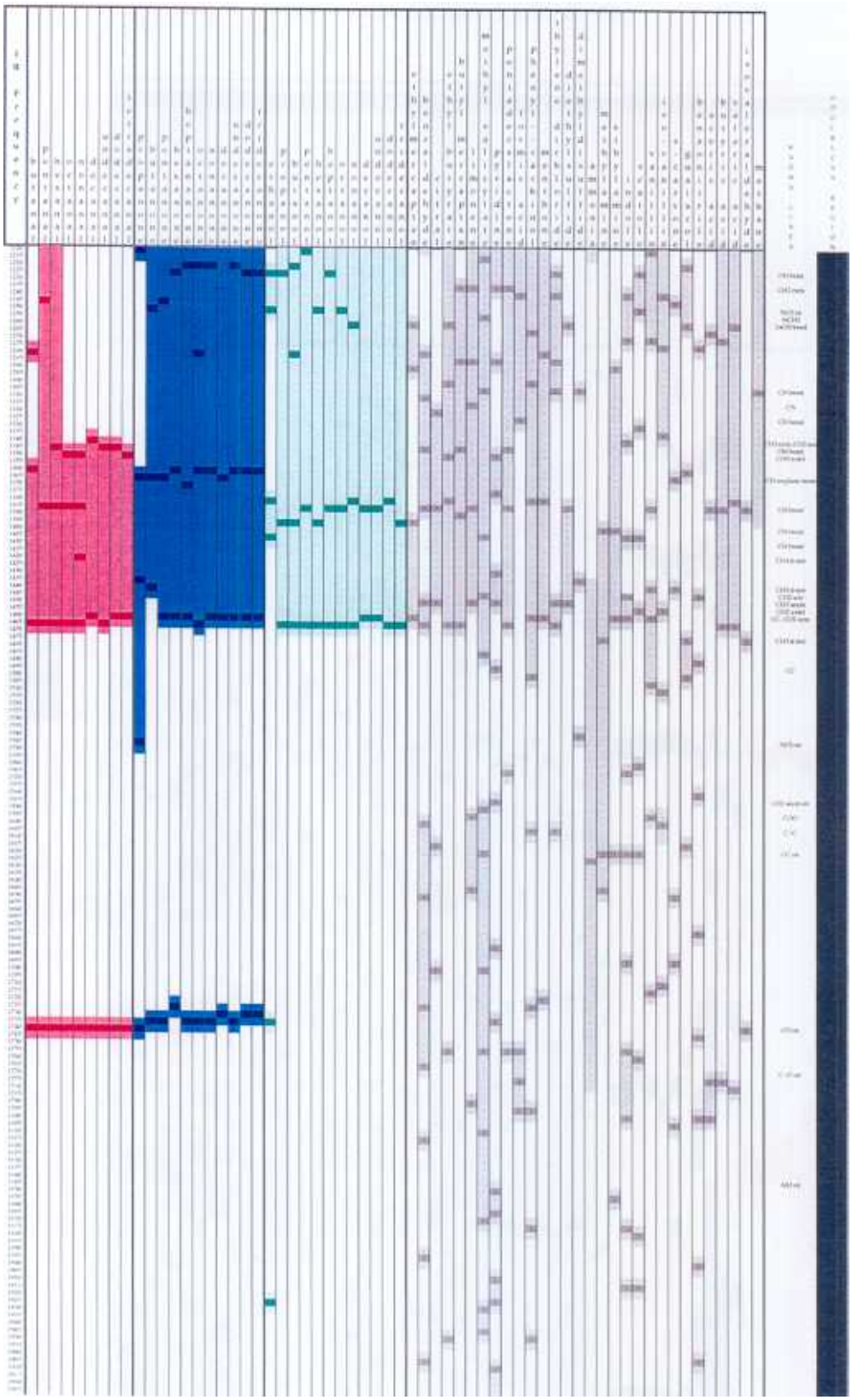
Species	Alt. Name	Reported Odour	IETS Absorption Frequencies (cm-1)
Acetaldehyde		pungent, fruity	597 678 918 1023 1319 1395 1432 1560 2883 2939 2979 3609
Acetic Acid		strong (vinegar)	896 1001 1303 1373 2903 2977
Acetic anhydride		strong, acetic	602 678 930 1043 1335 1412 1472 1576 2891 2967 2999 3609
acetone		frangrant, mint-like	550 661 851 911 948 1114 1295 1401 1447 1628 1748 1891 2867 2950 3010
acetonitrile	methyl cyanide	aromatic	698 920 980 1119 1392 1461 1655 1864 2321 2839 2909 2997 3052
acetyl acetone	pentanedione	?	244 388 535 625 743 1006 1178 1264 1336 1404 1516 2848 2905 3046
Acetyl Chloride		?	606 686 938 1039 1335 1404 1460 1596 2863 2923 2967 3609
acrylic acid		acrid	364 515 640 822 884 936 978 1035 1264 1352 1404 1436 1550 1623 2918 2980 3012 3043 3090 3605
adamantanol		?	293 338 408 442 471 560 642 713 828 906 954 1047 1106 1199 1280 1310 1366 1451 2850 2906 2980
aminobenzoic acid		?	251 439 545 684 766 819 901 973 1075 1128 1152 1253 1296 1345 1402 1436 1552 1725 1798 2896 3012 3055 3205 3369 3451
ammonia		pungent	648 915 1091 1594 1758 3086 3173 3272 3593
aniline	phenylamine	characteristic	420 506 609 671 728 786 852 905 1000 1107 1218 1263 1350 1407 1449 1535 1802 2835 2914 3000 3008 3169 3370 3580
anthracene		?	287 453 536 643 770 843 921 1062 1179 1325 1408 1471 1613 1866 2080 2836 3542
anthroic acid		?	211 386 469 561 662 745 837 966 1094 1122 1223 1315 1379 1480 1572 1637 2253 2529 2731 2878 3053 3163 3246 3347 3494
benzaldehyde		?	397 433 604 679 711 811 846 926 974 1021 1053 1085 1148 1347 1407 1434 1478 1589 2909 3016 3052 3167
benzene		?	257 445 504 633 717 756 836 920 984 1048 1172 1290 1370 1444 1602 1646 2195 2858 2932
benzoic acid		?	264 369 396 578 644 693 792 908 952 1062 1139 1309 1420 1480 1585 2872 3037 3246 3675
benzylalcohol	hydroxytoluene	faint, aromatic	304 408 463 489 597 630 712 771 860 931 997 1068 1086 1183 1201 1235 1335 1413 1483 1539 1643 2792 2929 3048 3111 3738
benzylamine	aminotoluene	?	282 412 471 493 597 634 716 775 860 938 1001 1064 1086 1187 1209 1238 1339 1409 1491 1528 1635 2992 3074 3118 3741
bromobenzaldehyde		?	120 262 323 512 618 770 839 937 1010 1159 1304 1464 1555 1704 2623 2794 2910 2986 3379 3477 3571
bromophenol		unpleasant	300 325 415 505 630 710 850 955 1010 1095 1195 1260 1395 1475 1570 2975 3065 3185 3600
butanoic acid		?	240 278 559 761 858 925 1068 1207 1253 1371 1438 1569 2738 2890 2923 2957 3087 3617
butyl benzene		?	289 719 874 1063 1309 1355 1435 1606 2895
carbon dioxide		odourless	628 929 1864 3693
carbon monoxide		odourless	348 407 470 969 1043 1661 1780 1965 2094 3648

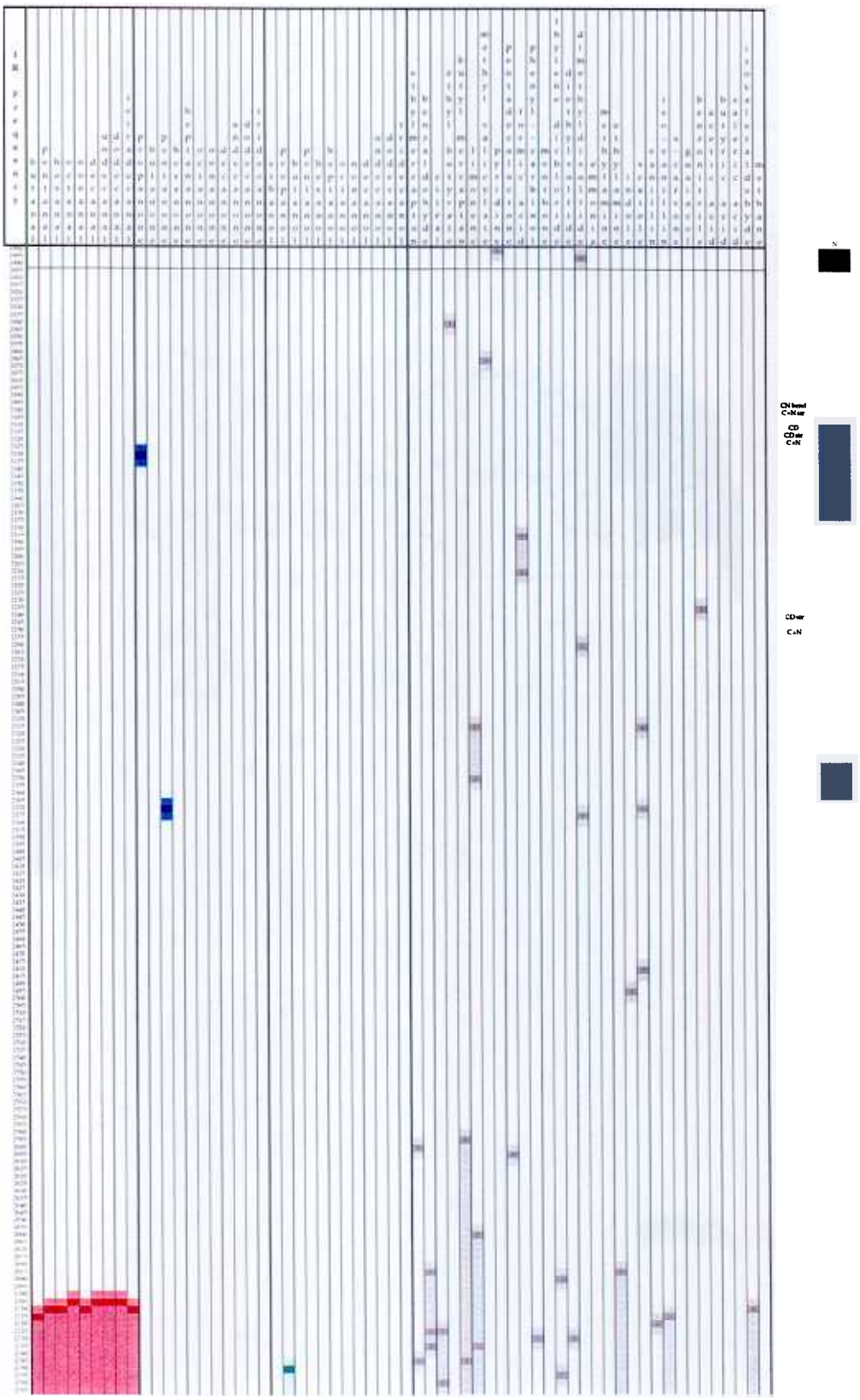
carbon tetrachloride		heavy, ethereal	273 342 360 443 522 604 657 735 776 881 929 965 1450 2900 3600
carbon tetrafluroride		?	756 1482 1909 2919 3293
carboxybenzoic acid		?	404 580 668 736 828 926 979 1101 1160 1311 1408 1423 1594 1715 2973 3065 3221 3674
catechol	benzendiol	?	289 440 559 603 733 906 1036 1121 1199 1258 1328 1439 1580 1672 2893 3008 3600
chlorobenzoic acid		?	272 413 487 531 623 689 738 764 847 953 1093 1146 1286 1423 1493 1594 2845 3030 3175 3640
chlorophenol		unpleasant	295 385 405 430 540 640 665 715 850 955 1040 1095 1190 1265 1415 1505 1590 2970 3045 3185
cinnamic acid		?	272 406 470 597 701 719 800 870 928 997 1154 1177 1264 1420 1565 1635 1681 3009
crotoic acid	methylacrylic acid	?	246 334 416 704 868 909 985 1044 1249 1367 1466 1595 1701 1777 2933 3595
Cyanoacetic acid		?	367 435 503 594 722 919 1070 1183 1274 1384 1448 1660 1860 2272 2915 2979 3074 3187 3493 3637
cycloheptatriene		?	250 300 342 542 584 692 757 803 857 934 1049 1145 1195 1237 1310 1375 1441 1514 1575 1637 2720 2762 2843 2962 3585
diaminoethane	ethylenediamine	ammonia-like	659 898 946 1046 1275 1361 1452 1571 2775 2827 2866 3238 3291 3587
diaminopropane		?	502 607 697 771 818 930 1047 1257 1366 1398 1444 1581 2838 2877 3219 3620
dihydroxyethane		?	936 1070 1113 1251 1376 1461 1576 2775 3587
dihydroxypropane	propylene glycol	Pratically odourless	502 607 697 771 818 930 1047 1215 1257 1366 1398 1444 1581 2838 2877 3620
dimethylsulphoxide		?	274 376 591 650 889 996 1280 1353 1548 2823 2891 3648
diphenylamine		floral	250 261 404 496 562 617 691 742 823 885 951 1029 1058 1164 1245 1491 1576 2869 3016 3600
ethanol		fragrant	304 907 1069 1385 1481 2878 2943 3552
ethylene		sweet	300 909 1054 1298 1388 1463 1663 2891
fluoroform		odourless	305 525 1432 1926 2874
formamide	methanamide	?	290 506 629 920 1048 1370 1435 1596 1662 1831 2718 2831 2928 3288 3573
Formic Acid		pungent	249 309 1028 1365 1444 1572 2702 2848 2958 3598
glycine		odourless	281 438 576 704 908 1018 1294 1394 1612 1655 1841 2892 3258 3577
Heptanoic acid		rancid	391 578 708 743 869 960 990 1068 1121 1203 1264 1307 1385 1464 1603 2879 2919 3735
heptene	heptylene	?	332 950 1060 1397 1480 2296 2945 3688
heptyne		?	459 559 645 927 1073 1118 1286 1355 1423 2086 2705 2800 2836 3273 3636
hexanoic acid	caproic acid	limburger cheese	391 593 732 854 887 967 1064 1123 1216 1295 1380 1455 1590 2864 3617
hexene		?	332 950 1060 1397 1480 2296 2945 3688
hexyne		?	550 650 736 877 900 923 1050 1105 1223 1264 1291 1359 1441 1605 2100 2859 2900 2950 3682
hydrogen		?	680 928 1924 3729

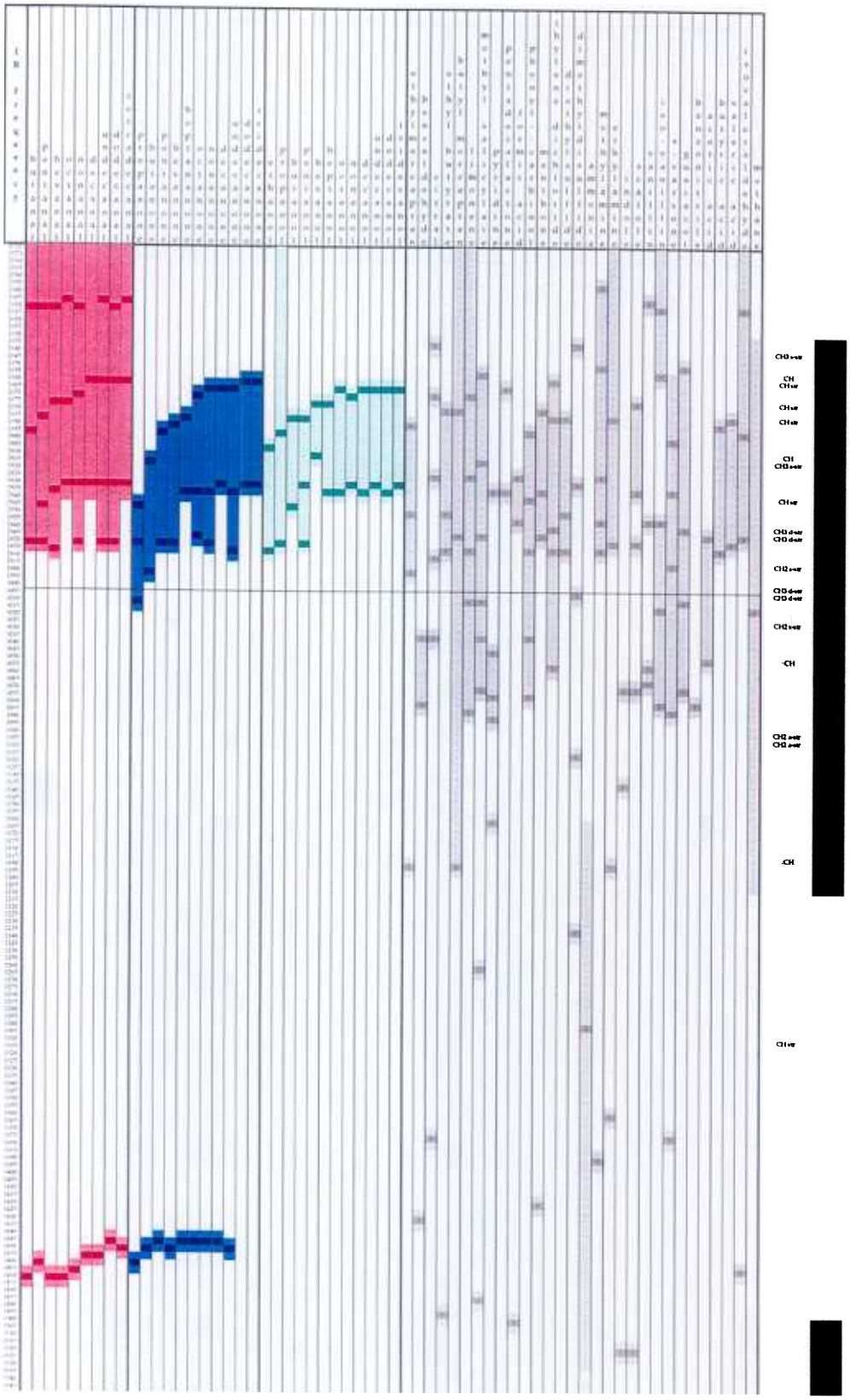
hydrogen cyanide		bitter almonds	652	904	2117	3622																													
lauraldehyde	dodecanal	?	737	883	932	1059	1112	1161	1215	1239	1312	1371	1429	1605	2839	2883	3678																	
mercaptobenzoic acid		?	229	365	417	470	643	692	748	801	868	977	1060	1135	1180	1293	1455	1579	2515	2579	3102													
methane		odourless	295	693	934	1271	1458	1833	2737	2829	2913	3552																							
methanol		?	304	925	1045	1188	1433	2931	3636																										
nitrophenol		aromatic	275	365	400	445	525	560	640	725	750	855	940	1050	1110	1150	1260	1300	1365	1440	1470	1580	2710	2845	2895	2935	3010	3615						
octene		?	332	950	1060	1397	1480	2296	2945	3688																									
oxygen		odourless	628	929	1864	3693																													
pentanoic acid	valeric acid	unpleasant	419	558	746	826	851	885	1006	1040	1086	1182	1216	1266	1338	1413	1556	2864	2897	3652															
phenol		distinctive	404	500	604	678	735	787	861	913	970	1048	1130	1248	1509	1600	2865	3004	3043	3604															
phenylethylamine		?	290	353	400	452	485	558	606	672	764	849	962	1051	1153	1212	1289	1370	1447	1499	1583	1605	2840	2887	2976	3005	3045	3651						
Propanoic acid		?	321	596	694	801	894	992	1066	1225	1295	1360	1462	1588	2882	2929	2957	3627																	
Propanoic acid		?	321	512	694	801	950	1076	1104	1211	1481	1611	2119	2231	3627																				
propiolic acid		?	182	551	619	739	1290	1514	2023	2835	3189	3532																							
pyridine		sharp, empyreumatic	338	384	545	594	632	685	768	805	908	1065	1230	1325	1362	1432	1812	2134	2241	2753	2807	2923	3591												
sorbic acid		?	249	307	603	713	800	870	922	1020	1096	1154	1217	1281	1386	1426	1565	1675	2916	3014															
tiglic acid		spicy	299	364	762	874	938	1015	1073	1173	1349	1408	1578	1654	1818	2862	3619																		
toluene		benzol-like	270	410	602	728	959	1112	1286	1373	1456	1548	1713	1822	2433	2873	3139	3483	3618																
trichloroethylene		chloroform-like	266	298	412	445	653	725	835	874	926	1052	1116	1151	1286	1358	1424	1556	1587	1630	1846	2695	2801	2838	2880	2934	3578								
trichlorophenol		?	365	422	489	545	710	782	838	1059	1121	1229	1291	1347	1445	1517	1553	2880	3024	3600															
urea	carbamide	?	308	554	611	795	899	999	1060	1382	1434	1595	1657	1841	2812	2907	3314	3375	3517																
water		odourless	319	644	810	892	1068	1378	1473	1626	2818	2942	3633																						
xylene		?	268	398	467	640	696	774	864	968	1167	1223	1305	1392	1457	1526	1638	1807	2559	2606	2762	2948	3082	3708											

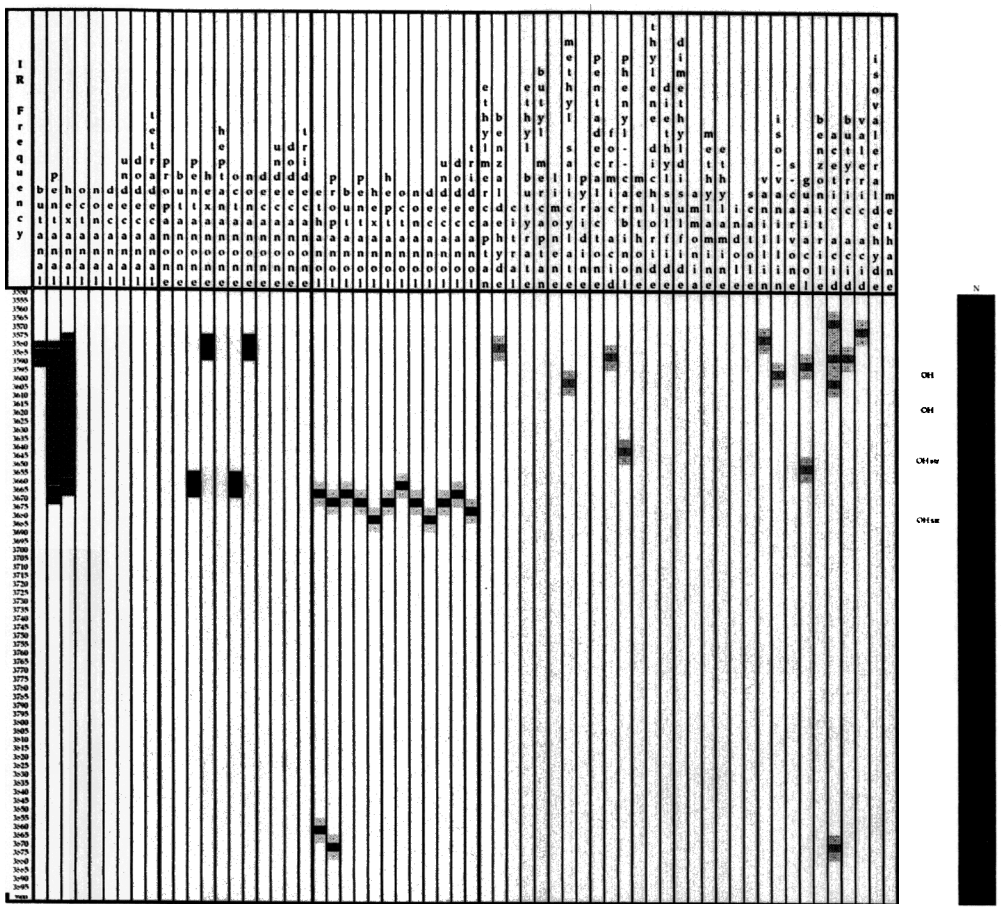
Table A4.2 Gaseous Infrared Absorption Frequencies for a Range of Species with Known Odour Characteristics










IR Frequency
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Pentanal
hexanal
octanal
nonanal
decanal
undecanal
dodecanal
tetradecanal
Propanone
Pentanone
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octanone
nonanone
undecanone
tridecanone
ethanol
Propanol
Pentanol
hexanol
octanol
nonanol
decanol
undecanol
dodecanol
tridecanol
ethylmercaptan
benzaldehyde
ethyl butyrate
butyl mercaptan
methyl salicylate
Pentadecanoic acid
phenyl-mercaptan
thylene dichloride
diethyl disulfide
dimethyl disulfide
methylamine
ethylamine
indole
scatole
vanillin
iso-valeraldehyde
guaiacol
benzothiazole
acetic acid
butyric acid
valeric acid
isovaleraldehyde
Methane
N
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ANNEX A5 –

SUMMARY FROM ELECTRONIC NOSE WORKSHOP

Summary of Workshop SIGII: Standards and Definition of Terms.

Friday 17 March 2000
National Physical Laboratory, Teddington, UK

This document summarises the discussions that took place during a workshop organised for the NOSE Network by Special Interest Group SIGII under the Chairmanship of Professor Barry Jones, Brunel University, UK, and hosted by the National Physical Laboratory. The workshop was attended by 24 people, mainly from the UK (14), but also from Germany (3), Italy (2), France (2), Norway, Finland and Latvia (1 each). The attendees represented industrial companies developing and/or exploiting electronic nose technology, academic and government research groups, and National Metrological Institutes.

Introduction – Professor Barry Jones

The aims of SIG II can be summarised as the establishment of the procedures required to bring the field of electronic nose measurement into a traceable framework. The purpose of this workshop was to review the current status of standardisation within the Electronic Nose Community, and to develop an action plan for further developments in this area.

E-mailed inputs had been received from a number of members of the network who were unable to attend the workshop, including Dr M. Klee (Agilent Technologies), Dr E.J Staples, and Dr J. Gardener. All indicated their support and interest in the workshop, and there was a general indication of the importance of developing a metrological basis for electronic nose measurements.

Dr Stephane Stathmann then gave a description of the work and objectives of the NOSE network, which has the primary goal of developing synergy within the field through collaboration and knowledge transfer within the network. The potential role of the network in providing support for a collaborative project was also discussed, in terms of information exchange, access to the network website and databases, and some financial support for workshop activities.

Short Presentations

Dr Paul Quincey from the National Physical Laboratory (NPL) discussed how standardization can support and enhance analytical measurements. The potential benefits that can arise from standardization include :-

- Consistent measurements over time
- Comparability of measurements between instruments and organisations
- Better knowledge of the potential problems and uncertainties, and their relative scales
- Versatility of measurement applications
- Improvements to effectiveness and efficiency.

He also described NPL's role in supporting industry through the National Measurement System, with particular reference to the Valid Analytical Measurement (VAM) programme. The main aim of the VAM programme is to improve the quality of analytical measurements and to facilitate mutual recognition of analytical data.

Dr Robert Wielgosz from NPL outlined different models of standardisation and, in particular, the use of calibration standards to achieve traceability to the SI system of units. In general, a user will require any measurement technique to be comparable (over time and location). Traceability is a method of ensuring comparability to a level determined by the uncertainty of the measurements. One of the main points raised for discussion is whether 'E-nose measurement space' can be defined and calibrated by traceable reference standards.

Dr John-Eric Haugen from the Norwegian Food Research Institute described his work on the calibration of electronic noses. The key issues highlighted were :

- *Calibration* – proper calibration is essential in obtaining accurate measurements, and experience shows that frequent calibrations are required to compensate for sensor drift.
- *Drift* – sensor drift is a major issue in electronic nose measurement, and is influenced by a large number of factors. Mathematical algorithms are being developed to compensate for drift using calibration data as a reference.
- *Recalibration* – the sensors in electronic noses have a limited lifetime, and ensuring batch to batch sensor comparability is crucial.
- *Calibration standards* – the calibration standards used need to be stable over time, and be closely related to the measurement samples, ie application specific.
- *Data transferability* – the goal of E-nose instrument manufactures is to achieve full reproducibility, ie obtain the same response for the same sample from different, but nominally similar, instruments. If this is not achievable directly then a mathematical algorithm will be required to transfer the data.
- *Calibration transferability* – practical e-nose applications have shown that, in general, calibration data sets are not transferable from one instrument to another. Again, the development of mathematical transfer algorithms may enable calibration transfer to take place.

Ms Quitterie Lucas from Alpha MOS described some of the work that has been carried out to charaterise Alpha-MOS Electronic Noses. This work has focussed on :

- The selection of the best combination of sensors and discriminate variables in order to give the optimum discrimination for a given application.
- The transferability of sensors and/or parameters to give measurement reproducibility. This is achieved through the measurement of a three chemical calibration kit, and comparison against standards responses.
- On-line monitoring of various system diagnostics
- Long term monitoring of drift, and the determination of drift correction parameters.

Dr Tim Pierce from Leicester University showed how sensor array models could be used to assess the discriminating powers and sensitivities for multiple sensor systems. The response of a sensor array to a range of chemicals can be described in matrix form. This response matrix can be used to transform concentration space ('odour space') into sensor space ('e-nose space'), and the volume of accessible sensor space (VASS) defined. This method is not limited to simple linear sensor response and can deal with different forms of response behaviour. A comparison of the sensor uncertainties to the VASS can be used to define the discriminating power of the sensor array (ie the maximum number of different mixtures that could be detected separately), and a reverse transform of the uncertainty volume in sensor

space back into concentration space can be used to give the sensitivity of the system for each chemical.
There then followed a general discussion on some of the issues raised during the talks. The main areas discussed were calibration, sensor panels and the requirements of manufacturers and users.

It was pointed out that the more sensors that are used the larger the volume of sensor space, and therefore the more reference points (ie calibration artefacts) required to characterise it. This is particularly the case where different types of sensors are used in a single instrument, as each type usually has very different response characteristics. A general calibration procedure would require the identification of key chemicals which can be used to characterise particular types of sensor. Another issue raised was whether calibration artefacts should be based on headspace samples, which it the usual type of measurement samples, or gas standards, which is the more usual type of traceable artefact.

The use of human sensor panels was discussed. The uncertainties of a sensor panel measurement can be 50 % to 100%, and therefore a large number of samples are required to validate the measurements. Also, sensor panels are very expensive and extensive training is required for each application. However, it was felt that the role of electronic noses was not to totally replace the use of sensors panels, but to work with them, for example as a pre-screening method. Sensor panels would still be required to define and/or grade the different product classes.

Supplier and users of electronic noses were asked what they would ideally like to come out of a programme of research into standardisation. From the suppliers point of view the main aim was to build customer confidence through greater credibility for the measurements technique. The ability to replace sensors without having to re-train the instrument was seen as an important part of this. In addition, current instruments are not sold of the basis of a performance specification, but rather through application-driven examples of case studies and test cases. From the users point of view, the main aim was to reduced costs and increase process efficiency. At the moment electronic noses are useful for rapid, on-line screening but do not provide a quantitative measure of authenticity. The main goal would be for electronic noses to provide quantitative forensic evidence in support of regulatory, legal and patent issues.

Discussion Groups

The meeting then broke in two separate discussion groups, one looking at Terms and Characteristics, and the other looking at Appropriate Standardisation Models and Practical Calibration. A summary from each group is given below.

Terms and Characteristics

In order to fit the field into a proper metrological framework is important to use and understand the internationally-accepted terms (as defined in the International Vocabulary of Basic and General Terms in Metrology) that are relevant to electronic nose measurements. These include :

- *Repeatability* – closeness of the agreement between the results of successive measurements of the same measurand carried out under the same conditions
- *Reproducibility* – closeness of the agreement between the results of measurements of the same measurand carried out under changed conditions of measurement
- *Uncertainty of measurement* – a parameter, associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand.
- *Sensitivity* – change in the response of a measuring instrument divided by the corresponding change in the stimulus.
- *Traceability* – property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties.

In order to apply these definitions to electronic nose measurement it will be necessary to properly assess various characteristics of electronic nose performance, including :

- *Drift* – sensor drift needs to be monitored and/or compensated for in order to achieve good reproducibility.
  Comparability of sensors - particularly in terms of comparability before and after sensor replacement.
- *Environmental influence* – the effects of temperature, pressure and humidity need to be quantified in order to define operation limits for a given level of performance.
- *Transfer of single sensor characteristics to overall instrument performance* – one possible option for standardisation would be to quantify the characteristics of each of the individual sensors and then extrapolate the results to the behaviour of the multiple sensor array.

Two of the key outstanding questions that would need to be investigated in order to proceed are :

- Is it possible to move away from application-specific calibration and validation, and develop generic procedures ?
- How should network training be included within a generic standardisation procedure ?

<u>Standardisation Model and Practical Calibration</u>

- Any calibration standards will need to include both polar and non-polar compounds
- Manufacturers and customers prefer samples that are generated from a headspace. Several current commercially available ENOSE systems will require modification to allow the introduction of gas samples. A chemical standard (liquid / solution) presented in a sealed vial may be a preferred option
- The detection limit of (LOD) ENOSE's to particular chemicals is not well defined; and stated LOD's for a compound such as n-butanol vary from the ppb to the ppm range (vapour phase). As manufacturers generally deal with headspace analysis, an LOD is usually quoted which refers to the concentration of compound within a solution.
- Chemical standards are required to test the stability of sensors, and will be needed at various concentration levels for application tests

The user community would like a 'smart' instrument which contains a facility for internal calibration

At present the ENOSE industry make comparison measurements. The specific chemicals which are in any mixture are not known. However, future 'gas standards' should reflect the major gas components in the head space. The list of chemicals used by an ENOSE manufacturer for sensor testing, was indicated as a good starting point for the development of standards:

Volatile component	Concentration Range/ ppm
Acetaldehyde	0.09 - 0.9
Ammonia	0.01 - 0.1
2-chloro-6-methylphenol	1 – 20
Ethyl Hexanoate	1 – 74
Methanthiol	0.14 - 1.4
	25 – 1000
1-octen-3-ol	1 – 20
Propanoic acid	0.06 - 0.6
Trimethylamine	0.01 -0.2
Toluene	25 – 1000

T.M. Hawkins and P.J. Travers, Proceedngs of ISOEN 99, Tuebingen (1999) pp. 113-116

- Measurements to determine interference from relative humidity were still considered necessary
- The diversity / orthogonality of sensors is an important factor
- Manufacturers have stated that standards are an important area that should be developed. However, at present it is unlikely that different manufacturers will come together to define an industry standard without careful consideration of IPR issues.

Conclusions and Future Actions

There is a clear requirement within the filed of electronic nose measurement for the development of a traceability framework. All areas of the community recognise this and are keen that such a framework be put in place. However, a significant amount of work needs to be done before an acceptable International Standard could be written. The proposed mechanism to achieve this is for a core group of partners to prepare and submit an Expression of Interest to the European Commission. If acceptable this would be followed by a Dedicated Call for a two to three year collaborative project into the feasibility of using a limited number of reference artefacts to provide calibration and traceability for the use of electronic noses in the food industry. This project would involve input from manufacturers, users, research organisations, and National Measurement Institutes, and would have the final objective of preparing a draft standard for CEN/ISO submission.

Although not covered at the meeting, a short description of the procedure for EC submission is included below for reference. The most suitable EC programme would be the Competitive and Sustainable Growth Programme which places regular calls for "Expressions of Interest" (EoI) proposals applicable to :

- Methodologies in support of European Standardisation
- Methodologies in support of the fight against fraud

Feasibilities studies for certified reference materials CRMs

A proposal covering the Standardisation of Electronic Noses would fit ideally into the first of these categories, but would also have strong relevance to the other two areas. Details of the relevant topics under each of these headings, and information on the Proposal Preparation guidelines are given on the Cordis website (http://www.cordis.lu/growth/). An EoI proposal is basically a six page (anonymous) document summarising the requirement and justification for the work, the benefits to the EC that will result from the work being carried out, and the technical objectives of the work. At this point there is no requirement to specify costs or details of the partnership undertaking the research. There are two calls remaining in Framework V with deadlines of 15/6/2000 and 30/4/2001, and the intention is to prepare a submission for the first of these deadlines.

ANNEX A6 –

'DEVELOPMENT OF STANDARD PROCEDURES AND PROTOCOLS FOR THE CHARACTERISATION OF 'ELECTRONIC NOSES'

EXPRESSION OF INTEREST SUBMITTED TO THE EC GROWTH PROGRAMME

EUROPEAN COMMISSION – GROWTH PROGRAMME

EXPRESSION OF INTEREST FOR THE NEEDS OF RESEARCH SUPPORTING DOCUMENTATION

Development of Standard Procedures and Protocols for the Characterisation of 'Electronic Noses'

1. CONFORMITY WITH THE WORK PROGRAMME

This topic is directly applicable to the R&D activities of the *Competitive and Sustainable Growth Programme* and concerns the development of *Methodologies in support of European standardisation.* It falls under *Generic Activity 2: Measurements and Testing*, and specifically under *Research Objectives 6.2.2 Measurements and testing anti-fraud methodologies and 6.2.3 Measurement and testing methodologies in support of quality.*

2. KEYWORDS

Electronic noses, Odour measurement, Sensor arrays, Pattern recognition analysis, Measurement Traceability, Instrument characterisation, Process control, Environmental Monitoring, Detection of fraud

3. SUMMARY OF OBJECTIVES AND JUSTIFICATION

The objective of this activity is to develop standard procedures and protocols to enable the quantitative characterisation of 'electronic nose' instrumentation. Specific parameters to be addressed include the repeatability, reproducibility, uncertainty, range, sensitivity and traceability of the measurements, together with associated calibration and QA/QC activities.

The field of electronic noses is an emerging technology with potential application across a wide range of application areas, including bacteriological and environmental monitoring, explosive detection, process monitoring and control, product quality control, and fraud detection. The development of standardization procedures is required to help the European Electronic Nose community realise the full potential of the measurement technique, and provide potential users with quantitative information on instrument performance.

4. BACKGROUND

An electronic nose can be defined as 'an instrument which comprises an array of electronic chemical sensors with partial specificity and an appropriate pattern recognition system, capable of recognising simple or complex odours (and other gaseous mixtures)[1]. The ability of an electronic nose to rapidly discriminate between slight variations in complex mixtures makes the techniques ideal for on-line process diagnostics and screening across a wide range of application areas. A recent international symposium on Olfaction and Electronic Noses

(ISOEN 99, Tubingen, Germany, September 1999)[2] highlighted the variety of monitoring applications currently being researched. Examples included :

- Detection and identification of micro-organisms in headspace samples
- Qualitative and quantitative analysis in the petroleum industry
- Detection of amniotic fluid in vaginal smears
- Detection of TNT
- Development of a field odour detector for environmental applications
- Quality control applications in the automotive industry
  Discrimination between clean and contaminated cows teats in a milking system
- Analysis of cosmetic raw materials
- Differentiation of wine aromas
- Classification and degradation studies of olive oils
- Flavour analysis in foods

This list of the different research areas shows the board potential market for electronic nose technology. However, it has been recognised by the R&D community that widespread uptake of the technology has been severely restricted by the lack of standardisation in this area (eg *'Performance definition and Standardisation of Electronic Noses', J.W. Gardner and P.N Bartlett* [3] and *'Electronic noses – specify or die', P. Mielle et al* [2]). There is therefore a need to develop internationally acceptable methodologies for the harmonization of electronic nose characterisation and performance testing. This requirement can be best met through the development of standardised procedures and protocols that enable quantitative and objective comparisons to be made between different types of instrument. These procedures could then form the basis of future international standards in this area.

The International Standards Organisation defines standards as 'documented agreements containing technical specifications or other precise criteria to be used consistently as rules, guidelines, or definitions of characteristics, to ensure that materials, products, processes and services are fit for their purpose'. The combination of multiple sensors, partial specificity and pattern recognition analysis make the usual techniques of instrument characterisation and calibration difficult or impossible to apply to electronics nose instrumentation. As a result of this issue there are, to date, no international standards (or drafts) which directly refer to electronic nose measurement.

Research into electronic nose development and application is particularly strong within Europe. Since the beginning of 1999 a European network (funded under the European Commision's ESPRIT 4 Programme) has been in place covering the general topic of artificial olfaction – the Network of Excellence on Artificial Olfactory Sensing 'NOSE' (project reference : 29526)[4]. The aims of the NOSE network are to:

- Stimulate information exchange
- Develop synergy in the artificial olfaction community
- Orient technology innovation towards the operational needs, and
- Stimulate the use of development of standards.

The network, which currently has 89 member organisations, provides a forum for knowledge transfer between users, researchers and instrument developers and it is anticipated that work on this activity would draw upon the facilities provided by NOSE.

In order to fit the field into a proper metrological framework it is important to use and understand the internationally-accepted terms (as defined in the International Vocabulary of Basic and General Terms in Metrology) that are relevant to electronic nose measurements. The most important of these include :

- **Repeatability** – closeness of the agreement between the results of successive measurements of the same measurand carried out under the same conditions
- **Reproducibility** – closeness of the agreement between the results of measurements of the same measurand carried out under changed conditions of measurement
- **Uncertainty of measurement** – a parameter, associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand.
  Sensitivity – change in the response of a measuring instrument divided by the corresponding change in the stimulus.
- **Measuring Range** – set of values of measurands for which the error of a measuring instrument is intended to lie within specified limits
- **Traceability** – property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties.

The primary requirement for the project is to develop suitable techniques and procedures that will enable the metrological parameters defined above to be determined for electronic nose instrumentation, in a way that is acceptable to both the instrument developers and to the user community.

5. ECONOMIC AND SOCIAL BENEFITS

The field of electronic nose research is an area of technological development where Europe has a world-leading position. A recent review of patents in electronic nose technology (T. Talou and B. Dubreuil[2]) showed that over 50 new patents had been deposited over the last decade, with the majority coming from European companies and Universities. The development of appropriate standardisation will be a key factor in enhancing world trade in this area, where International Standards are vital as they represent the core of the World Trade Organisation's Agreement on Technical Barriers to Trade, while protecting European IPR. The diverse and dispersed nature of the different groups involved in the development and exploitation of electronic nose technology means that this benefit could only be realised if the project is undertaken as a collaborative European project rather than taking place at a National level.

Other important beneficiaries of such a project would be the wide range of users who could benefit from the availability of standardised performance characterisation of electronic nose technology. This would enable potential users to properly assess the application of the technique in their area. Examples of application areas where this would be of direct relevance include :

- **Industrial process monitoring and control** – electronic noses have demonstrated their potential applicability to on-line process control and production QA/QC activities across diverse industrial sectors, including the petrochemical industry, food and beverage production, the automotive industry, and the perfume and cosmetics industry. The availability of improved process control techniques with specified performance levels would have a direct impact on industrial efficiency and competitiveness.
- **Environmental monitoring** – odour nuisance is one of the major causes of public complaints about atmospheric pollution, and electronic noses offer the potential for field odour detection and characterisation. They have also demonstrated their applicability in the analysis of water quality and waste-water treatment, another important environmental issue.
- **Detection of fraud and consumer protection** – the ability of electronic noses to discriminate between slight changes in complex vapour mixtures gives them the potential to identify illegal copies of a range of products from wines and spirits to perfumes and cosmetics.
- **Law and Order** – there are potential applications in the rapid detection of vapours from explosives and drugs.
- **Health and Safety** – the use of electronic noses in the detection of bacteriological contamination is one of the possible H&S applications of the technique.

As indicated above, the potential market for electronic nose technology is large. An estimate of the world-wide market size (made in 1998[1]) showed a hundred-fold growth in sales between 1993 and 1997, and predicted an annual market of 2500 instruments with an approximate value of 160 million Euro around the turn of the millennium.

6. SCIENTIFIC AND TECHNOLOGICAL OBJECTIVES

The principal objective of the project will be the development and dissemination of a set of procedures that enable the characteristics of any electronic nose to be quantifiably assessed. The characteristics to be determined should include all of the metrological parameters defined in Section 4, namely repeatability, reproducibility, measurement uncertainty, sensitivity, measuring range and traceability.

It is anticipated that the first phase of the project should consist of a thorough review of the QA/QC and calibration work currently carried out for electronics nose measurements, and the general specification requirements of users. This review should draw upon experience from across the electronic nose community. The results of this review could then be used to prepare draft procedures that were generally acceptable to the developers and suppliers of electronic nose instrumentation, and met the requirements of users.

A programme of experimental work should be undertaken to demonstrate the validity and practicality of the draft procedures, with reporting of the experimental results to be included as part of the project deliverables. As part of this process, it will be necessary to properly assess various characteristics of electronic nose performance, including :

- **Drift** – sensor drift needs to be monitored and/or compensated for in order to achieve good reproducibility.
- **Comparability of sensors** - particularly in terms of comparability before and after sensor replacement.
- **Environmental influence** – the effects of temperature, pressure and humidity need to be quantified in order to define operation limits for a given level of performance.
- **Transfer of single sensor characteristics to overall instrument performance** – one possible option for standardisation would be to quantify the characteristics of each of the individual sensors and then extrapolate the results to the behaviour of the multiple sensor array.

Another important element of the experimental work will be the realisation of suitable calibration artefacts. At present the majority of electronic nose measurements are based on application-specific comparison measurements, and the specific chemicals which are in any mixture are not known. Any new 'calibration standards' will need to consist of generic mixtures that reflect the gas components typically found in the sample head-space, and which have a significant effect on the various detector responses. The list of chemicals used by an electronic nose manufacturer for sensor testing is included here as a possible starting point for the development of such standards:

Volatile component	Concentration Range/ ppm
Acetaldehyde	0.09 - 0.9
Ammonia	0.01 - 0.1
2-chloro-6-methylphenol	1 – 20
Ethyl Hexanoate	1 – 74
Methanthiol	0.14 - 1.4
Methanol	25 – 1000
1-octen-3-ol	1 – 20
Propanoic acid	0.06 - 0.6
Trimethylamine	0.01 -0.2
Toluene	25 – 1000

Source : T.M. Hawkins and P.J. Travers[2]

The results of the experimental work would be used to revise the draft procedures, and the final deliverable of the project would be the dissemination of the final procedures. These should be in form that would make them suitable to be the basis of future international standards in this area.

In order to meet the requirements for general applicability and acceptability it is anticipated that partners from a range of organisations would be directly involved in the project, possibly including contributions from manufacturers, users, research organisations, and National Measurement Institutes.

7. ADDITIONAL INFORMATION

The details of the information sources referred to in this document are given below :

1) 'Electronic Noses – Principles and Applications'; Julian W. Gardner and Philip N. Bartlett; Oxford University Press, 1999

2) Proceedings of ISOEN 99; published by the Institute of Physical Chemistry, University of Tubingen, Germany; ISBN 3-00-004819-7

3) 'Performance definition and standardization of electronic noses'; Julian W. Gardner and Philip N. Bartlett; Sensors and Actuators B 33 (1996) 60-67

4) http://nose.uia.ac.be : Homepage of NOSE – Network of Excellence on Artificial Olfactory Sensing

ANNEX A7

GLOSSARY OF ODOUR DESCRIPTIVE TERMS

Aldehydic	a floral bouquet harmonised with a complex of fatty aldehydes which contribute to the fragrance blend.
Animal	reminiscent of either musk Tonkin, castoreum, civetor ambergris and contains a warm, vibrant nuance.
Balsamic	sweet vanillic note with a slightly woody background
	the main fragrance theme
Citrus	reminiscent of citrus fruits, clear
Cloying	extreme or excessive sweetness, or the ability of an odour to linger long after contact
	rich, full bodied and profound
	the absence of sweetness, including woody, grassy and ferny odours
Earthy	the musty stale smell of freshly turned soil
Ferny	special green quality punctuated with a woodiness from the stem
	devoid of stimulating or interesting qualities
Floral	odour of flowers, one or a mixture
Fresh	an invigorating odour, reminiscent of the outdoors and typified by green citrus notes
Fruity	suggestive of any of the edible fruits
Fungal	reminiscent of mushrooms
Grassy	green and leafy with a slight touch of sweetness reminiscent of the odour of freshly cut grass
Green	fresh leafy scent
Harsh	crude, unbalanced, rough, pungent odour
Hay	sweet clover odour reminiscent of coumarin
Heady	powerful, stimulating and intoxicating
Heart	the heart of a perfume is its central and decisive part; the main constituent, core or base of a composition which gives it character
Heavy	generally sweet and balsmic

Herbaceous	grassy green, spicy and somewhat medicinal
Honey	sweet, heavy and syrupy with a waxy background
Leather	pungent and smoky with a slight sweetness
Lift	brilliant top note with wide diffusiveness
Light	neither sweet nor cloying with a fresh note that is predominant
Liqueur	sweet and fruity with a flavour top note and alcoholic overtones
Mellow	aged, balanced, smooth and rich
Mushroom	pungent, musty with some earthy-green tones
Musty	mouldy, damp and possibly even fungal
Rounded	balance, smoothness and harmony
Sharp	strong, penetrating and often pungent
Tobacco	primarily pungent, with a light touch of green
Top note	the initial fragrance impression, the first odour perceived
Velvety	soft and smooth, lacking harsh chemical notes