# CHAPTER 1

# INTRODUCTION

## 1.1 BACKGROUND

The increased pollution of the environment has generated a need for the continuous improvement of existing methods and for the development of new, reliable and sensitive methods for air, water and soil quality control.

Volatile aldehydes in air such as formaldehyde, acetaldehyde and acrolein have received attention as hazardous air pollutants. Formaldehyde (HCHO) is classified by the Environmental Protection Agency (EPA), the American Council of Governmental Industrial Hygienists (ACGIH), the National Institute of Occupational Safety and Health (NIOSH) and the Occupational Safety and Health Administration (OSHA) as a probable human carcinogen [1,2].

Airborne concentrations of HCHO above 0.1 ppm can cause irritation of the eyes, the nose and throat, the upper respiratory tract and the lacrimation glands [1,2,5,6]. It is also thought that HCHO can cause nausea, dizziness and lethargy at levels as low as 50 ppb [7].

Aldehydes are present in exhaust gases due to incomplete combustion of hydrocarbons and in photo-oxidation processes occurring in the atmosphere [8]. Sasol has recently added alcohol to their fuel [9], which has the advantage of reducing particulates, carbon monoxide and nitrous oxide emissions. However, this measure leads to an increase in aldehyde emissions, in particular formaldehyde and acetaldehyde [10-12].

This problem, however, is not localised to our external environment. Since people in developed countries spend up to 90% of their time indoors, exposure to air pollutants in the indoor environment can be high. In the 1970's, concerns were raised that certain organic compounds found in non-industrial buildings could cause health problems similar to those of Sick Building Syndrome [4,13]. As a result, formaldehyde has been the most widely studied compound in indoor air. Average HCHO levels in office buildings range from 10 ppb to 78 ppb. Several studies point to formaldehyde predisposing children to respiratory tract infections. 1 to 2% of children exposed to 60-120ppb HCHO at home may develop asthma; with an increased likelihood if also exposed to tobacco smoke [4]. Concentrations of formaldehyde were found to be 10 or more times higher indoors than outdoors [4]. Tobacco smoke, combustion gases from gas appliances, disinfectants and water based paints [4,14] release formaldehyde indoors. The main culprits however, are products manufactured using urea-formaldehyde (UF) resins including particleboard used in flooring and furniture, hardwood plywood panelling and UF-foam insulation [1,4,7,13,15]. Table 1.1 lists the Permissible Exposure Limits (PEL) for airborne HCHO in the workplace (indoors).

Table 1.1 Indoor Personal Exposure Limits (PEL) for airborne formaldehyde [3,4].

| | PEL | STEL | CEILING |
|---|---|---|---|
| OSHA | 0.75ppm[#] | 2ppm[##] | 0.5ppm* |
| NIOSH | 0.016ppm | | 0.1ppm |
| ACGIH | | | 0.3ppm |
| WHO | | 0.1ppm** | |

[#] Time Weighted Average (TWA) over 8 hours.

[##] Short Term Exposure Limit (STEL) during 15 min period.

* action level measured over 8 hours.

** 30 min average.

Acetaldehyde also causes irritation of the eyes, nose and throat. However, acetaldehyde is usually handled in industry under closed systems, as it is an explosive hazard. In industry exposure to acetaldehyde is not known to be continuous or at high levels, hence the recommended threshold limit for acetaldehyde is 100ppm with a Short Term Exposure Limit (STEL) of 150ppm [6].

Higher aliphatic aldehydes, such as propanal and butanal, are typically components of the exhaust of internal combustion engines. They are characterised by a lower general toxicity and as such, no exposure limits have been set for them [6].

The toxicity of the aliphatic aldehydes generally decreases as the chain length increases [6].

Acrolein and crotonal, are acute eye and respiratory irritants. The toxicity of these aldehydes is enhanced by the presence of the double bond. The threshold limit for acrolein is 0.1ppm with a STEL of 0.3ppm for 15min. Crotonal is ten times less toxic than acrolein, hence the threshold limit of 2ppm [6].

Thus increasing awareness of the effects that certain aldehydes, particularly formaldehyde, can have on human health, indicates a need to be able to detect and quantify the level of aldehydes in the environment, both indoor and outdoor. Research into the determination of formaldehyde in air, still continues despite the several methods already developed. Although detection of exposure limits can be reached with these methods, they prove tedious and time consuming.

With the aim that no sample preparation be required, methods for analysing aldehydes directly would be ideal, but they make use of bulky and complicated instrumentation. Although direct analysis of HCHO gas, using Gas Chromatography (GC) would also be ideal, we are hampered by the fact that common detectors in GC like the Flame Ionisation Detector (FID) and the Thermal Conductivity Detector (TCD) lack sensitivity for this compound [16]. Mass Spectrometry for low masses, such as

30amu for HCHO, would not show sufficient sensitivity either, as this mass falls in the same mass region as air (nitrogen 28 amu and oxygen 32 amu).
Similarly, the detection of acetaldehyde particularly in beer is also difficult, yet important to monitor, as acetaldehyde and other carbonyl compounds are known to contribute to the stale flavour in beer [17]. Acetaldehyde has a mass of 44 amu coinciding with that of carbon dioxide ($CO_2$), which is prevalent in both beer and air. In addition, a high vapour pressure and polarity make acetaldehyde a difficult compound to pre-concentrate on non-polar sorbents. Chromatography on non-polar thin film stationary phases often leads to co-elution of acetaldehyde with the ethanol in the beer.

Indirect methods using derivatising reactions remove these detection and concentration difficulties, while introducing new ones. Problems encountered are determined principally by the sample preparation techniques used. These involve the pre-concentration device, the derivatising reagent and the desorption method.
The collection of gaseous samples in impingers and bubblers is not very portable and convenient for field-work. Hence, much attention has been given to tubes packed with sorbents, where the gaseous sample can be sucked through the tube using a portable pump.

Indirect methods make use typically of the following procedure: The derivatising reagent either coats the sorbent or is present in solution. In the former case, formaldehyde gas reacts with the reagent on the surface of the sorbent. The product is often extracted from the sorbent or solution using a solvent. The extract is then concentrated to a small volume by evaporation and injected into the instrument for analysis. However, the use of toxic solvents is undesirable. Dilution of the product to be analysed, results in a decrease in sensitivity since only a tiny portion of the extract is finally transferred onto the column. An alternative product transfer method is desired. Thermal desorption of the entire contents of the sorbent trap directly onto the column eliminates the above-mentioned concerns.

Adsorbents unfortunately are known to have several disadvantages. They possess active sites, which allow for chemical reactions with the sorbed analytes being analysed, or in this case, the reagent being used for derivatisation. Tenax, for example, is known to release benzaldehyde as one of its thermal degradation products, thereby making it unsuitable for use in benzaldehyde analysis [18]. Some compounds may be irreversibly adsorbed on the sorbent, especially polar compounds on carbon sorbents [19]. Additionally, sorbents must undergo several steps of pre-treatment before being packed into collection tubes. After the analysis, the sorbent must once again undergo several reconditioning and preparation steps before it can be re-used. This entire process becomes time consuming. Thus, the ideal sorbent should be chemically inert, thermally stable and immediately reusable.

Polydimethylsiloxane or silicone rubber, has recently become popular as a liquid-like sorbent [18]. Analytes dissolve into the phase as they would in a solution. The silicone absorbent has a larger capacity or concentration range for which the partition isotherm is linear. For adsorbents once all available sites are occupied by a mono-layer, the adsorbent shows less retention for any further analytes entering the trap (non-linear partition isotherm). Thermal degradation of the silicone, during thermal desorption, produces polysiloxane compounds with reproducible retention times. In addition, these compounds are easily distinguished by their Electron Impact (E.I) mass spectral fragments. After thermal desorption, the silicone rubber is ready for use again.

Several derivatising reagents have been used for the reaction with HCHO and other low molecular mass aldehydes. By far the most popular reagent is 2,4-

DiNitroPhenylHydrazine (DNPH). HCHO is collected on a sorbent or in an impinger containing the reagent, followed by solvent extraction and separation by High Performance Liquid Chromatography (HPLC) with Ultra Violet (UV) detection. HPLC cannot match the desired resolution, speed of analysis, compound identification and quantification of Gas Chromatography (GC). 2,4-DNPH however, is not suitable for use in GC analysis either, as it requires high temperatures to be volatilised (which may decompose the derivative) and regular cleaning of the inlet liner [11,20,21]. Recently, in-situ derivatisation of HCHO, using a SPME fibre coated with O - (2,3,4,5,6-PentaFluoroBenzyl) HydroxylAmine (PFBHA), analysed with GC-FID or Gas Chromatography – Electron Capture Detection (GC-ECD), showed promising results [22]. The method uses a Polydimethylsiloxane (PDMS) – divinylbenzene (DVB) polymer fibre as the sorbent for PFBHA. Formaldehyde again, as with other adsorbents, reacts on the surface of the fibre. As long as the PFBHA remains minimally consumed, the oxime formation rate is limited by the HCHO concentration. The method is ideal for grab sampling and as a passive sampler for time weighted averaging in indoor air analysis. Oximes, in general are volatile and ideal for analysis using GC. The SPME fibre is desorbed directly in the hot inlet of the GC and no special desorption equipment is required. SPME fibres however are fragile and expensive. A more rugged sampling system is required, that would allow many samples to be taken in the field before being transported to the laboratory. Hence, the possibility of performing in-situ derivatisation on our silicone rubber traps using PFBHA, which show a number of advantages over SPME, was investigated.

## 1.2 OUR APPROACH

Sampling methods are required that (1) reduce the complexity and cost of the sampling system involved (2) reduce the experimental uncertainties/errors (3) lower the limit of detection for formaldehyde in the outdoor environment [23].

On this basis, our research was carried out to find a pre-concentration method for formaldehyde gas and other aldehydes, which could fulfil the above requirements using the Silicone rubber traps developed in our laboratories [24-27] in combination with Gas Chromatography – Flame Ionisation Detection (GC-FID) and Gas Chromatography – Mass Spectrometry (GC-MS).

Our aim is (1) to prepare stable gas standards of volatile aldehydes. (2) Select and load a derivatising reagent onto our silicone rubber traps in a convenient, repeatable manner. (3) Demonstrate the efficient pre-concentration of the aldehyde gas standards on the reagent-coated silicone rubber trap. (4) Quantitatively recover and analyse the contents of the trap. (5) Demonstrate *in-situ* derivatisation on our silicone rubber traps with real gaseous indoor and outdoor air samples and headspace analysis of beer.

## 1.3 ARRANGEMENT AND PRESENTATION

Chapter 2 will introduce the methods already available for the determination of formaldehyde and other aldehydes in air. Chapter 3 follows with sample preparation focussing on pre-concentration devices and techniques. Preparation of aldehyde gas standards is described in chapter 4. The instrumentation is briefly discussed in chapter 5. The characteristics of the trap in terms of completeness of reaction on the absorbent, trapping efficiency and complete transfer onto the column are examined in chapter 6. The application of the trap on real gaseous samples is shown in chapter 7.