# Odour Measurement and Characterisation

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ISSN 1475 6684

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# Odour Measurement and Characterisation

## Executive Summary

This report reviews work published on the measurement and characterisation of odorous species.

The three main areas covered are:

- an investigation into the validity of objective methods for characterising odour and establishing odour scales;
- quantitative experimental studies to determine the limits of currently available techniques in measuring common odorous gases at ambient levels, and
- an assessment of the requirements for gaseous odour standards to meet industrial and regulatory requirements for odour monitoring.

CONTENTS

# 1 INTRODUCTION AND BACKGROUND

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 has never been successfully defined in terms of simple physico-chemical properties of the molecules concerned. Therefore, any true assessment of odour depends ultimately on the use of people and their subjective olfactory response.

This report outlines the current understanding of the olfaction process and describes some of the empirical odour scales and models that have been developed. It goes on to describe the performance and limitations of the main sampling and analysis techniques that can be used for the measurement of odorous species. The report concludes with a discussion of the requirements for standards of odorous gases.

# 2 OBJECTIVE ODOUR SCALES

It is estimated[2] 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 research in this area, the final answers to these questions remain undetermined.

The following sections contain a description the biological processes that occur during odour detection; give details of some of different classification schemes that have been applied to different odours and the theories of odour perception that lie behind them; and discuss some of the issues associated with the use of human odour panels to quantify and classify different odours.

## 2.1 BIOLOGICAL MECHANISM FOR ODOUR DETECTION

The basic anatomy of the human nose and olfactory system have been understood for some time. Figure 2.1 is a schematic diagram of the mammalian olfactory system[3]. The initial detection of odours takes place at the posterior of the nose in the region known as the olfactory epithelium. Odour molecules travel through the mucous layer – a 40 micron thick fluid layer with a high concentration of lipids – until they reach one of the olfactory cilia, where molecular reception occurs. The odour molecule must be soluble in the mucous layer for this transport to take place. The receptor cells are connected via axons to the olfactory bulb in the brain. In the bulb the axons converge at sites called glomeruli.

Human DNA research[4] has shown that approximately 1000 genes encode 1000 different odour receptors, and that each receptors must therefore respond to several different odour molecules. Further experiments have shown that these receptors are distributed randomly

within the olfactory epithelium. However, there is strong evidence[5] to suggest that the receptors connecting to each individual glomerulus are of the same type. 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.

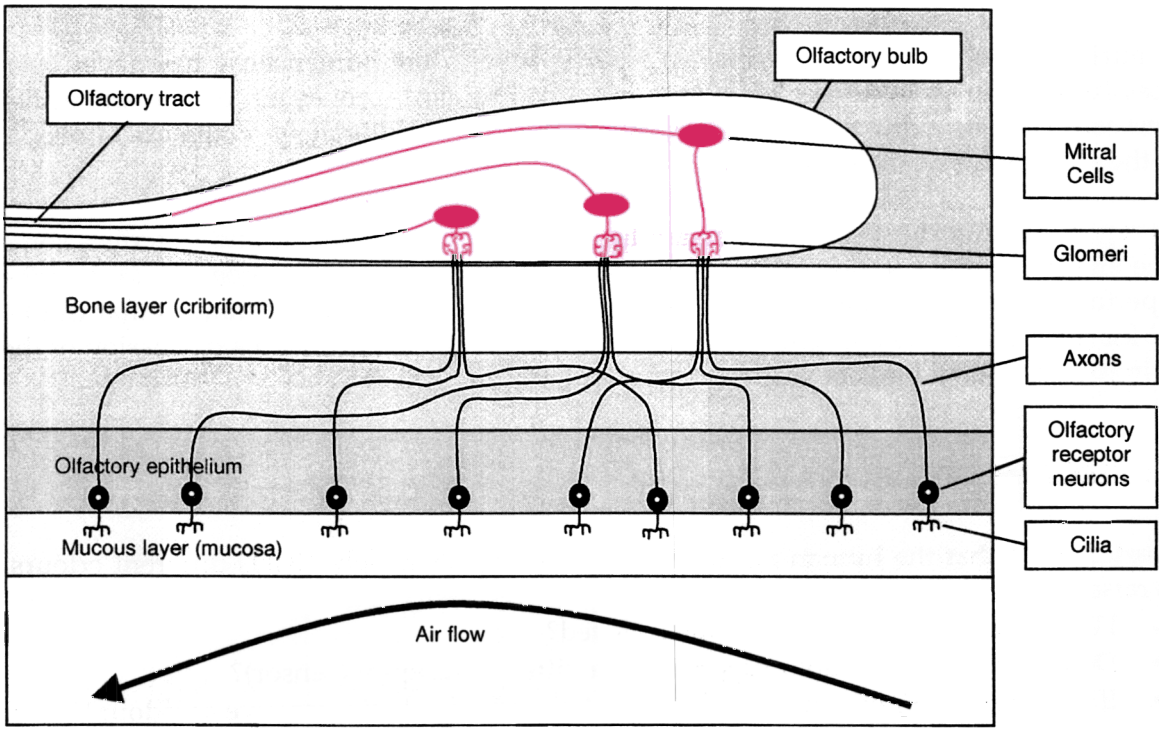



*Figure 2.1 Mammalian Olfactory System*

There are two other areas in the nasal cavity which respond to inhaled 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 is though to be vestigial in humans.

### Odour Reception Process

The basic process of odour reception within the receptor cell follows a cascade process that is analogous to that of many other biological systems, including photoreception, neurotransmitter reception and hormone reception[6]. Figure 2.2 shows the key elements of the odour receptor cell in its rest state.

Reception of an odorous molecule triggers a cascade of reactions within the olfactory receptor neurons which ultimately leads to the transmission of an action potential down the olfactory nerve. A simplified description of this transduction cascade is given below, and illustrated in Figure 2.3.

### The cAMP Transduction Cascade

i) The cell remains in its rest state until an odorous molecule binds with one of the G-protein coupled receptors. The receptor then changes shape and couples to a G-protein

(G-olf). The G proteins consist of three sub-units: the active alpha sub-unit, and the regulating beta and gamma sub-units. In the rest state the alpha sub-unit binds to Guanosine Di-Phosphate (GDP).

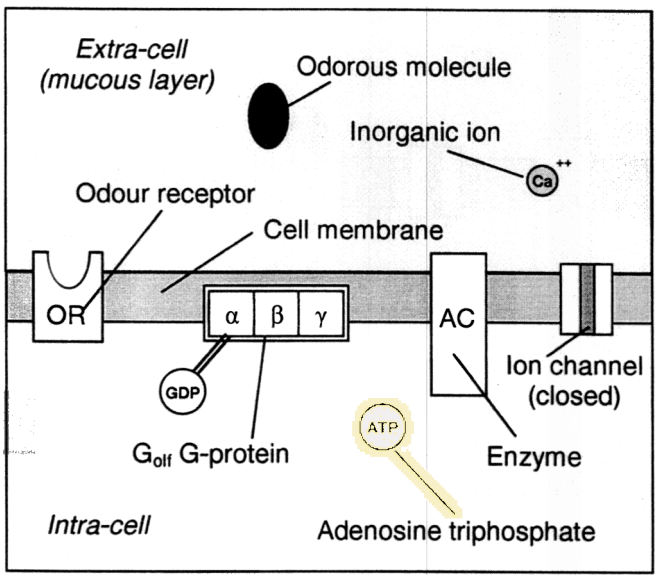



*Figure 2.2 Key Elements in Cellular Odour Reception and Transduction*

ii) When the G protein is activated by the odour receptor the GDP in the alpha sub-unit is replaced by Guanosine Tri-phosphate (GTP). This process causes the alpha sub-unit to disassociate from the beta and gamma subunits.The released alpha subunit now associates with and activates an enzyme – adenylyl cyclase (AC).

iii) The enzyme activation process hydrolyses the GTP to GDP. The alpha subunit then re-binds with the beta and gamma sub-units, returning the G-protein to its rest state.

iv) The activated enzyme cyclizes Adenosine TriPhosphate (ATP) into cyclic-3'-5'-AdenosylMonoPhosphate (cAMP), which acts as a intracellular hormone (commonly know as a "second messenger").

v) The intracellular concentration of cAMP increases dramatically and this activates (opens) gated ion protein channels in the cell membrane. The open channels allow extracellular inorganic ions ($Ca^{++}$) to flow into the cell, causing it to polarise.

vi) The cell is depolarised by a flow of chloride ions, and this $Cl^-$ whole cell current is the source of the odour reception signal which is carried to the olfactory bulb via the axions[7].

The original odorous molecule can be cleared from the receptor by a number of processes including interaction with an odour biding protein and chemical conversion by UDP-glucuronosyltransferase (UDP-GT) or cytochrome P-450 monooxygenase (P-450). Without further activation the cAMP concentration in the cell falls as the cAMP is hydrolysed to Adenosine MonoPhosphate (AMP), and as a result the ion channel closes.

The process described above is not the only transduction cascade in olfactory reception. Another G-protein mediated process involving Inositol TriPhosphate (IP3) and diacyl glycerol (DAG) has been shown to act directly on the ion channels and the intracellular $Ca^{++}$ concentration. Both cascade processes can occur in the same cell, and may be activated by different odorants[8].

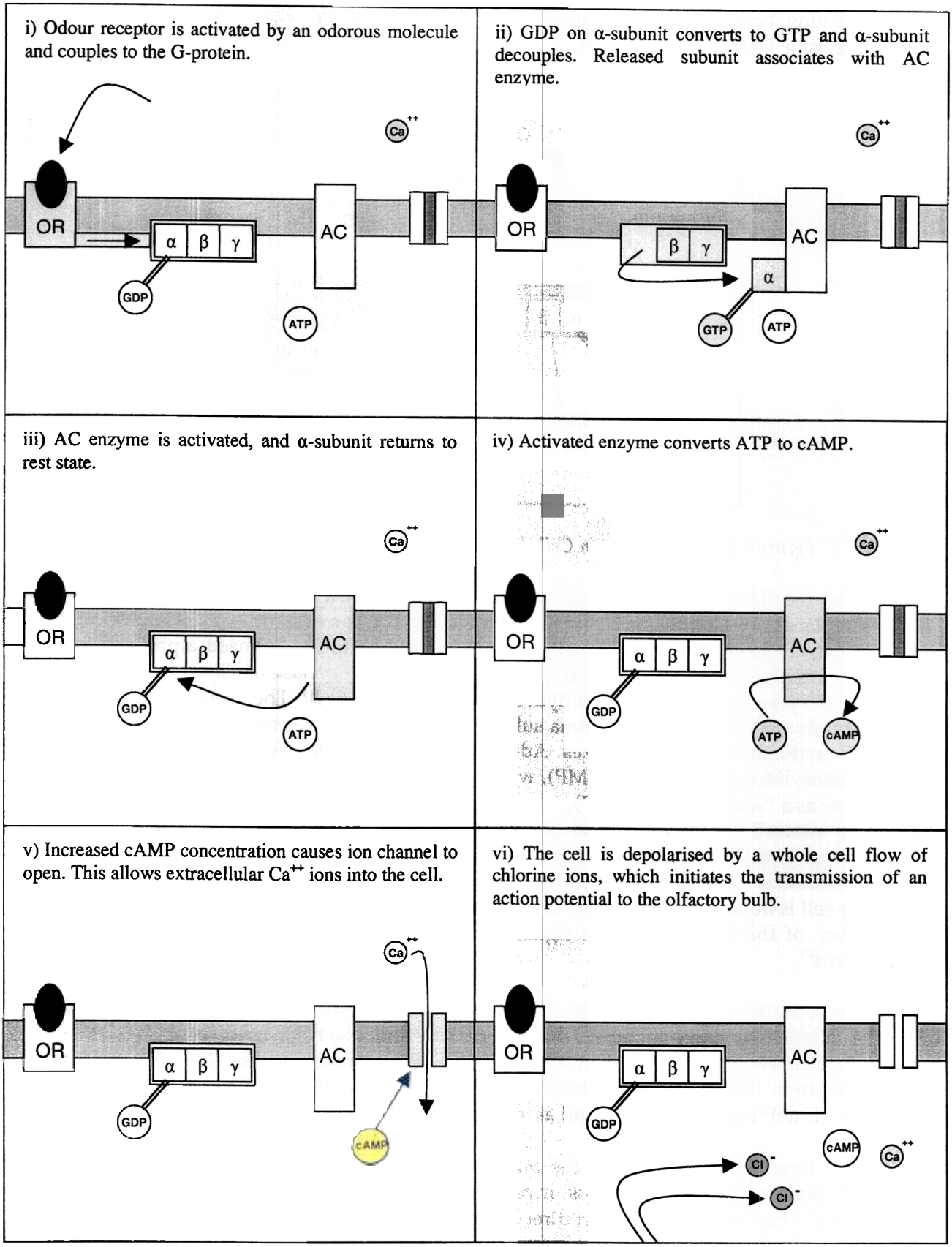



*Figure 2 3. The cAMP Transduction Cascade*

## 2.2 CLASSIFICATION OF ODOURS

A fundamental question which arises when investigating odour character is whether human (mammalian) odour classification is based on a set of primary odours and, by implication a discreet set of primary odour receptors, or on a continuum of odour sensing. These two modes of sensing are best described by means of an analogy with colour vision, where the eye responds to three primary colours, and 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 models of odour are based on the premise that discreet primary odours exist with respective primary odour receptors. Given this assumption, 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[9] in the 1950s. The method used was to rationalise the different descriptions of odour types and classify 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 primary odour categories are given in Table 2.1.

*Table 2.1 - 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 descriptions relating to 1573 organic compounds, gives 19 categories or clusters of odour[10]. 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.

An alternative model references odour quality to specific odoriferous molecules based on a classification of odour descriptor and structure[11]. The approach was based on the analysis of 1,400 molecules from which the authors concluded that 42 reference points (odours) are sufficient to define this structural olfactory relationship continuum (odorous space).

Other methods of classifying odoriferous molecules have also been presented, including physicochemical parameters such as solubility, entropy or energy to classify odours[12,13]. Although parameters such as solubility can affect the ability of the nose to detect an odour, it is generally considered that these sorts of parameter are not directly responsible for odour quality.

## 2.3 THEORIES OF ODOUR PERCEPTION

In Section 2.1 the biological mechanism for odour reception was described. However, the key question that is not addressed is :

*What are the property of a specific chemical that define the odour that is perceived ?*

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[14-20]. 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.

### 2.3.1 Stereochemical Theory

A 'stereochemical theory' of odour was postulated by Amoore[9] in the early 50's as part of his research into odour classification. Amoore related odour quality to molecular shape, and having listed 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[22]. 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[23]. 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.

A significant number of QSARs relating to odour have been published and recently reviewed[24]. For example, the benzaldehyde-likeness of the odour of 25 alkyl-substituted benzaldehydes and nitrobenzenes, and benzonitrile has been assessed, and the results correlated with molecular shape. QSAR techniques have been applied to various characteristics of odorous species including odour quality, intensity and threshold.

### 2.3.2 Molecular Vibration – Odour Relationships

Originally postulated in 1937 by Dyson[25], Wright[26] 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 $cm^{-1}$. This approach has not been accepted universally. For example, 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[27] 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[28] 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 $cm^{-1}$ appears to be arranged along a 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[29].
  Pungent sensations (detected by the Trigeminal nerve) 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[30] 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)[31,32]. 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.

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.

A study was carried out to investigate the relationships between IETS and infrared spectra of various odour species and their associated odour characters[xx]. The conclusion of this review was that there is no obvious relationship between odour and absorption frequency, particularly given the predicted low resolution of the odour receptors. 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 used in the study. However, without more detailed knowledge of the interaction between the odorous molecules and the odour receptors it seems unlikely that a deterministic relationship between the properties of a molecule and its perceived odour will be realised in the near future.

### 2.3.3 Odour Perception - Conclusions

Although the mechanism for odour reception and transduction is understood, significant questions remain about the relationship between the perception of a particular odour and the receptor response to that chemical. Most models of odour perception attempt to relate certain characteristic of the odour species to its perceived odour. However, other, perhaps critical, factors in odour perception 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[34] 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.

## OLFACTOMETRIC ANALYSIS (HUMAN ODOUR PANELS)

### Background to Olfactometric Analysis

Although the details of human odour perception not yet clearly understood various methods do exist for quantifying and classifying odours. These are generally based around 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[35], which is closely based on the approach developed in the Netherlands 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.

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.

### 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

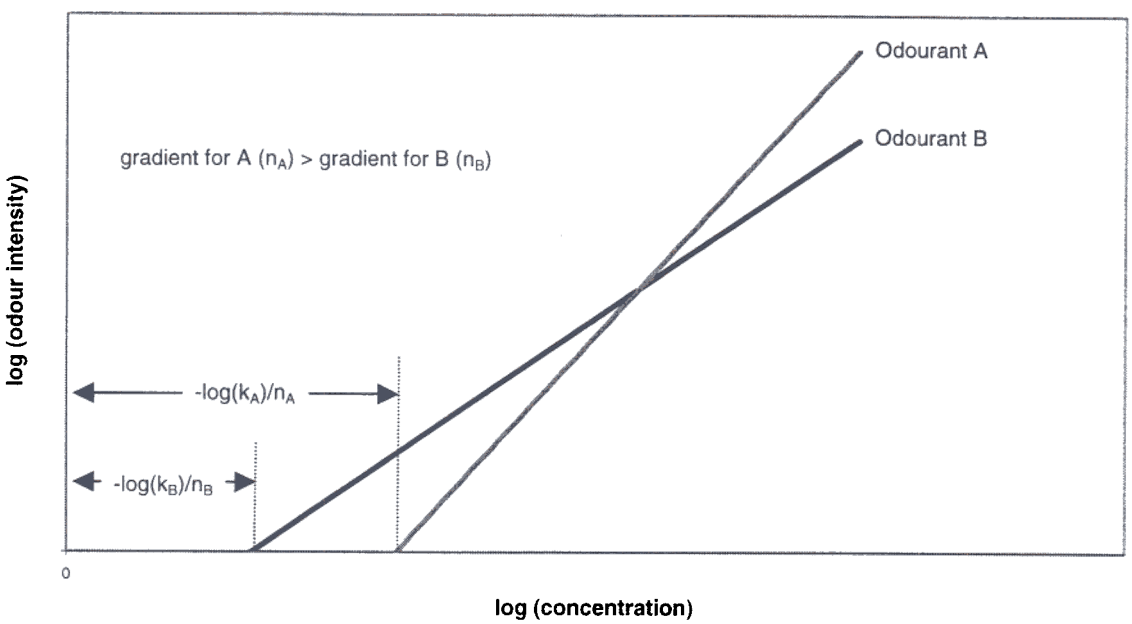
The odour intensity, I, is a measure of how strong a particular odour is. Odour intensity can in general only be defined in relative, subjective terms, by comparing one odour to another. Steven's law (1957) is usually quoted when referring to odour intensity, where the relationship between odour intensity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

$$I = kc^n$$

or

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

*Figure 2.4 - Diagram of the Perceived Intensity vs. Concentration Relationships between two Odourants A and B*




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 2.4.

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 one indicates that an odourant's perceived intensity increases linearly with increasing concentration. Values of $n$ other than one show the deviation from linearity.

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

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[36-38]. The value of $k$ is known to vary over six orders of magnitude for different chemicals.

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).

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[39]. 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[40]. However, as with other areas of olfaction research, there is as yet no generally accepted model.

### 2.4.3 Odour Values

The odour value for a particular odourant gives a measure related to its odour intensity[41]. The odour value (OV) of a substance, is defined as the ratio of its actual concentration to 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[42]. However, later they have been applied as a quantitative measure to specify an odourant's intensity[43], 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 2.4.2.

- 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.

### 2.4.4 Olfactometers

An olfactometer is an instrument for the preparation and delivery of an odour stimulus to a chemoreception system – usually a human assessment panel. Various reviews[44,45] 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[46,47] 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 elsewhere (see Table 4.3), 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').

### 2.4.5 Odour 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[48] 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 2.2.

*Table 2.2 – 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 |

### Gas Chromatograph (GC) Sniffing

Human sniffing at the exit ports of GC-columns is a well established technique[49] 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.

## 3 VALID FIELD SAMPLING AND MEASUREMENT METHODS

### 3.1 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.

### 3.2 SAMPLING METHODS

#### 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 air samples into previously-evacuated gas cylinders (with a volume of a few litres) at a flow rate of around a litre a minute. If metal cylinders are used, then these require specially-passivated internal walls (eg electro-polished) to ensure that their interiors are inert to the species being sampled. A typical 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 (less than one ppb) before the final evacuation stage.

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.

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.

A recent development in 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 silicon-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.

### 3.2.2 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[50].

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 3.1 gives examples of the sorbents that can be used for various classes of odorous molecules:

*Table 3.1 - 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 |

Desorption of the compounds of interest is usually performed thermally. This involves heating the sample 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 can be a major issue 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[51,52].

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 an effective desorption mechanism is not known, and useful measurements cannot be made until a suitable mechanism is identified.

## 3.3 MEASUREMENT METHODS

### 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.

### 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.

FID detection is suitable for a wide range of volatile organic compounds. Table 3.3 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.

*Table 3.3 – 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 | |

### 3.3.3 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 sulphurous odour standards were performed to assess the applicability and sensitivity of this technique to some of the key odour species.

The first measurements were made using a 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. 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. The sensitivity of these measurements was limited by the methane and carbon dioxide matrix. This was due to 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 3.4 summarises the result of the GC-SCD measurements, with the detection sensitivities normalised to a sample volume of 1 ml. 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).

*Table 3.4 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 Table 3.4 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 3.3.1.

### 3.3.4 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 many different 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 3.5 and 3.6 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 3.4. 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 3.5 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 3.6 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. This is particularly the case for primary thiols, such as methanethiol and ethanethiol, which are easily oxidised into the disulphide form[53]. 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-butyl 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.

### 3.3.5 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[30].

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)[54]. A recent review[55] 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[56]. Several reviews have been published the odour qualities of chiral compounds[57-59], including the role of chirality in structure-odour relationships[60].

## 4 REQUIREMENTS FOR ODOROUS GAS STANDARDS

### 4.1 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 4.1 gives examples of the types of odorous species that can be produced during the manufacturing processes in different industries.

*Table 4.1 - Examples of Odorous Pollutants in Various Industrial Areas*

| Industry | Sulphur Compounds | Nitrogen Compounds | Aldehydes and Ketones | Acids and alcohols | Hydrocarbons |
|---|---|---|---|---|---|
| Pharmaceutical | - | Acrylonitrile | - | Phenols<br>Acrolene | Benzene<br>Toluene |
| Insecticides | Hydrogen sulphide | - | - | Alcohols | Chlorobenzene<br>Chlorine |
| Foundries | | Ammonia<br>Amines | Formaldehyde | Phenols | |
| Oil/asphalt plant | Thiols,<br>Sulphides | | | | Various |
| Aircraft industry | | | Formaldehyde<br>Acetaldehyde<br>Benzaldehyde | | 1-pentene<br>1-butene |
| Perfumes | - | - | Aldehydes<br>Ketones | - | - |
| Textile | - | Amines | Formaldehyde | - | Solvents |

| | | | | | |
|---|---|---|---|---|---|
| Paper | Hydrogen sulphide<br>Thiols<br>Dimethylsulfide<br>Dimethyldisulfide | - | - | - | - |
| Fish Processing | - | Trimethylamine<br>Cadaverine<br>Putrescine<br>Ammonia | - | Fatty acids<br>Butyric acid | - |
| Slaughter-houses | Hydrogen sulphide<br>Thiols | Ammonia<br>Amines | Aldehydes | Fatty acids | - |
| Pig farming | Hydrogen sulphide<br>Thiols | Ammonia | Aldehydes | Fatty acids | |
| Manure Treatment | Disulfides | Trimethylamine | - | Propionic and Butyric acids | - |

As indicated above, a major area of odour pollution is in the sewage and waste treatment industries. Table 4.2 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.

*Table 4.2 - 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 | $C_8H_6NH$ | Fecal, nauseating | 0.0006 |
| Scatole | $C_9H_8NH$ | 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 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.

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.

## 4.2 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 have been identified to provide a cross section of the types of chemicals, and which also targetted some specific industrial requirements.

The CEN standard on olfactometry[61] specifies n-butanol as a reference species for odour measurement. 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 that is suitable for the dilution systems commonly used for olfactometry.

Some other odorous mixtures with industrial relevance have already being addressed elsewhere in the VAM programme, these include carbonyl sulphide, formaldehyde, ammonia, benzene, toluene and xylene.

Based on the industrial requirements outlined in Section 4.1 the most important class of species identified for further research were volatile organic compounds with active sulphur groups, for example ethanethiol, 2,2-dimethyl ethanethiol, dimethyl sulphide, and hydrogen sulphide. Sec-butylamine was also identified as key nitrogenous odorous species.

Another priority area is odorous species with specific industrial relevance, for example 1-pentene, which has been identified as a key odour component in engine emissions. Another industrial sector 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'[63] identified a sub-set of gases which provide a useful multi-component standard.

Table 4.3 shows the odour threshold (OT) data for some of the key species identified for further research [62]. 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 4.3 – Odour Threshold Data for Key Pollutant Species*

| Species | Reported Threshold Range | Best Estimate of Threshold | |
|---|---|---|---|
| | (µg/m$^3$) | (µg/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 |

# 5 CONCLUSIONS

## 5.1 ODOUR CHARACTERSATION

Basic models of odour perception probably over-simplify the actual mechanism for the detection and identification of different odours. Continuing research into odour perception suggests that the establishment of a deterministic odour scale is unlikely in the near future. However, improved knowledge of the sensing mechanism, and the properties of the molecules that trigger the odour response, should provide important advances in the study of olfaction, including insight into the vast range of odour thresholds observed for different species, and possibly provide the ability to predict the likely smell of unknown chemicals.

## 5.2 MEASUREMENT OF ODOROUS GASES

The results of an investigation are reported 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.

### 5.3 REQUIREMENTS FOR ODOUR STANDARDS

Key species have been identified for which there is a requirement for trace-level odour standards. These are required to provide reference artefacts for the main types of odorous species, as well as targeting a number of specific industrial and environmental monitoring applications.

## 6 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 (RvA). The author would also like to acknowledge the contributions of staff in the Analytical Science Group at NPL, including Robert Wielgosz, Paul Holland, Andrew Brown, Des Alphonso, Hansa D'Souza, Malcolm Henderson, Paul Quincey and Martin Milton.

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