# CHAPTER 4

# GAS STANDARDS

## 4.1 INTRODUCTION

In order to determine unknown quantities of formaldehyde and other aldehydes in the environment, it is important to test the method on controlled aldehyde atmospheres. Although there are commercial formaldehyde gas standards available, several methods for their generation in a laboratory do exist [101-104,23,32,39,40].

The gas standard used should provide stable, accurate, reproducible and controllable concentrations of the aldehyde studied, at the part-per-million (ppm) and part-per-billion (ppb) levels. It should be simple and ensure that sufficient amounts of the standard will always be available.

There are two types of methods for generating gas standards namely, static and dynamic methods [101,105-107].

## 4.2 STATIC METHODS

Static methods [101,105-107] involve the addition of a known amount of pure analyte gas or vapour to a known volume of diluent gas (nitrogen or purified air) into a closed container, e.g. Teflon bags [22,55], stainless steel cylinders or glass

vessels [32,108]. Mixing of diluent and pure gas then occurs. Although this method is simple and inexpensive, losses of the analyte may occur due to adsorption and condensation on the walls of the container. Leaks can occur and pressure changes will exert an effect on the final concentration. Only limited volumes can be prepared, and poor accuracy arises with the introduction of a small volume of analyte into a dilution gas. Because of these difficulties static methods are not suitable for the preparation of low concentration gas standards of polar analytes.

## 4.3 DYNAMIC METHODS

Dynamic methods [101,105-107] provide a constant concentration of analyte gas over a long period of time. They involve the continuous addition of analyte gas or vapour, having a known generation rate, into a flowing stream of diluent gas with a known flow rate. Once an equilibrium has been reached, these methods have an advantage over static methods. Losses due to adsorption or condensation against the walls are now negligible, since all surfaces are coated with the analyte. Additionally, a wide dynamic range can be obtained by varying the concentrations. These methods also provide flexibility of collection volumes and flow rates used. The main disadvantage is that the equipment used for this set-up is more elaborate and expensive.

Dynamic methods can be divided into 2 groups namely permeation and diffusion methods [101,105-107].

### 4.3.1 PERMEATION METHODS

In this method the idea is to mix a small known volume of the analyte gas or vapour, which passes through the membrane of a permeation device, with a known volume of diluent gas [23,39,40,101,105-107,109-113].

The permeation device normally consists of a PolyTetraFluoroEthylene (PTFE, Teflon®) tube, which is sealed on both ends with Teflon plugs or glass beads, after the analyte gas, liquid or solid is introduced. Teflon is chosen for the construction of the device, because it is chemically inert. After a certain period, if the temperature is held constant, the vapour will continuously permeate through the membrane of the tube at a constant rate. A standard mixture can then be obtained if the permeation tube is immersed in a flowing stream of a purge gas, with a known flow rate.

At equilibrium, the permeation rate(r) of the analyte gas through a membrane is given by [101,105,107]:

$$r = DS\,(P_1 - P_2)\,(A / d) \qquad (4.1)$$

Where D is the diffusion coefficient, S is the solubility constant, $P_1$ and $P_2$ are the partial pressures of the permeant gas on the two sides of the membrane, A is the membrane area and d is the membrane thickness.

By using the Arrhenius equation, the permeation coefficient, B, for a particular gas can be expressed as [101,105,107]:

$$B = DS = B_0\, e^{(-Ep / RT)} \qquad (4.2)$$

Where $E_p$ is the permeation activation energy, R is the gas constant and T is the absolute temperature of the membrane.

The following equation can now be obtained by substituting equation 4.2 into equation 4.1 [101,105,107]:

$$r = B_0 \, e^{(-Ep/RT)} \, (P_1 - P_2) \, (A/d) \qquad (4.3)$$

As shown by this equation, the permeation rate is proportional to the area and membrane material type and inversely proportional to the thickness of the membrane.

To maintain a 1% accuracy in the permeation rate, it is necessary to control the temperature of the permeation tube to within ± 0.1°C, since it can be seen from equation 3 that the permeation rate varies logarithmically with the inverse temperature (1/T) [101,109].

Quite often the above constants are not available to allow prediction of the permeation rate. However, a gravimetric method exists which can also be used to determine the permeation rate. In an environment where the temperature is constant, and a flowing stream of diluent gas is present, the mass loss of the tube is equal to the mass of permeating analyte. The mass loss of the permeation tube must be weighed at room temperature to the nearest 0.01mg. Several measurements will allow the construction of a mass *versus* time graph. The first few points that deviate from the straight line are excluded as these indicate that a steady state has not been reached. The slope of the straight line best fitting the points obtained provides the permeation rate, which can also be described by the following equation [101,109]:

$$r = W / t \qquad (4.4)$$

where W is the mass loss (g) over the time interval t (min).

Errors in the concentration are generated when the permeation rate is not accurately determined. Since the permeation rate is dependant on the temperature, it remains very important that during calibration the temperature remains constant to within 0.1°C. The tube should always be used at that calibration temperature [101,109].

Permeation methods used to generate formaldehyde gas standards have been used previously [23,39,40,101]. One method involves the thermal depolymerisation of paraformaldehyde or α-polyoxymethylene inside the permeation tube [23,39,40,101]. Thermal depolymerisation occurs when the permeation tube is inserted into a glass gas-tight chamber, which is then placed inside a system where the temperature can be controlled at 80°C, e.g. in a thermostated oven or oil bath. There is an inlet for the purging and dilution gas, which allows the gas to be conditioned to the same temperature before entering the chamber. At this stage the dilution gas mixes with the permeated formaldehyde in the chamber and forms a standard gaseous mixture [23,101]. Another method involves the generation of formaldehyde inside a permeation cell. Paraformaldehyde is loosely packed into a gas-tight glass or stainless steel cell with quartz wool. A PTFE permeation tube is placed inside the cell, with one end connected to the purge gas flow and the other end to the mixing chamber. The temperature of the cell was controlled as above. Formaldehyde diffuses into

the teflon tube where it mixes with the diluent gas, then moves on into the chamber. The formaldehyde concentration is monitored over time by a UV spectrometer. Once the concentration (absorbance) over time becomes constant, the standard can be used. In this method, the formaldehyde concentration is inversely proportional to the total flow rate of the diluent gas [101].

It should be noted that, at moderate temperatures, formaldehyde can decompose into carbon monoxide and hydrogen, particularly when in contact with metal surfaces. Hence a modification of this method was made using a silicone membrane and thermally depolymerising $\alpha$-polyoxymethylene therein [101,103].

### 4.3.2 DIFFUSION METHODS

Gas standards are most commonly prepared via diffusion methods [58,101,105-107]. These methods involve the maintenance of a saturated vapour pressure in a reservoir and diffusion through a capillary tube into a stream of purging gas to make a mixture of known concentration. Diffusion of the vapours through the capillary tube will occur at a constant rate, if the tube geometry and temperature remain constant. If it can be assumed that the concentration of the vapour generated at the upper part (mixing chamber) of the diffusion tube is nearly zero and the lower part (reservoir) is saturated, then the following equation can be used to describe the diffusion rate r, in grams per second [101,105-107,114].

$$r = ( DMPA / RTL ) \ln [ P / (P - P_v) ] \qquad (4.5)$$

D is the diffusion coefficient ($cm^2/s$) at pressure P (atm) and temperature T (K). M is the molecular mass (g/mol). P is the pressure at the open end of the capillary

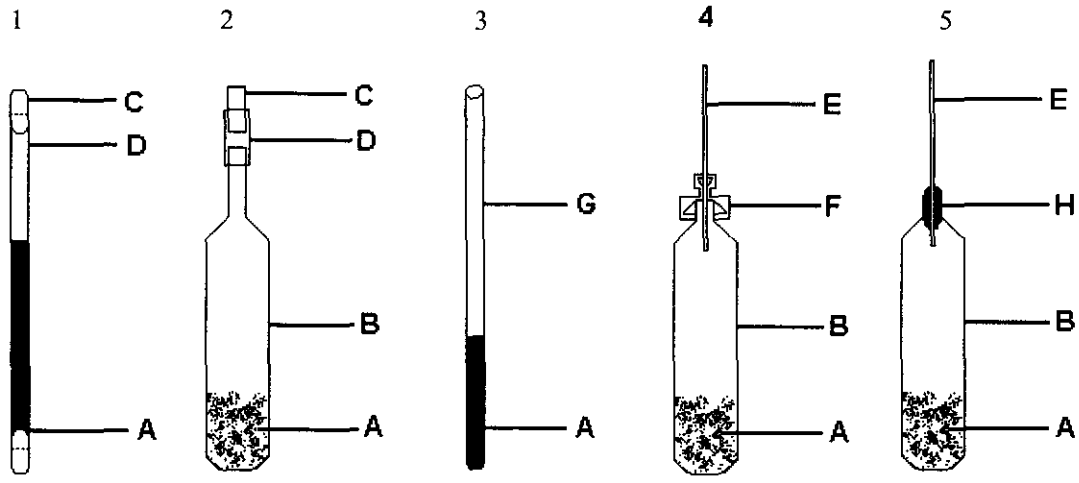
tube (atm), A is the cross-sectional area of the diffusion path ($cm^2$) and R is the gas constant ($cm^3$.atm/mol.K). T (K) is the absolute temperature of the diffusion cell, L is the length of the diffusion path (cm) and $P_v$ is the partial pressure of the diffusion vapour (atm) at the temperature T. From this equation, it can be seen that the diffusion rate is dependent on the geometry of the diffusion path, pressure and temperature.

Diffusion methods have been used to generate formaldehyde gas standards [101,114-116]. One method uses a diffusion cell made of pyrex glass consisting of a reservoir and a long-neck capillary tube. The desired concentration range is obtained by varying the dimensions of the diffusion tube, the temperature of the system and the flow rate of the diluent gas. The paraformaldehyde, or trioxane [102], thermally depolymerises in the reservoir to form the formaldehyde vapour, which diffuses through the tube into the mixing chamber where it mixes with the purging gas flowing above the opening of the capillary tube. The diffusion coefficients can be obtained from literature and the diffusion rate can be calculated using equation 4, and alternatively, calibration of the diffusion tube can be done gravimetrically, as for the permeation tube [101].
Lower concentrations of formaldehyde can be obtained by diluting the gas mixture again further downstream [101].

## 4.4 EXPERIMENTAL

Gas standards of selected saturated aldehydes, namely formaldehyde, acetaldehyde, propionaldehyde (propanal) and butyraldehyde (butanal) were prepared as well as a few unsaturated aldehyde gas standards of acrolein, crotonaldehyde and benzaldehyde.

A diffusion and permeation tube was prepared, to provide a high and low concentration respectively for each compound, and also to determine which generation method provided the more stable standard.




A - ALDEHYDE
B - GLASS AMPOULE
C - GLASS PLUG
D - TEFLON TUBE
TYPE 1,2 - PERMEATION STANDARDS
TYPE 3,4,5 - DIFFUSION STANDARDS

E - FUSED SILICA CAPILLARY
F - REDUCING UNION
G - GLASS CAPILLARY
H - POLYIMIDE RESIN

Figure 4.1. Aldehyde gas standard devices.

The diffusion standards, see figure 4.1, type 3, were prepared by placing a certain amount of a compound into a glass capillary tube, sealed at one end only. Formaldehyde gas had to be prepared at a higher temperature, so it was handled separately from the other aldehydes. All the diffusion standards, excluding formaldehyde, were then collectively placed in a closed glass container, having an inlet and outlet, where nitrogen gas could flow over the open-ends of the capillary tubes, allowing diffusion of the aldehydes to occur over the length of the capillary. Diffusion rates were determined by measuring the mass loss of each capillary over a time period. The entire set-up, excluding that for formaldehyde, was placed under a fume hood as several of these compounds are toxic by inhalation [6], and simultaneously this kept the temperature constant.

Permeation standards, see figure 4.1, type 1, were prepared by placing a certain amount of aldehyde into a thin-walled teflon tube, which is then sealed at both ends with pieces of sealed glass capillary. All the permeation tubes, excluding formaldehyde, are placed in a glass tube, large enough to allow nitrogen to flow over the PTFE surfaces of each tube as for the diffusion standards. The permeation rate was also determined gravimetrically, as above.

The diffusion and permeation tubes for the preparation of the formaldehyde gas standard were placed in a GC oven, thermostated at 80.05°C, allowing simultaneously, for the thermal depolymerisation of paraformaldehyde and preventing the repolymerisation of liberated formaldehyde. The permeation tube for formaldehyde was prepared as for the other aldehydes, figure 4.1, type 1. The diffusion tube was prepared differently, see figure 4.1, type 4. A 1/16 " to 1/4" reducing union was fitted to a glass vessel consisting of a reservoir and short

1/4" neck. A length of fused silica capillary was inserted into the union and held in place with a column ferrule. Since the diffusion rate is dependent on the diffusion path length and cross-sectional area, the diffusion rate could be varied by changing the length and/or bore of the fused silica capillary.

Mass loss versus time graphs were plotted for each device, see Figure 4.2.a,b. From the slope of the curves it could be seen that the aldehyde diffusion and permeation tubes made did not provide low enough mass loss rates. How would it be possible to lower the mass loss rate? Firstly, of the two generation methods the permeation tubes provided the lower mass loss rate. Secondly, it could be possible to modify the permeation device. From equation 1, the permeation rate is directly proportional to the area of the membrane (A) and inversely proportional to the thickness of the membrane(d). With this in mind, it was decided to decrease the area through which the aldehyde could permeate by decreasing the length of the tube, see figure 4.1, type 2. For acrolein, which has an extremely high mass loss rate, we decided to use a thick-walled teflon membrane, which increases the term, d (membrane thickness), resulting in a proportional decrease in permeation rate, r, as seen from equation 4.3. Results obtained are shown in Figure 4.2c. Since these permeation standards were larger in size they could no longer be inserted into the glass tube with the nitrogen blowing through it. They were placed, instead, in an impinger type device. Table 4.1, shows a summary of the results obtained for all the gas standards prepared.

Table 4.1 - Summary of gas standard devices prepared and results obtained

| | ACETALDEHYDE | | | PROPANAL | | | BUTANAL | |
|---|---|---|---|---|---|---|---|---|
| type | 3 | 1 | 2 | 3 | 1 | 2 | 3 | 1 |
| length (cm) | 9 | | | 9 | | | 9 | |
| I.D (mm) | 1.2 | 1.6 | 1.6 | 1.2 | 1.6 | 1.6 | 1.2 | 1.6 |
| wall width (mm) | - | 0.25 | 0.25 | - | 0.25 | 0.25 | - | 0.25 |
| **mass loss (ng/min)** | **40** | **60** | **40** | **100** | **30** | **7** | **40** | **10** |
| $r^2$ | 0.9744 | 0.9563 | 0.9922 | 0.9956 | 0.9921 | 0.989 | 0.9899 | 0.9806 |

| | ACROLEIN | | | | CROTONAL | | | BENZALDEHYDE | |
|---|---|---|---|---|---|---|---|---|---|
| type | 3 | 1 | 1 | 2 | 3 | 1 | 2 | 3 | 1 |
| length (cm) | 9 | 5 | 4 | 1 | 9 | 5 | 1 | 9 | 5 |
| I.D (mm) | 1.2 | 1.6 | 1.6 | 1.6 | 1.2 | 1.6 | 1.6 | 1.2 | 1.6 |
| wall width (mm) | - | 0.25 | 1.6 | 1.6 | - | 0.25 | 0.25 | - | 0.25 |
| **mass loss (ng/min)** | **4000** | **300** | **90** | **20** | **900** | **100** | **30** | **50** | **9** |
| $r^2$ | 1 | 0.9947 | 0.9991 | 0.997 | 0.9874 | 0.9989 | 0.9902 | 0.9969 | 0.9984 |

| | FORMALDEHYDE | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| type | 4 | 4 | 4 | 4 | 5 | 1 | 1 | 1 | 2 |
| length (mm) | 74.25 | 77.8 | 84.1 | 74.5 | 64.5 | 54.65 | 51.2 | 50 | 10 |
| I.D (mm) | 0.54 | 0.32 | 0.25 | 0.1 | 0.1 | 4.55 | 1.6 | 1.6 | 1.6 |
| wall width (mm) | - | - | - | - | - | 0.25 | 0.25 | 1.6 | 1.6 |
| **mass loss (ng/min)** | **400** | **100** | **80** | **200** | **400** | **600** | **200** | **80** | **10** |
| $r^2$ | 0.9991 | 1 | 0.9943 | 0.9825 | 1 | 0.9956 | 0.9908 | 0.997 | 1 |

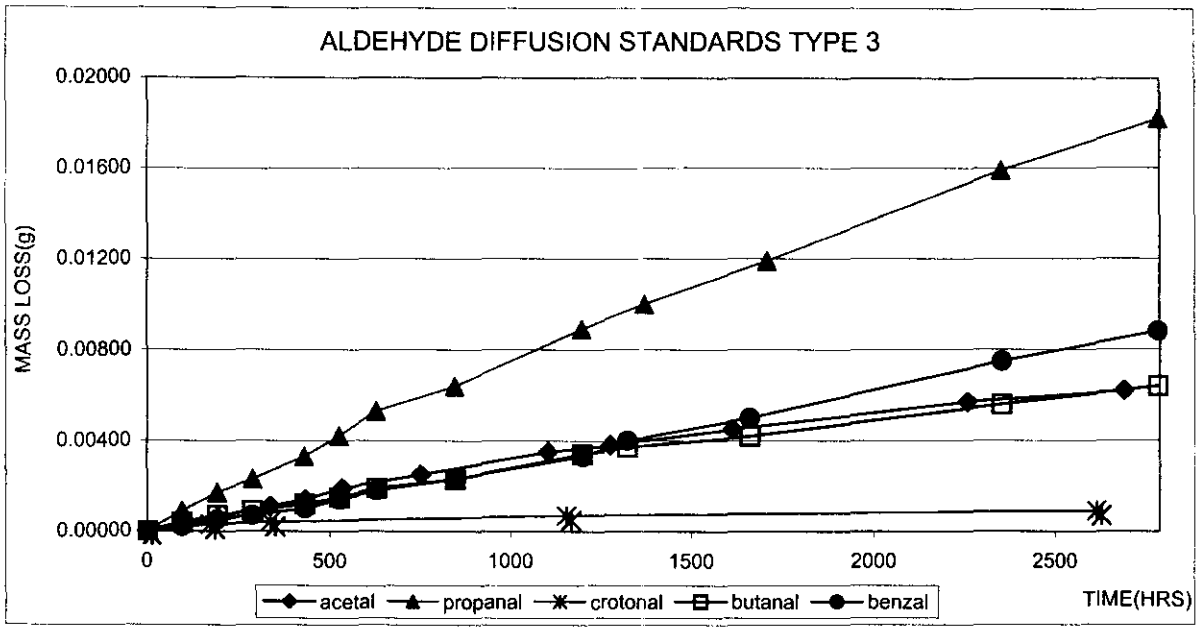



Figure 4.2 a* - Mass loss curves for the aldehyde diffusion gas standards prepared.
* Acrolein mass loss curve not shown, as diffusion was too rapid.

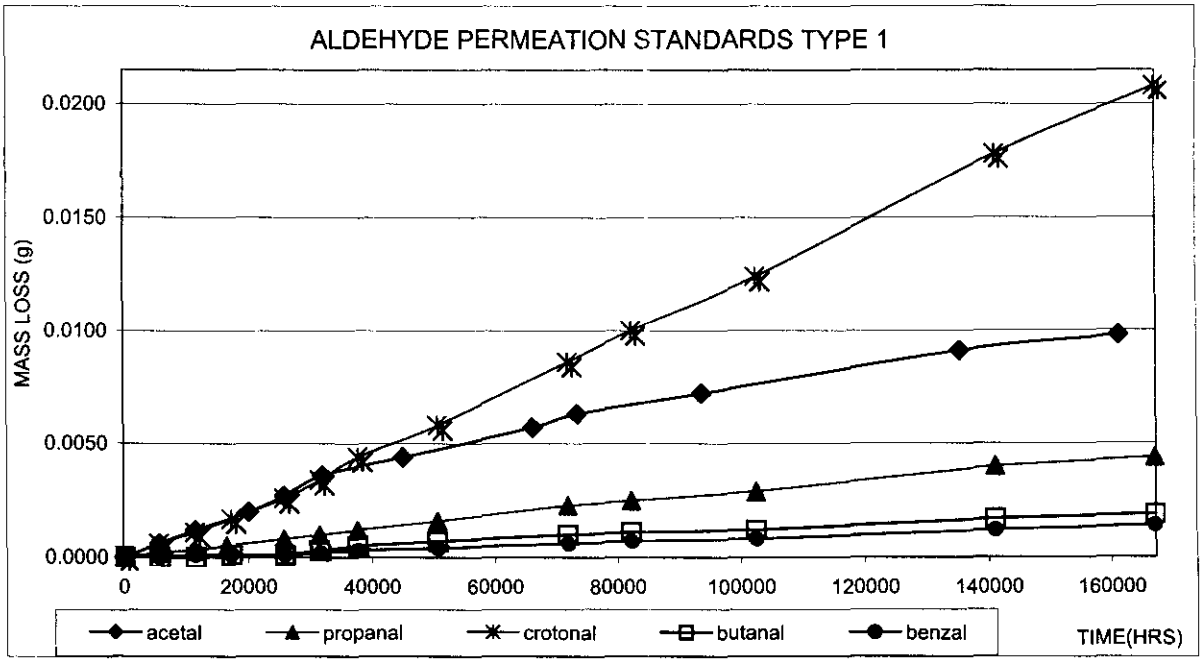



Figure 4.2 b# - Mass loss curves for the aldehyde type 1 permeation gas standards.
# Acrolein mass loss curve not shown, as permeation was too rapid.

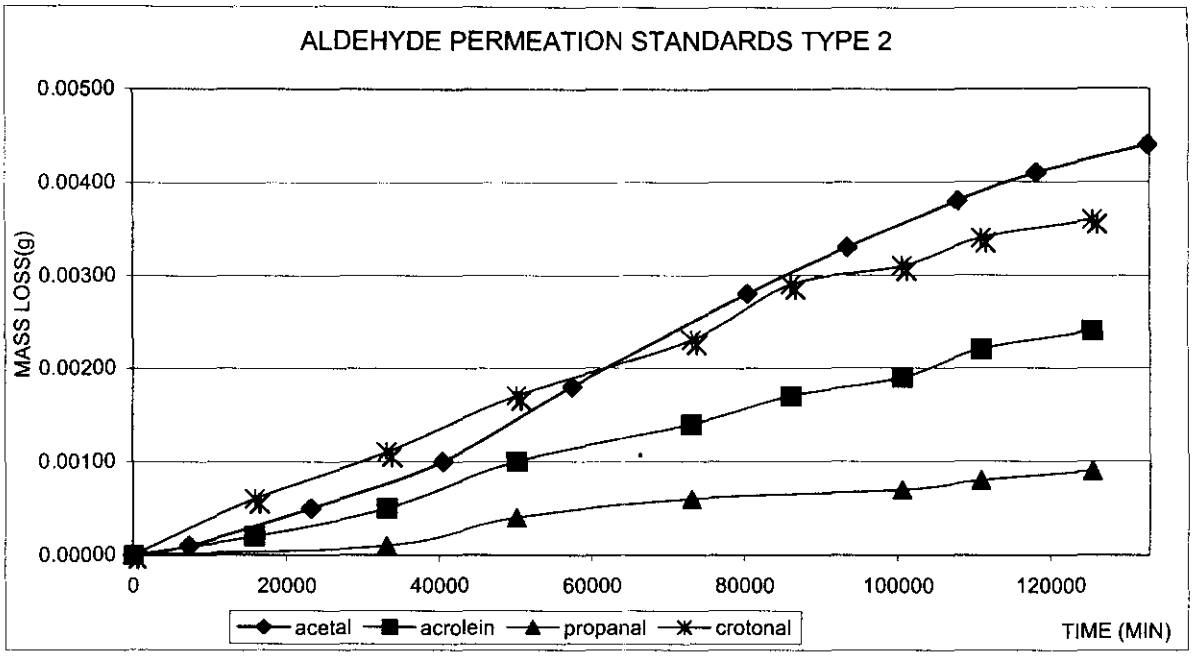



Figure 4.2 c** - Mass loss curves for the aldehyde type 2 permeation gas standards.
** No butanal and benzaldehyde gas standards of this type were prepared.

The formaldehyde gas standards mass loss rates were too high (400 - 100 ng/min) to be used without an additional dilution step. The mass loss curves for the HCHO gas standards prepared are shown in figure 4.2.d. A diffusion standard with a longer length of fused silica capillary was attempted, but proved too cumbersome and delicate to be inserted into the PTFE vessel used at the time. For the HCHO diffusion vessel (Table 4.1,type 4), a proportional decrease in diffusion rate had already been observed for the change from the 0.54mm (400ng/min) to the 0.25 mm i.d capillary (80ng/min). This trend was expected to continue when moving from the 0.25mm i.d fused silica capillary to the 0.1mm i.d fused silica capillary, but this was not the case. Most likely, the ferrule around the narrow bore capillary was not leak-tight. Polyimide resin (Figure 4.1,type 5) was used as an alternative to the column- nut and ferrule in order to obtain a leak tight seal. A diffusion rate of 400ng/min indicated that this was not achieved.

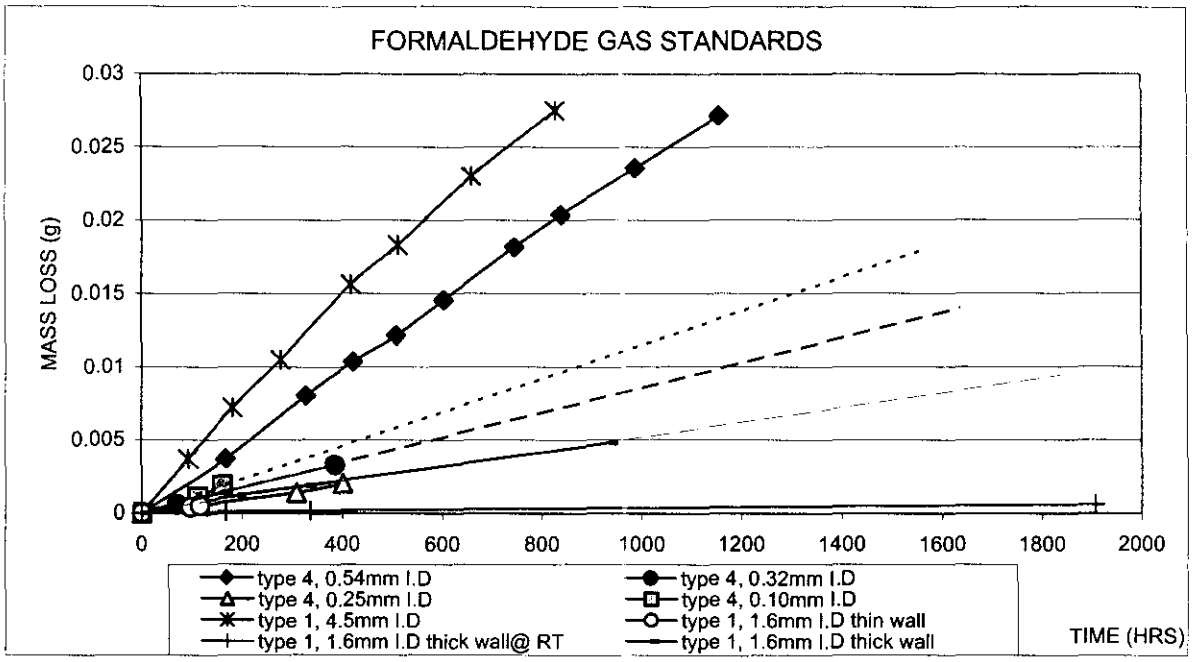



Figure 4.2 d - Mass loss curves for the formaldehyde gas standards.

It was then decided to substitute the thin-walled HCHO permeation device (200ng/min), with a thick-walled membrane, figure 4.1, type 1. This provided a mass loss of 50ng/min, but as yet was not low enough. The only alternative remaining was to use a lower temperature.

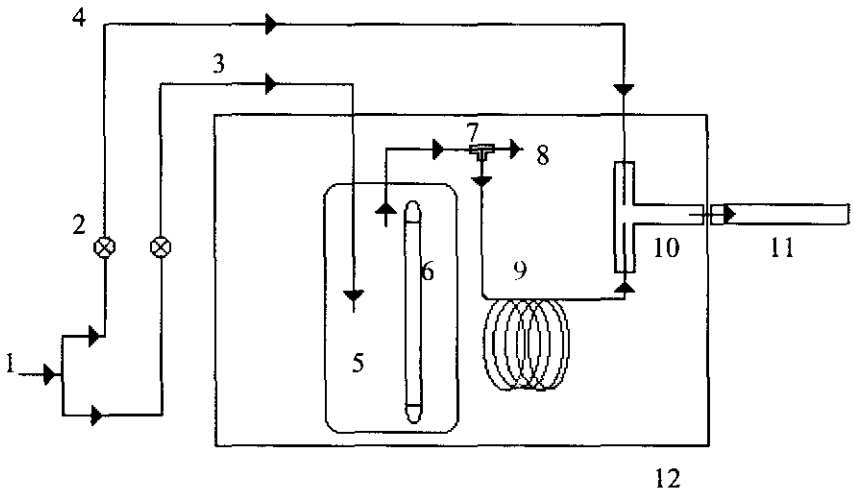
As Paraformaldehyde is a polymer built up with formaldehyde monomers,

$$HO - (CH_2O)_n - H \ (n = 8 - 100)$$

it was then considered that perhaps it was not necessary to fully depolymerise the paraformaldehyde, but rather to use its vapour pressure at room temperature instead, which is well above atmosphere. HCHO, however polymerises easily at temperatures below 80°C, it will not repolymerise between 80°C and 100°C [15]. Now assuming that the HCHO concentration is low enough once it has permeated through the membrane, repolymerisation should theoretically not be

able to take place at lower temperatures. With this assumption, the thick-walled permeation tube (figure 4.1, type 2) was calibrated at room temperature and provided a mass loss of 10ng/min which was ideal. With time, however, it was discovered that there was no longer any mass loss even though the paraformaldehyde was still clearly present. While the HCHO permeated through the membrane, it managed to concentrate in the membrane and repolymerise. All the pores were thereby blocked, making it impermeable to any further HCHO moving through. The low temperature method thus had to be abandoned.

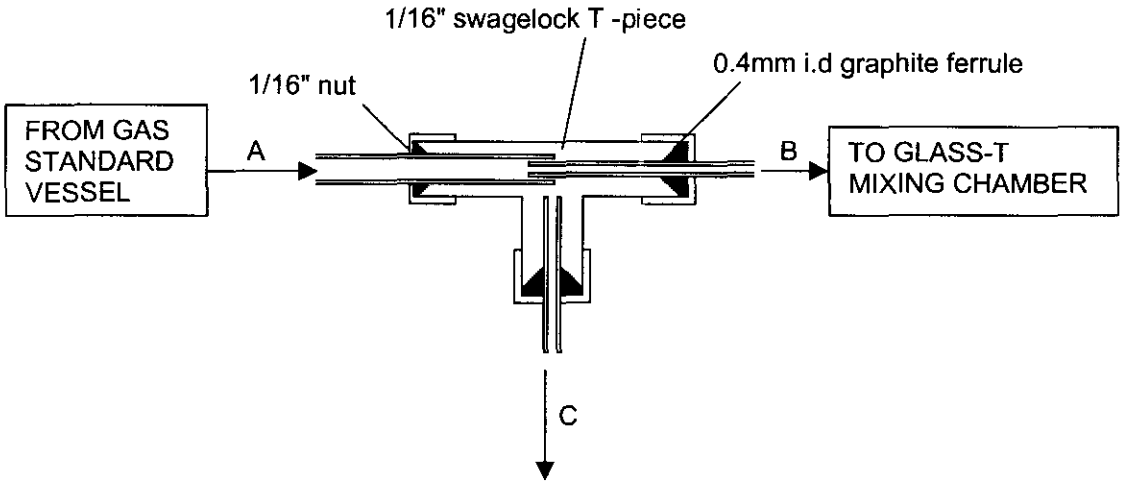
A description of all the HCHO gas standards prepared as well as their mass loss rates are summarised in Table 4.1.




1 - HIGH PURITY NITROGEN GAS
2 - MASS FLOW CONTROLLERS
3 - PURGE GAS
4 - DILUENT GAS
5 - GLASS VESSEL
6 - GAS STANDARD
7 - T-PIECE SPLIT
8 - SPLIT VENT
9 - RESTRICTOR
10 - GLASS T-PIECE
11 - SILICONE RUBBER TRAP
12 - GC - OVEN

Figure 4.3. Dilution system for the gas standard.

Since no attempted gas standard for HCHO could reliably provide low enough concentrations, it was decided to include a dilution system. Figure 4.3, shows the set-up arranged to fit inside a GC-oven so that the temperature of all the components could be maintained at 80°C. If the temperature were to fall below 80°C, HCHO could repolymerise and deposit as the polymer onto the cooler surfaces. A 100 ng/min HCHO permeation standard was placed inside a closed glass vessel. A 74:1 split ratio then provided a 1.33ng/min HCHO atmosphere.




A - 0.54mm i.d F.S capillary, 30 ml/min

B - 2m 0.25mm i.d F.S capillary, RESTRICTOR 0.4 ml/min

C - 1cm 0.25mm i.d F.S capillary, SPLIT VENT 29.6 ml/min

Figure 4.4. T-piece split.

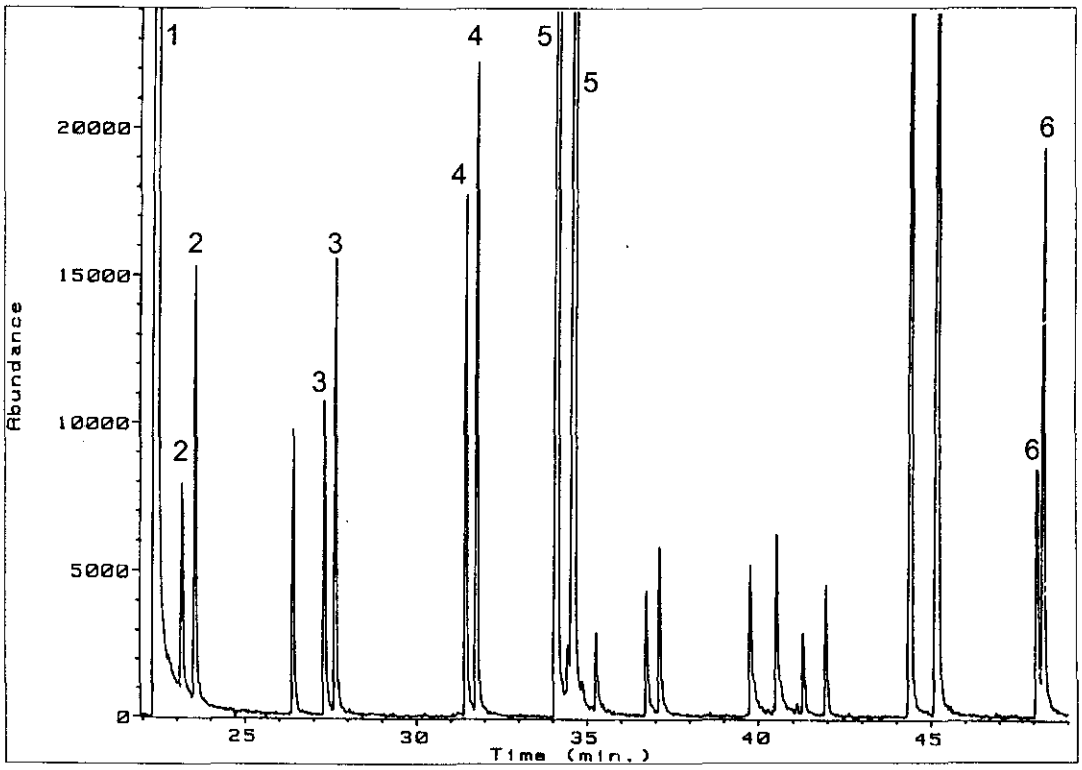
The split was prepared using a 1/16 " swagelock T-piece and 2 differing lengths of 0.25mm i.d. fused silica capillary. Figure 4.4 shows the inside of the T-piece. The 2m long 0.25mm i.d fused silica capillary was inserted into the wider bore (0.54mm i.d) capillary leading from the glass vessel which contained the

standard. The 2m length of fused silica capillary served as a restrictor so that the bulk of the flow was split through the 1cm fused silica capillary (inserted on the third leg of the T-piece). The split ratio is dependant on the lengths of the two 0.25mm i.d fused silica capillaries. The longer the length of the split vent capillary, the smaller the split ratio. In addition, the shorter the length of restrictor capillary the smaller the split ratio. The flow rate through the split had to be set before the diluting flow could be added. The restrictor length was then inserted into a 4mm i.d glass T-piece where it joined up with the diluting flow entering from the other end. The gas mixture could then be collected at the exit of the glass T-piece on the outside of the GC-oven. A 1/4" swagelock union was used at the exit to allow for easy collection with the trap.

The concentration of the HCHO atmosphere could be changed by adjusting the dilution flow. A diluting flow of 10ml/min provided a concentration of 0.1ppm. Appendix 2 demonstrates the calculation method used to determine aldehyde gas concentrations.

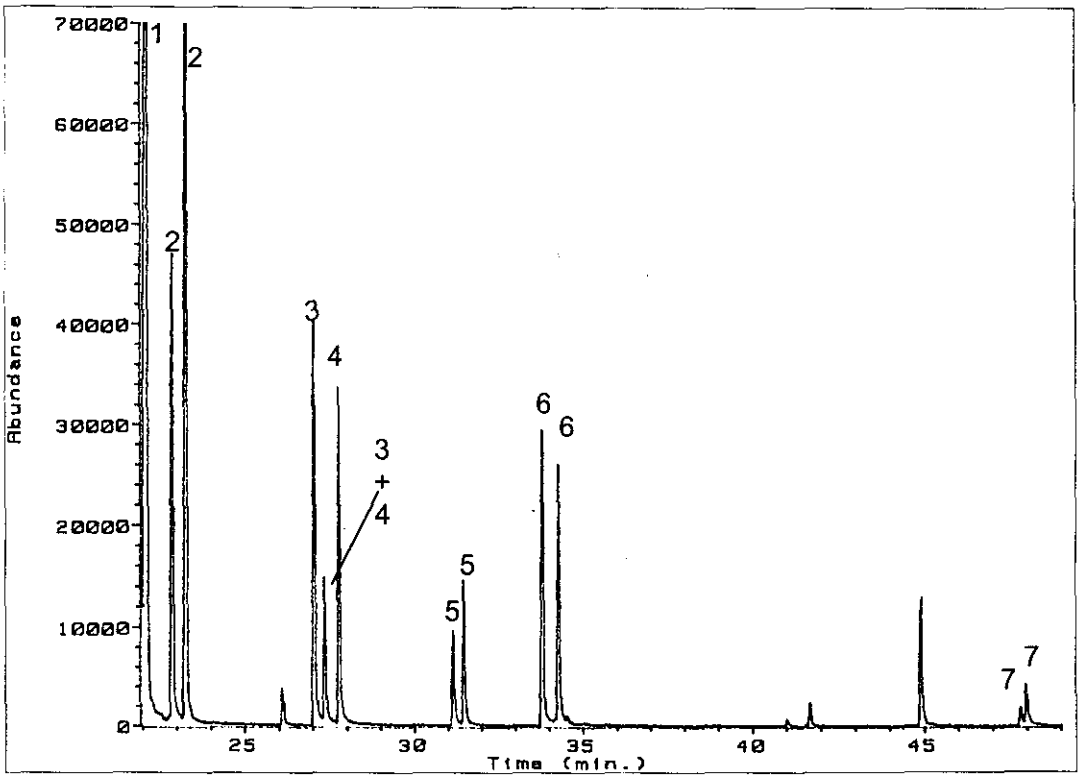
The diffusion and permeation (type 1) aldehyde standards (excluding HCHO) were tested using a 100% PDMS SPME fibre. See table 4.1 for their respective mass loss rates. The fibre was exposed to the dynamic headspace of a 10g/L PFBHA aqueous solution for 2 min. Thereafter the fibre was exposed to the diffusion standards for 5 min, desorbed at 250°C in the HP 5890 GC-inlet. Instrument parameters are listed in table 6.1. The temperature program used was 30°C/5min ramped at 3°/min to 180°C then ramped again at 50°/min to 280°C and held there for 4 min. The permeation standards were tested similarly, except the fibre was exposed to the standards for 10min. Figure 4.5 and 4.6

show the Reconstructed Ion Chromatograms using m/z 181, for the diffusion and permeation aldehyde gas standards respectively. The oxime products could be identified based on an earlier study discussed in section 6.2. From these chromatograms we could clearly see that the gas standards were functioning. Notice that the acrolein-oxime was not detected from the diffusion standards sampled, upon further inspection the acrolein diffusion tube was empty.




1. PFBHA 2. Acetal-oxime 3. Propanal-oxime
4. Butanal-oxime 5. Crotonal-oxime 6. Benzaldehyde-oxime

Figure 4.5. Reconstructed Ion Chromatogram using m/z 181 of SPME-PFBHA coated fibre exposed to aldehyde diffusion gas standards (type 3).




1. PFBHA 2. Acetal-oxime 3. Propanal-oxime 4. Acrolein-oxime
5. Butanal-oxime 6. Crotonal-oxime 7. Benzaldehyde-oxime

Figure 4.6.Reconstructed Ion Chromatogram using m/z 181 of SPME-PFBHA coated fibre exposed to aldehyde permeation gas standards (type 1).

## 4.5 CONCLUSION

We have successfully prepared stable and continuous gas standards for formaldehyde, acetaldehyde, acrolein, propanal, crotonal, butanal and benzaldehyde. A dilution set-up allowed lower concentrations of the formaldehyde gas standard to be obtained.