CHAPTER 2

METHODS FOR DETERMINING ALDEHYDES IN AIR

2.1 INTRODUCTION

Several reviews have been written on the various methods for the measurement of aldehydes in the environment [8,11,21]. These methods may be classified into two groups namely direct and indirect methods. Direct methods analyse the aldehydes during collection and therefore show great potential as the risk of sample contamination is greatly reduced. However, the cost and complexity of the instrumentation, as well as the properties of aldehydes make these methods, on the whole, unsuitable. Indirect methods, on the other hand, utilise these properties to improve ease of detection. Indirect methods analyse the aldehydes after they have been collected by some means. A brief summary of these methods that have been developed follows.

2.2 DIRECT READING METHODS

These methods give immediate results. Long-Path Fourier Transform Infrared Spectroscopy and differential absorption in the near UV region from a high pressure Xenon lamp, has been applied to the detection of formaldehyde. However, long optical paths are required (meters to kilometres) to obtain sensitivities of a few ppb. The laser fluorescence technique, with the aid of a photomultiplier, can monitor aldehyde concentrations as low as 40ppb. A tuneable diode laser may be used to monitor

formaldehyde in air at the 1-2ppb level, using hourly data averaging. An electrochemical fuel detector can instantaneously determine formaldehyde over the 0.3-5ppm range. Most of these methods require expensive, complex equipment and highly skilled operators. Several other direct reading methods have also been developed, but show poor sensitivity [11].

A novel reactive passive sampler monitoring card system was developed for on-site determination of formaldehyde in air. Formaldehyde diffuses through a polymeric membrane and reacts with a chemically impregnated sorbent layer. A colour-change is produced which is proportional to the exposure amount. Its working range is between 0.1 and 2ppm[28].

2.3 INDIRECT READING METHODS

2.3.1 NON-CHROMATOGRAPHIC METHODS

2.3.1.1 COLORIMETRIC METHODS

These methods rely on absorption spectrophotometry. The reaction product's absorbance can be measured and related to the concentration of the aldehyde collected, using Beer's Law. A brief introduction to some colorimetric methods follows.

CHROMOTROPIC ACID METHOD

Formaldehyde is collected on an adsorbent trap, or in an impinger containing either distilled water or a bisulphite solution. Chromotropic acid (4,5-dihydroxynaphthalene-2, 7-disulphonic acid), followed by concentrated sulphuric acid is then added to the extracted formaldehyde solution. A violet-coloured product forms, and its absorbance is measured at 580nm. Unfortunately, long collection times are required. Interferences from compounds such as phenols, ethanol, high mass alcohols and olefins inhibit the reaction, leading to negative bias in the results. The detection limit has been improved to 0.3-0.03 ppm, by changing the collection medium, the collection device, reaction temperature and storage [11,21]. NIOSH Method 3500[1] uses this technique, which has a working range of 0.02 to 4 ppm in an 80L air sample.

PARAROSANILINE METHOD

This method shows a two-fold increase in sensitivity over the chromotropic acid method. An impinger containing a sodium sulphite solution is used to collect formaldehyde. Sodium tetrachloromercurate and pararosaniline are added to the solution producing a purple-coloured product, which can also be determined spectrophotometrically at 560nm. Interferences from propanal, acrolein and acetaldehyde cause a positive bias in the results at 5ppm and above. In addition, the use of the toxic mercurate salt was not desired so the method was modified to exclude the salt. The modified method is sensitive to temperature, at the same time gaining interference from hydrogen cyanide, sulphite ion, hydroxylamine and sulphur dioxide. This method was also used to analyse formaldehyde collected on molecular sieve sorbent tubes. A disadvantage of these

tubes, however, is the decrease in breakthrough volume for HCHO as the water in the environment increases. The detection limit was found to be 0.03ppm[11,21]

PURPALD® REAGENT

Purpald® also known as 4-amino-3-hydrazino-5-mercapto-1,2,3-triazole, is a new reagent for the sensitive and specific spectrophotometric test for aldehydes. The reagent reacts with both aldehydes and ketones, as shown in figure 2.1. However, only the aldehyde-product can be oxidised to give the conjugated, purple-coloured, bicyclic ring system determined at 532 nm and 549 nm. The working ranges are 0.5 - 5ppm HCHO or 5 - 20 ppm HCHO after suitable dilution [29].

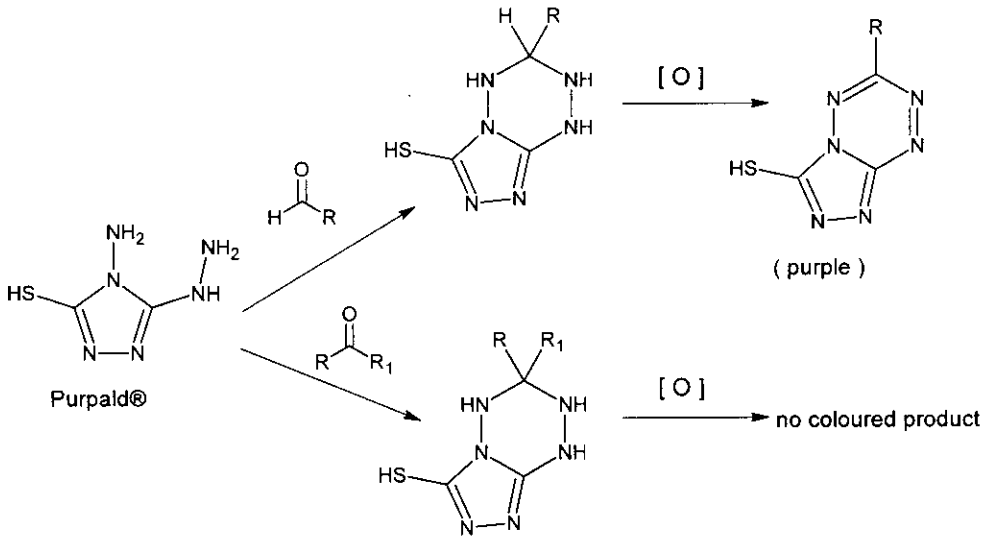

Figure 2.1 Reaction scheme for Purpald® reagent with an aldehyde or ketone [29].

3-METHYL-2-BENZOTHIAZOLONE HYDRAZONE (MBTH) METHOD

Formaldehyde reacts *in-situ* when it is collected in an impinger containing a 0.05% MBTH aqueous solution. Ferric chloride and acid are added to this product forming a blue cationic dye, which can be determined spectrophotometrically. This method's sensitivity is reported to be 30ppb formaldehyde in air. The dye is unstable after 4 hours. Other aldehydes collected will cause a positive interference. Aromatic amines, amino heterocyclics, azo dyes, stilbenes and Schiff bases may interfere by also reacting with MBTH [11,21]. The method is normally used for sum total aldehyde level determination.

2.3.1.2 POLAROGRAPHIC METHODS

GIRARD T METHOD

A bubbler filled with Girard T reagent (Trimethylammoniohydrazide chloride) is used to collect the formaldehyde. The formaldehyde-hydrazide reaction affords a hydrazone, which is then determined by Polarography. Other volatile aldehydes also collected cause interference in the analysis. The reported limit of quantitation is 0.3ppm[21]

HYDRAZINE METHOD

Formaldehyde collected in a bubbler filled with aqueous methanol is allowed to react with hydrazine. Differential Pulse Polarography at a dropping mercury electrode is used to selectively determine the formaldehyde hydrazone. Even though the detection limit is as

low as 0.01ppm, the sample collection set-up is not very portable, limiting its use to the lab [21].

2.3.2 CHROMATOGRAPHIC METHODS

2.3.2.1 ION CHROMATOGRAPHY

OXIDATIVE CHARCOAL TUBE METHOD

Formaldehyde is collected and partially oxidised to formate, on an oxidant-coated sorbent. Aqueous hydrogen peroxide is used to extract the formate, which is then determined by ion chromatography. Collected samples are not stable for more than 5 days. The method shows a limit of quantitation of 0.03ppm[21].

PULSED AMPEROMETRIC DETECTION

Aldehydes in solution are separated on a cation exchange resin in the potassium form, and are then detected electrochemically by oxidation with a platinum electrode. Detection limits range between 1 and 3ppm, though no application to airborne aldehydes has been made [11].

2.3.2.2 CAPILLARY ELECTROPHORESIS (CE)

Current applications involve substituted benzaldehydes, which react in-column with sodium bisulphite to produce charged complexes, which can be separated using CE [30]. The reaction scheme is shown in figure 2.2.

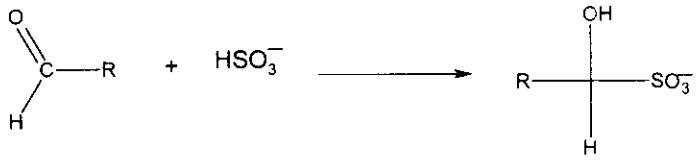

Figure 2.2 Reaction scheme for bisulphite with an aldehyde [30].

2.3.2.3 DIRECT GAS CHROMATOGRAPHIC METHODS

Whole air samples are injected onto a Porapak Q pre-column, hydrocarbons are not collected and pass through. This allows the aldehydes (C2-C5) collected to be diverted to another Porapak Q column followed by a "methanizer" where they are converted to their corresponding alkanes. Detection is with an FID, providing a method sensitivity of 0.3-0.08ppm[11]. Similarly, formaldehyde, acetaldehyde, and other volatile gases in a non-corrosive gas matrix, are converted to methane and ethane, respectively, using a nickel coated catalyst in a hydrogen atmosphere, and analysed using an FID, shown in figure 2.3. A detection limit of 0.1ng for formaldehyde and 0.06ng for acetaldehyde was obtained [16].

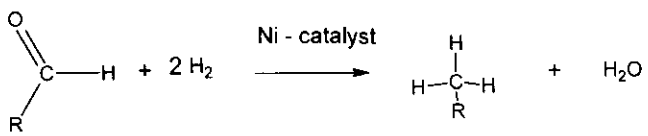

Figure 2.3 Reaction scheme for the conversion of an aldehyde to an alkane [16].

Carbonyl compounds have also been efficiently reduced to their corresponding alcohol, by sodium borohydride ($NaBH_4$), shown in figure 2.4, followed by GC on porous polyaromatic resin beads and FID detection [31].

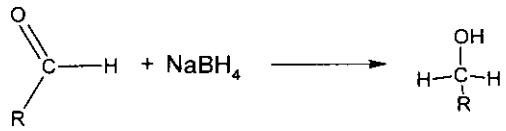

Figure 2.4 Reaction scheme for the reduction of an aldehyde to an alcohol [31].

A helium ionisation detector (HID) was used for the direct analysis of formaldehyde (HCHO) in the ppb-ppm range. The HID shows a marked increase in sensitivity over the FID for HCHO. However, due the HIDs large response to water in the air, the number of samples that can be analysed using the HID are limited as it takes 40min to fully elute the water isothermally before the next sample can be analysed [32].

Various adsorbents have been used to collect aldehydes, followed by either solvent extraction or thermal desorption with cryogenic focussing. Emphasis is placed on the GC column and detector used. Formaldehyde may, at the nanogram level, interact with the stationary phases of certain WCOT columns to form dimers and trimers [16]. Analysis of free carbonyls on commonly used GC-columns suffers from overlapping by dominant hydrocarbons. A new PLOT column (CP-LOWOX), which separates the interfering hydrocarbons, was successfully applied in the separation of semi-volatile aldehydes (C6-C11) pre-concentrated on various sorbents, thermally desorbed and analysed on an FID/MS [33]. A mixture of 10 short chain aldehydes were separated within 1 minute on inert spherical silica particles encapsulated with polyethylenimine (PEI) with CO_2 as the mobile phase, under solvating gas chromatography conditions [34]. C2-C5 aldehydes were trapped on a pre-column cold trap, heated from –183°C to 120°C in 3.5minutes and analysed simultaneously by 4 detectors [35]. Cryogenic trapping was also used in the

dynamic headspace analysis of volatile reaction products during the curing of urea-formaldehyde (UF) coatings [36].

2.3.3 DERIVATISATION AND CHROMATOGRAPHIC SEPARATION

In-situ derivatisation of aldehydes has several advantages over direct aldehyde analysis. Special storage is no longer required, because the aldehydes are stabilised as their derivatives. Background and interferences are reduced by the specific selective nature of the chemical reaction. Special detectors can be used since the derivative now has enhanced detectability. Use of *in-situ* derivatisation for the measurement of aldehydes has been studied extensively. Two common methods involve the reaction of a carbonyl with a hydrazine to form a hydrazone, or with an amine to yield an oxime.

2.3.3.1 HYDRAZONES

2,4-DINITROPHENYLHYDRAZINE (DNPH)

Formaldehyde has been collected in an impinger [37] and bubbler [38] containing DNPH, on DNPH coated sorbents [39-41], DNPH coated glass fibre [20], sintered glass [42] and PDMS SPME fibre [43]. HCHO reacts *in-situ* with the DNPH solution to form the 2,4-Dinitrophenylhydrazone chromophore which can be determined using HPLC with UV detection or GC-ECD/MS/FID/TSD [20,40,43]. The reaction takes place under strongly acidic conditions. Although this reagent has been used with GC analysis, removal of excess DNPH is required prior to injection (which leads to column and detector deterioration) [11,20,21], and frequent cleaning of the inlet liner [10]. High oven

temperatures are required because of the low volatility of the derivative [8]. Hence, HPLC-UV is favoured for this method, being both sensitive and easy to implement [10,11,21]. This technique is employed as a standard method for formaldehyde determination by the EPA, (EPA-TO11)[1], and NIOSH, (Method 2016)[3]. To further enhance the resolution and detection of an HPLC, a new detection method using Diode Array Ultraviolet Spectroscopy and Atmospheric Pressure Negative Chemical Ionisation Mass Spectrometry for liquid chromatography was introduced. The set-up showed a significant increase in resolution (34 carbonyls) and sensitivity in the ppb range [44]. Figure 2.5 shows the reaction scheme.

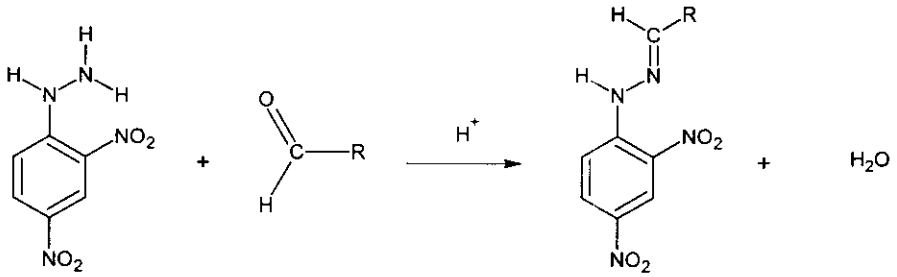

Figure 2.5 Reaction scheme for 2,4-DNPH with an aldehyde [20, 37-45].

DANSYLHYDRAZINE (DNSH) – (1-Dimethyl-aminonaphthaline-5-sulfonylhydrazine)

Schmied, et.al, developed a method for determining aldehydes and ketones simultaneously by derivatisation on silica gel coated with DNSH. The reaction scheme is shown in figure 2.6. The reaction is highly efficient and allows for collection flow rates of 2L/min. After collection, the hydrazones are extracted and separated by HPLC with fluorescence detection. DNSH was purified before each use. Detection limits are in the picogram range [46].

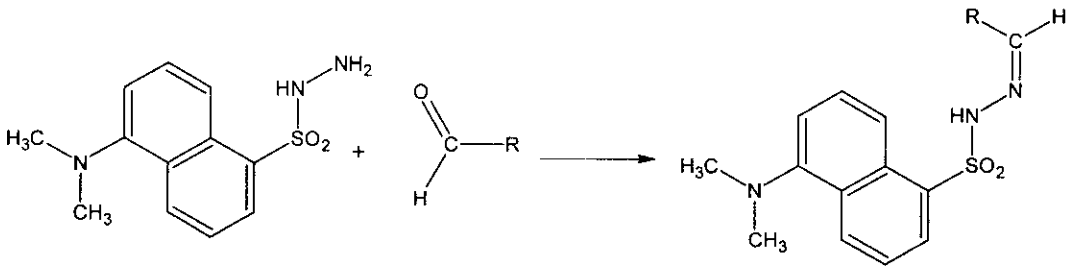

Figure 2.6 Reaction scheme for DNSH with an aldehyde [46].

O- (2,3,4,5,6-PENTAFLUOROPHENYL) HYDRAZINE (PFPH)

The hydrazine's detectability using ECD is enhanced by the pentafluoro-moiety. At this stage, the reagent has only been used in the study of lipid peroxidation in which volatile carbonyl compounds are formed [47,48]. Stashenko et al [47] heated a vegetable oil sample in a test tube and added PFPH solution. After the carbonyls reacted at room temperature with the PFPH, they were extracted into non-polar phases using either LLE or SPE. The extracts were analysed by GC-FID/ECD/MS-SIM. Detection limits of 10^{-14} and 10^{-12} mol/ml per aldehyde were obtained using ECD and MS-SIM respectively. More recently, using the same concept used by Pawliszyn [22], a SPME fibre was used to pre-concentrate carbonyls using *in-situ* derivatisation on a PFPH coated PDMS/DVB fibre which, following desorption in the GC inlet, was analysed by GC with ECD to obtain a detection limit of 10-90 fmol [48]. The reaction scheme is shown in figure 2.7 below.

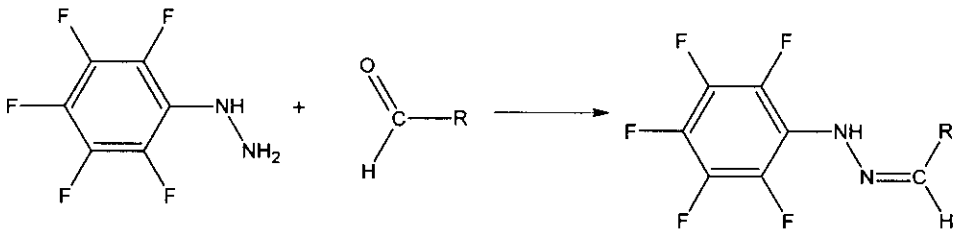

Figure 2.7 Reaction scheme for PFPH with an aldehyde [47,48].

2,4,6-TRICHLOROPHENYLHYDRAZINE (TCPH)

This reagent was introduced to reduce the problems experienced using 2,4-DNPH and GC analysis. An octadecyl silica cartridge impregnated with TCPH was used to collect HCHO. Thereafter the cartridge was held at 100°C for 6 min to allow for complete reaction. The cartridge is eluted with acetonitrile followed by GC-ECD analysis. Detection limits are determined by the blank, in the case of HCHO the limit of detection is 0.1ppb in 10L, while other carbonyls have even lower limits. An ozone scavenger had to be used to eliminate the interference of ozone above 300ppb[49]. The reaction scheme is shown in figure 2.8 below.

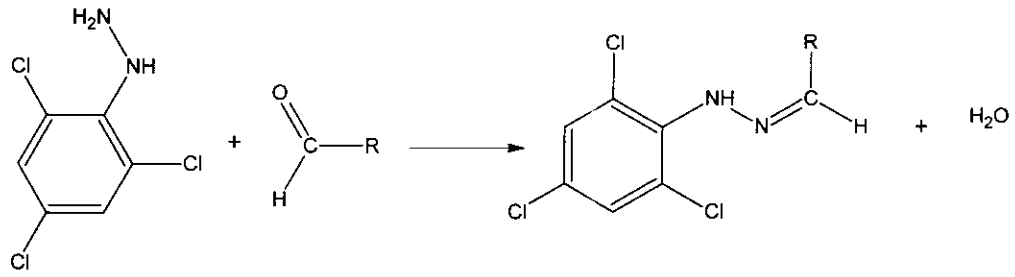

Figure 2.8 Reaction scheme for TCPH with an aldehyde [49].

2.3.3.2 OXIMES

Oximes are ideal for GC analysis due to their volatility, providing good separation, while the reaction conditions are mild, unlike those for hydrazone formation [8]. Typical amine reagents used in HCHO derivatization reactions followed by GC analysis are discussed below.

BENZYLHYDROXYLAMINE AND METHOXYAMINE

Benzylhydroxylamine and Methoxyamine can be applied to automobile exhaust and stationary source analysis. The reagents however, are not suitable for ambient air measurements since their reaction with low molecular mass aldehydes yield volatile products, hence detection limits were not reported for benzyloximes. Figure 2.9 shows the reaction scheme for benzylhydroxylamine with an aldehyde, and the scheme for methoxyamine with an aldehyde. The carbonyls were collected on silica gel, eluted with water, derivatised with benzylhydroxylamine and analysed using GC-NPD. Derivatives were well separated and could be detected to the picogram level. O-Methyloximes provided detection limits of 40ppb for aldehydes in air. For the determination of unsaturated aldehydes, particularly acrolein and crotonal, their respective O-methyloximes and benzyloximes are brominated and analysed using GC-ECD. The brominated acrolein methyloxime was detected at 0.5ppb in a 40L air sample [8].

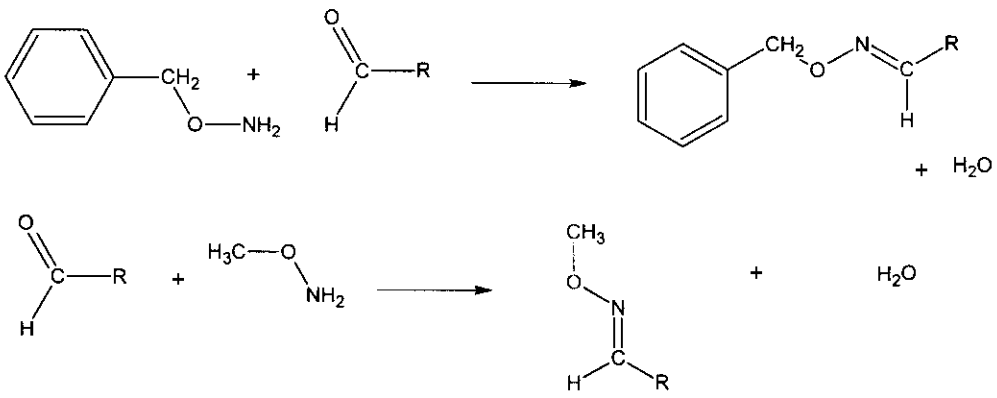

Figure 2.9 Reaction scheme for first, benzylhydroxylamine with an aldehyde. Second, methoxy amine with an aldehyde [8].

O -(2,3,4,5,6-PENTAFLUOROBENZYL) HYDROXYLAMINE (PFBHA)

This reagent is ideal for the determination of trace amounts of volatile aldehydes in air samples [8]. The oximes that are formed are volatile and stable to high temperatures allowing for GC analysis. All the oximes have a common base peak of m/z 181, which allows for easy identification with Mass Spectrometry [50]. The reagent has been used typically for determining aldehydes in drinking water with Electron-Capture Detection (ECD) [51] (EPA method 556) and Mass Spectrometry (MS) [50] as well as in beer [17], Cognac [52] and vegetable oils [53]. Recently PFBHA has also been used for indoor air and headspace sample analysis. C-18 silica gel cartridges coated with PFBHA were used to determine aldehydes in air emitted by vegetation as terpene oxidation products. After elution of the derivatives with hexane, a 50L air sample provided a detection limit of 2ppb using GC-MS [54]. Wu and Que Hee [55] developed a dynamic personal air sampler consisting of Tenax-GC solid sorbent coated with PFBHA, which was eluted with hexane and analysed by GC-MS. The detection limit for acrolein was 0.025ppm. Later, Wu and Que Hee [56] developed a passive sampler by applying the same concept. Martos and Pawliszyn introduced the use of a SPME PDMS/DVB fibre, for the *in-situ* derivatisation of HCHO. The headspace of an aqueous PFBHA solution coats the fibre, which is then exposed to the HCHO atmosphere or headspace of a sample. The fibre is then desorbed in the inlet of a GC oven. The technique is excellent for grab sampling and time weighted averaging for indoor air. Detection limits were as low as 15 ppb using GC-FID [22,57]. Figure 2.10 shows the reaction scheme.

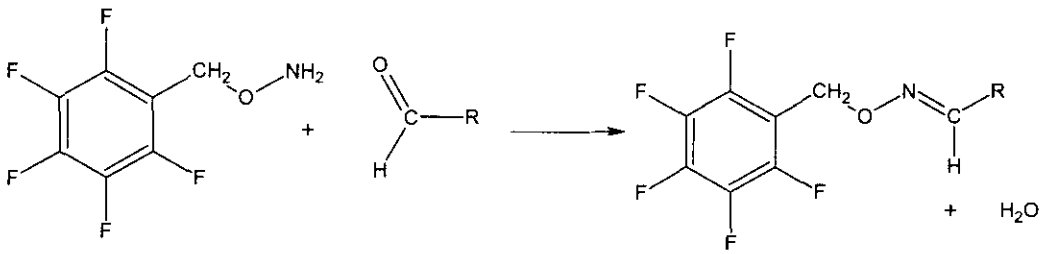

Figure 2.10 Reaction scheme for PFBHA with an aldehyde [50].

2.3.3.3 CYCLISATION REACTIONS

N - (BENZYLETHANOL) AMINE (BEA) -COATED SORBENT TUBE METHOD

Formaldehyde and most carbonyl compounds react rapidly with secondary aminoethanols to form the cyclic oxazolidine derivative, as shown in figure 2.11. Formaldehyde was collected on BEA coated Chromosorb sorbent. The derivative was extracted with isooctane and separated using GC-FID. Detection was in the range of 0.55-4.71mg/m^3 [8]. The method lacks sensitivity caused by the low sampling rate required to ensure derivative formation, and high blank levels. Thus, the reagent is not suitable for ambient air analysis. The use of a Nitrogen specific detector enhances sensitivity slightly. Acid gases/mists will react with the BEA and convert it to the ammonium salt, resulting in lower BEA reagent availability [21].

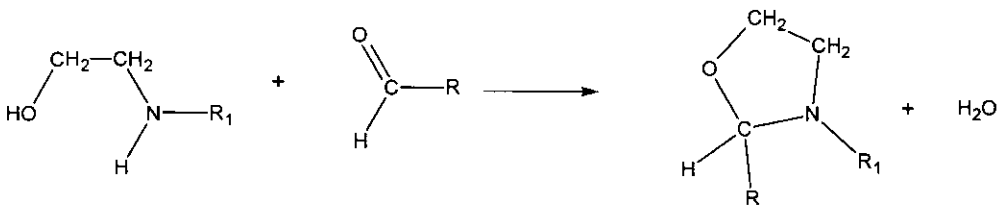

Figure 2.11 Reaction scheme for ethanolamine with an aldehyde [8,21].

2-HYDROXYMETHYLPIPERIDINE (HMP)

Kennedy, et al. determined acrolein in air by pre-concentration on a XAD-2 sorbent tube coated with 2-HMP. Acrolein forms a bicyclo-oxazoline, which can then be determined by Gas Chromatography - Nitrogen Specific Detection (GC-NSD) in the 0.13-1.5 mg/m^3 range [58]. Formaldehyde can also be determined by conversion to hexahydrooxazolo [3,4-a] pyridine in a denuder tube coated with 2-HMP (with a back-up tenax sorbent tube). Figure 2.12 shows the reaction scheme. Recovery can be done by thermal desorption followed by GC-MS analysis for which the limit of detection is in the range of 0.03 to 0.51 mg/m^3 [23]. NIOSH uses this technique for the determination of formaldehyde and acrolein in air (Method 2541) with a detection range of 0.3-20mg/m^3 [59], as well as aldehyde screening (Method 2539)[60] using GC –FID/MS detection.

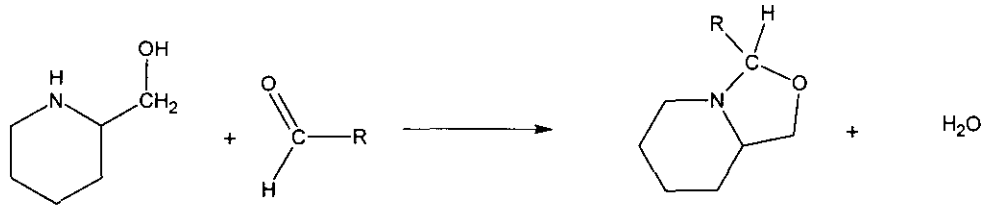

Figure 2.12 Reaction scheme of 2-HMP with an aldehyde [58-60,23].

CYSTEAMINE (2-AMINOETHANETHIOL)

Cysteamine reacts readily with carbonyl compounds at room temperature and neutral pH. However, it does not react with β-unsaturated aldehydes such as acrolein and crotonaldehyde. Unlike certain derivatising reagents, no cis-trans isomers of the reaction product are formed making quantitation easier [8]. This reagent has been used in the determination of volatile carbonyl compounds in cigarette smoke [61] and automobile exhausts [62]. The smoke/exhaust is collected in a vessel containing an aqueous

solution of cysteamine. The carbonyl compound is converted to the thiazolidine as shown in figure 2.13, followed with analysis by GC with NPD. Detection limits are in the picogram range.

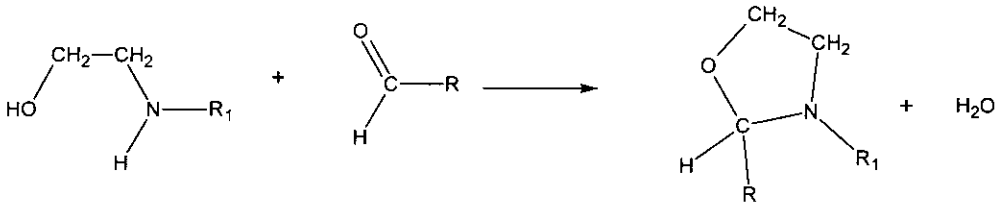

Figure 2.13 Reaction scheme of cysteamine with an aldehyde [8,61,62].

AMMONIA

Formaldehyde is collected on a silica gel sorption cartridge that was coated with polyethylene glycol (PEG-400), to increase the polarity of the adsorbent. The pre-concentrated HCHO is extracted using aqueous ammonia, which HCHO reacts exclusively with to form a hexamethylenetetramine, shown in figure 2.14, which is analysed using GC-FID. Detection limits fall in the same range as for the use of 2,4-DNPH, but with the use of thermionic detection, the limit can improve [63].

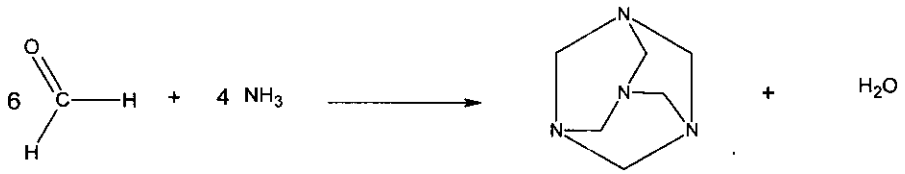

Figure 2.14 Reaction scheme for formaldehyde with aqueous ammonia [63].

ACETYLACETONE OR DIMEDONE (5,5-DIMETHYL-1, 3 -CYCLOHEXANDION)

Aldehydes in air were determined by pumping air through a bubbler to which dimedone, ethanol and piperidine are added. An extensive sample workup consisting of washing, refluxing for 20 minutes, a triple extraction with diethyl ether and drying leads to an extract, which is analysed by GC-ECD. This method, unlike the 2,4-DNPH for GC method, can separate o-, m- and p-tolualdehyde as well as acrolein, propanal and acetone which are poorly separated by HPLC. The detection limit for acrolein was 80pg and benzaldehyde was 17pg[64]. Figure 2.15 shows the reaction scheme.

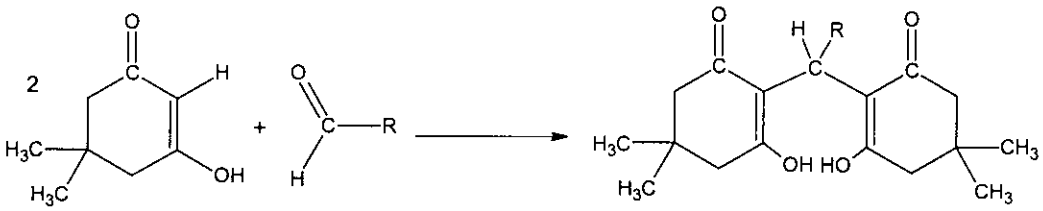

Figure 2.15 Reaction scheme for Dimedon with an aldehyde [64].

The reaction of the dimedon reagent above with HCHO in the presence of ammonia is otherwise known as the Hantzsch reaction. The reaction scheme is shown in figure 2.16. Formaldehyde has been simultaneously derivatised in, and extracted by CO_2 supercritical fluid using the Hantzsch reaction [65]. LC-MS has also been used to determine the derivatives of the Hantzsch reaction. An advantage of this reaction is that only the product exhibits fluorescent properties. Problems with increasing fluorescence in the reagent blank were experienced [66].

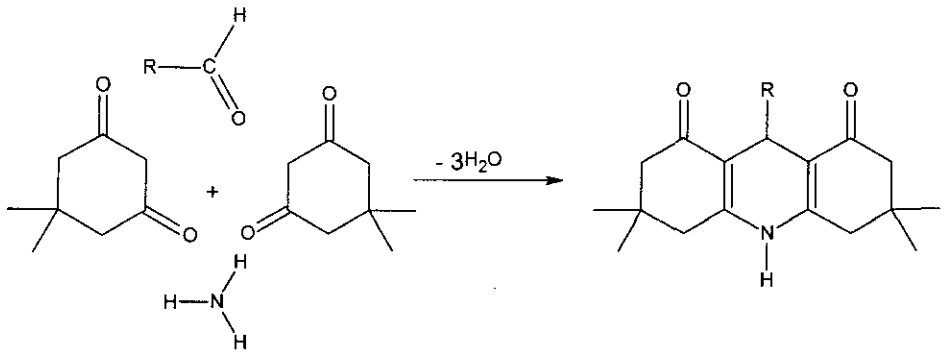

Figure 2.16 Hantzsch reaction scheme [65-66].

2.4 CONCLUSION

Despite all the available methods, not one of them can satisfy all the criteria for concurrent aldehyde analysis. The need for a field method, which is cheap, sensitive, selective and most importantly simple, is greater than ever.