Developing a Reliable Method for Airborne Aldehydes Monitoring in Confined Spaces in Polluted Environments

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Declaration

The candidate confirms that the work submitted is her own, except where work which has formed part of jointly-authored publications has been included. The contribution of the candidate and the other authors to this work has been explicitly indicated below. The candidate confirms that appropriate credit has been given within the thesis where reference has been made to the work of others.

Publications

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Research produced for the article appears in Chapter 4. The candidate performed all the experiments, analysis and write up. Dr. Li, Dr. Ross and Dr. Hargreaves contributed with comments, guidance and proof reading.

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Abstract

Airborne aldehydes are measured by drawing a volume of air through a cartridge containing silica coated with 2,4-dinitrophenylhydrazine (DNPH), which is eluted with a solvent and analysed using high performance liquid chromatography with UV detection. The method cannot measure acrolein, and suffers from interferences from ozone and nitrogen dioxide, making sampling difficult in polluted environments. Using this method to measure the aldehydes in the London Underground maintenance sites, where the exhaust emissions are high, the method failed to deliver results.

The aim of the thesis was to fully understand the limitations of using the DNPH method in a polluted environment, and to develop an improved measurement method. It was found that the DNPH not only suffers from interference from ozone and nitrogen dioxide, but carbon monoxide also causes interference and destroys the DNPH. The destruction of the DNPH by NO_2, CO and ozone was quantified and an equation for the calculation of the amount of DNPH required for sampling of aldehydes in a polluted environment was proposed.

Based on these findings, several other derivatisation reagents (3-methoxybenzothiazolin-2-one hydrazine (MBTH), 2,3,4,5,6-pentafluorophenyl hydrazine (PFPH), O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine (PFBHA), 2-diphenylacetyl-1,3-indandioine-1-hydrazine (DAIH), 4-hydrazinobenzoic acid (HBA)), were evaluated in the presence of NO, NO_2 and CO. The evaluation of alternative derivatisation reagents resulted in the identification of PFBHA to be the superior alternative to DNPH due to its low reactivity towards NO_2, NO and CO. A method using PFBHA as the derivatisation reagent was developed, using silica gel coated with hydroquinone as the sorbent material. The new method has a 100 % method recovery as well as collection efficiencies above 90 % for all three of the aldehydes.

The LOD for formaldehyde, acetaldehyde and acrolein were determined to be 2.40, 6.49, and 2.70 $\mu g/m^3$, respectively, when sampling at 1.0 L/min for 8 hours. The concentrations of these aldehydes were measured at a train maintenance depot. The results were compared to those obtained using the DNPH method. The DNPH method underestimated the aldehyde concentrations by between 18 – 93 %, depending on the concentration of NO_2, and CO present. A reliable method for the measurement of airborne aldehydes in polluted environments was developed.

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List of Abbreviations

2-BPE	Trans-1,2-bis(2-pyridyl)ethylene
2-HMP	2-(Hydroxylmethyl)piperadine
4-APEBA	4-(2-((4-Bromophenethyl)-dimethylammonio)ethoxy)-benzenaminium dibromide
AA	Acetaldehyde
ACR	Acrolein
ACR-D	Acrolein-DNPH
AFME	Animal fat methyl ester
BD	Biodiesel
CE	Capillary electrophoresis
CE-FLD	Capillary electrophoresis with fluorescence detector
CE-UV	Capillary electrophoresis with ultraviolet detector
CI	Compressed ignition
CRM	Certified reference material
DAIH	2-Diphenylacetyl-1,3-indandione-1-hydrazine
DCM	Dichloromethane
DEEE	Diesel engine exhaust emissions
DEFRA	Department of Environment Food and Rural Affairs
DI	Direct injection
DMU	Diesel multiple unit
DNPA	2,4-Dinitrophenyl azide
DNPH	2,4-Dinitrophenyl hydrazine
DNSH	1-Dimethylaminonaphthalene-5-sulfonylhydrazide
DOAS	Differential optical absorption spectroscopy
DOC	Diesel oxidation catalyst
DPF	Diesel particle filter
ECD	Electron capture detector
EI	Electron ionisation
EPA	Environmental Protection Agency
FA	Formaldehyde-DNPH
FID	Flame-ionisation detector
FLD	Fluorescence detector
FT	Fischer-Tropsch

FTIR	Fourier-transform infrared spectroscopy
GC	Gas chromatography
GC-ECD	Gas chromatography with electron capture detector
GC-FID	Gas chromatography with flame-ionisation detector
GC-MS	Gas chromatography mass spectrometry
GC-NPD	Gas chromatography and a nitrogen phosphorous detector
GC-TCD	Gas chromatography with thermal conductivity detector
GTL	Gas-to-liquid
HBA	4-Hydrazinobenzoic acid
HDV	Heavy duty vehicle
HETP	Height equivalent to a theoretical plate
HPLC	High performance liquid chromatography
HPLC-FLD	High performance liquid chromatography with fluorescence detector
HQ	Hydroquinone
HSE	Health and Safety Executive
IC	Ion chromatography
ICE	Internal combustion engine
ISO	International Organisation for Standardisation
LC-MS	Liquid chromatography mass spectrometry
LC-MS/MS	Liquid chromatography – tandem mass spectrometry
LDV	Light duty vehicle
LIFS	Laser-induced fluorescence spectroscopy
LOD	Limit of detection
LOQ	Limit of quantification
LPG	Liquefied petroleum gas
LTE	Long-term exposure
MBTH	2-Methoxybenzothiazolin-2-one hydrazine
MDHS	Method for the determination of hazardous substances
MDMNTH	N-Methyl-4-N’,N’-dimethyl-amino-6-(4’-methoxy-1’-napthyl)-1,3,5-triazine-2-hydrazine
MDNA	N-Methyl-2,4-dinitroaniline
MDNPH	N-Methyl-2,4-dinitrophenylhydrazine
MEKC	Micellar electro kinetic chromatography

MFC	Mass flow controller
MNBDA	N-Methyl-4-amino-7-nitrobenzofuran
MNBDH	N-Methyl-4-hydrazino-7-nitrobenzofurazan
MS	Mass spectrometry
NBEA	N-Benzyl ethanolamine
NIOSH	National Institute for Occupational Safety and Health
NMR	Nuclear magnetic resonance
NO_x	Oxides of nitrogen
NPD	Nitrogen phosphorous detector
OSHA	Occupational Safety and Health Administration
PAH	Polyaromatic hydrocarbon
PDA	Photodiode array detector
PFBHA	O-(2,3,4,5,6-Pentafluorobenzyl)-hydroxylamine
PFPH	2,3,4,5,6-Pentafluorophenyl hydrazine
PN	Particle number
PTR-MS	Proton-transfer-reaction mass spectrometry
PTV	Programmed temperature vaporisation
RH	Relative humidity
RP	Reversed phase
RSD	Relative standard deviation
Rt	Retention time
SCOEL	Scientific Committee on Occupational Exposure Limits
SCR	Selective catalytic reduction
SIFT-MS	Selected ion flow tube mass spectrometry
SIM	Selective ion monitoring
SMEP	Soy-bean oil methyl esters blended with palm oil
SO_x	Oxides of sulphur
SPME	Solid phase micro extraction
STE	Short-term exposure
TD	Thermal desorption
TD-GC-MS	Thermal desorption gas chromatography mass spectrometry
TDLS	Tuneable diode laser spectroscopy
THF	Tetrahydrofuran
TIC	Total ion current

TWA	Time-weighted average
TWC	Three way catalyst
UDMH	Unsymmetrical dimethyl hydrazine
UFOME	Used frying oil methyl ester
ULSD	Ultra-low sulphur diesel
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
VOC	Volatile organic compound
WEL	Workplace exposure limit

Chapter 1
Introduction and background

1.1 Aldehydes and their occurrence

Carbonyls are partially oxygenated organic compounds, and aldehydes have the carbonyl functional group in the terminal position, as shown in Figure 1.1. R could represent hydrogen (formaldehyde), an alkyl group or an aromatic group[1]. Formaldehyde is the most abundant atmospheric aldehyde, followed by acetaldehyde[2].

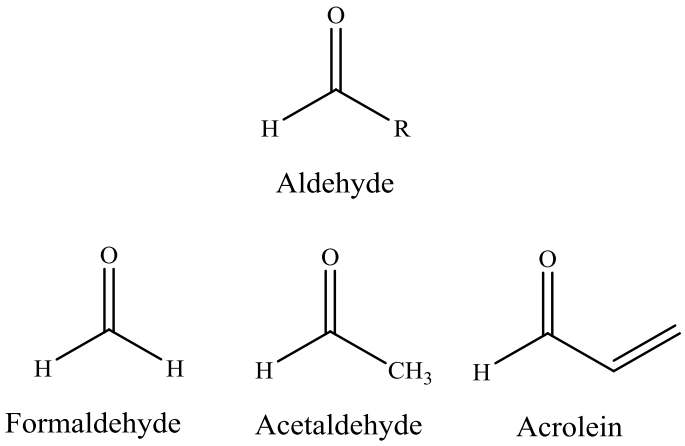

Figure 1.1: Structure of aldehydes

Short term exposure to formaldehyde, acetaldehyde or acrolein causes irritation of the eyes, skin and the upper respiratory tract, resulting in symptoms such as nausea, headaches and coughing[3]. Exposure to high concentrations of these compounds causes injury to the lungs and other organs. Acrolein is highly toxic, and at levels as low as 23 mg/m^3, exposure could be fatal[4]. Formaldehyde, acetaldehyde and acrolein, as well as other low-molecular-mass aldehydes, are suspected to be carcinogenic and mutagenic. Aldehydes are also a major cause of unpleasant odours in polluted environments[5]. Aldehydes have an effect on the environment as they are precursors of oxidants such as ozone, peroxyacyl nitrates, and other photochemical air pollutants[6].

Airborne aldehydes are emitted through biogenic and man-made processes, although natural sources of aldehydes are not an important contributor to air pollution[7]. Formaldehyde is one of the carbonyl compounds formed on thermal decomposition of

cellulose which occur during forest fires and burning of wood in house-hold ovens. In indoor environments, the primary sources of formaldehyde are building materials and wood-based furniture, construction materials, floor coverings, urea-formaldehyde spray foam and mineral wood insulation, preservatives in museums and disinfectants in medical laboratories[8, 9]. Acetaldehyde is a by-product of the alcoholic fermentation process[7]. The major source of acrolein is through emissions from incomplete combustion processes such as wood burning and engine emissions[10]. Aldehydes are secondary pollutants as a result of photo oxidation of gas-phase hydrocarbons[2, 11].

1.2 Air quality and Health and Safety legislation

The Air Quality Standards Regulations 2010, as made by the Department of Environment Food and Rural Affairs (DEFRA)[12], for ambient air, states that certain levels of pollutants in the outdoor environment should not be exceeded either annually or daily for the health of humans. These are tabulated in Table **1.1** and compared to exposure limits for workplaces in the UK (HSE)[13], EU (Scientific Committee on Occupational Exposure Limits - SCOEL)[14] and USA (Occupational Safety and Health Administration - OSHA)[15]. The WELs are set to protect the health of the worker by setting a maximum concentration of hazardous substances in indoor air over a time-weighted average (TWA), normally eight hours.

While there are no limits set for aldehydes in the ambient Air Quality Standards Regulations, strict limits have been set by the various governing bodies in the UK, Europe and the United States of America for workplace exposure. This is in sharp contrast to the limits for pollutants such as carbon monoxide, and nitrogen oxides, where the air quality limits are an order of magnitude lower than the workplace limits. Formaldehyde is the only aldehyde that is monitored for air quality purposes, as it is an ozone precursor substance, and therefore contributes to higher ground ozone levels. A large contributing factor to air pollution and the increased levels of these pollutants is the use of vehicle engines. Diesel engine exhaust gases are composed of about 67 % nitrogen, 12 % carbon dioxide, 11 % water, 9 % oxygen and 1 % polluting gases called diesel engine exhaust emissions (DEEE). DEEE is made up of 1.5 g/kWh carbon monoxide, 0.4 g/kWh oxides of nitrogen (NO_x), oxides of sulphur (SO_x), and 0.13 g/kWh total volatile organic compounds (VOCs) which include aldehydes[16].

Table 1.1: Comparison of Air quality limits with workplace exposure limits

Substance	mg/m^3						
	Ambient Air Quality[12]	UK HSE[13]		OSHA[15]		SCOEL[14]	
		LTE[a]	STE[b]	LTE[a]	STE[b]	LTE[a]	STE[b]
Acetaldehyde	-	37	92	366	-	-	-
Acrolein	-	0.05	0.12	0.23	0.7	0.05	0.12
Formaldehyde	Monitored	2.5	2.5	0.94	2.5	0.25	0.5
CO	10[c]	23	117	40	230	23	115
O_3	0.12[d]	-	0.4	0.2	0.6	-	-
NO_2	0.2[e]	0.96[f]	1.91[f]	9.4	1.9	0.9	1.9
NO	37[f]	2.5	-	31	-	2.5	-

[a] LTE – Long-term exposure (8 hour TWA reference period)
[b] STE – Short-term exposure (15 minute reference period)
[c] 8 hour daily mean
[d] 8 hour daily mean, not to be exceeded more than 25 days per calendar year averaged over three years
[e] 1 hour average, not to be exceeded more than 18 times a calendar year
[f] Does not apply to underground, mining and tunnelling industries until 21/8/23

The concentration of the gases in DEEE will be influenced by the type of engine, maintenance of the engine, the fuel used, the workload of the engine, and the engine temperature[17]. Gas turbine engines also emit aldehydes, specifically formaldehyde, acetaldehyde and acrolein, with formaldehyde emissions up to three times higher at idle than at full power[18]. Using a gas-to-liquid (GTL) fuel resulted in a reduction in the aldehyde emission levels from gas turbine engines[19]. Aldehyde concentrations in DEEE have also been shown to be dependent on the biodiesel content i.e. the type and blend concentration[20-24] with fossil fuel based diesel.

The engine emissions from road vehicles are regulated by the European Union (Euro 1 to Euro 6), which aims to reduce the levels of nitrogen oxides, carbon monoxide, hydrocarbons and particulate matter from road transport to improve the air quality. These standards do not make provision for the direct aldehyde emissions, which form part of Internal Combustion Engine (ICE) emissions[17], although the total hydrocarbon emission limit does include aldehydes. It is worth noting that all modern road vehicles are equipped with exhaust aftertreatment systems, including TWC (Three Way Catalyst), DOC (Diesel Oxidation Catalyst), DPF (Diesel Particle Filter) and SCR (Selective Catalytic Reduction) etc., which can reduce those harmful emissions to very low levels.

Off-road engines such as diesel powered trains and construction machines have separate emission regulations to on road cars and light duty trucks as set by the EU (Euro I – V). Similarly to road vehicles, non-road engine emission standards were also introduced through a tiered approach, however, it lagged behind the road vehicle standards by at least 5 years. Initially the standards did not include ship, railway locomotives, and aircraft engines and generating sets. The standards were set for CO, hydrocarbons, NO_x and particulate matter emissions. In 2006, railroad locomotives and inland waterway vessel engines were included in the Euro III standard, but was only applicable to new engines. Euro V, which came into effect in 2019, widened the scope of regulated engines to include most off-road engines, and also adopted a particle number (PN) emission limit for certain categories of compressed ignition (CI) engines. Measures being considered for future standards and lowering of emissions is the retrofitting of emission control devices in existing in-use non-road engines[25].

In certain workplace environments, such as mines, train and bus depots, diesel engines and generators (non-road engines) are regularly running in confined spaces, with the workers being exposed to the accumulated emissions, which are known sources of aldehyde emissions[17]. The accumulation of the aldehydes in these confined spaces is of particular concern to the health of the workers at these sites.

Exposure to engine exhaust emissions, which would include the aldehydes, can occur in the workplace where diesel operated heavy machines and vehicles are utilised, or in tunnels or construction sites where diesel operated stationary power sources are used[26]. Formaldehyde, acetaldehyde and acrolein are included in the list of substances with Workplace Exposure Limits (WEL)[13] set by the UK Health and Safety Executive (HSE). Since there is a risk of exposure in these DEEE environments, it is necessary to monitor the personal exposure of workers to aldehydes in the workplace.

Although aldehyde emissions from diesel engines are not specifically regulated, several aldehydes do have WELs. The UK HSE requires that exposure to all substances that are hazardous to human health be prevented or adequately controlled in an indoor or confined environment. It also requires that employers assess the health and safety risks to workers, which would include the measurement of aldehydes in the environment. These results will indicate the necessity to take action to control the levels of aldehydes in the workplace[17].

1.3 The measurement of formaldehyde and other aldehydes

The UK HSE recommends a method (*MDHS 102 Aldehydes in air, 2010*)[27] for the measurement of aldehydes. The method makes use of a cartridge containing a sorbent, usually silica gel, which is coated with 2,4-dinitrophenyl hydrazine (DNPH) to capture and derivatise the aldehydes (Figure **1.2**). The aldehyde-DNPH derivatives are eluted from the cartridge with acetonitrile and analysed using high performance liquid chromatography (HPLC) with ultraviolet (UV) detection. The DNPH method is used for the measurement of formaldehyde, acetaldehyde, propionaldehyde, acetone, butyraldehyde, valeraldehyde, isovaleraldehyde, hexanal, benzaldehyde, 2,5-dimethylbenzaldehyde, o-, m-, and p-tolualdehyde and glutaraldehyde[27]. The method cannot be used for the measurement of acrolein and crotonaldehyde[28], and ozone and nitrogen dioxide interfere with the method[27]. Ozone is removed using a cartridge containing potassium iodide, which is placed before the DNPH cartridge during sampling[28].

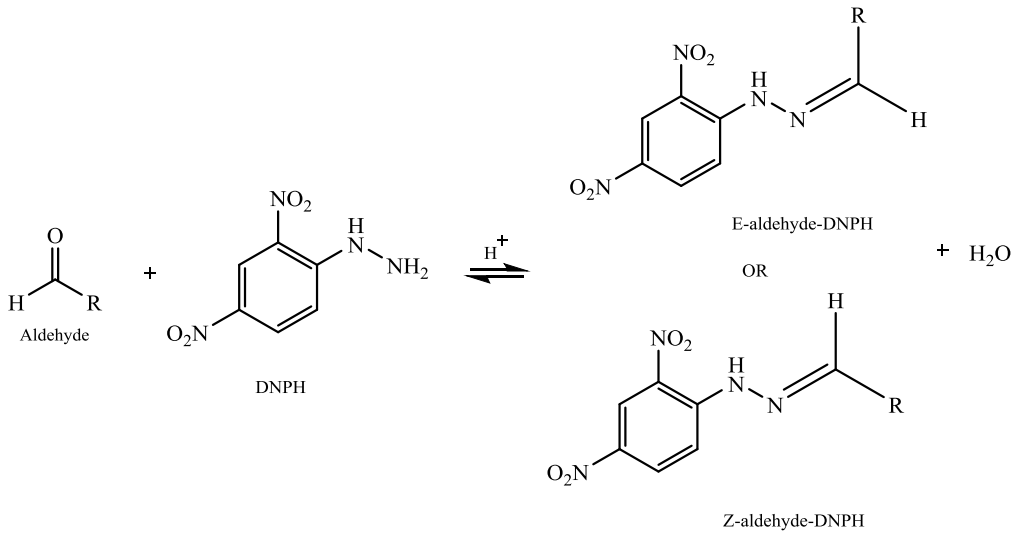

Figure 1.2: Reaction of aldehydes with DNPH[29]

Both NIOSH (National Institute for Occupational Safety and Health) and OSHA, in the USA, recommend an alternative method for the measurement of acrolein using 2-(hydroxylmethyl)piperadine (2-HMP) as the derivatisation reagent on XAD-2 followed by analysis with gas chromatography and a nitrogen phosphorous detector (GC-NPD)[30, 31].

1.4 Background and Industrial request

The London Underground maintenance sites are mobile sites that move along the train tracks as they are being repaired or replaced. All the equipment required for maintenance is brought to the site, and is removed afterwards. The electrical supply to the equipment comes from diesel engines and generators. These maintenance sites are classified as confined spaces.

> *"Confined space" means any place, including any chamber, tank, vat, silo, pit, trench, pipe, sewer, flue, well or other similar space in which, by virtue of its confined nature, there arises a reasonably foreseeable specified risk. - CONFINED SPACES REGULATIONS 1997*[32]

The risk in the London Underground maintenance site is the loss of consciousness or asphyxiation arising from exposure to diesel engine exhaust emissions. This risk is mitigated with the use of temporary fan installations at the work sites. No sunlight reaches the tunnels, therefore, no secondary reactions and pollutants are expected.

During maintenance work on the train tracks in the London Underground the NO, NO_2 and CO are monitored. Despite measures put in place to control the emission of NO and NO_2 from the engines, and thereby maintaining levels of the NO_x gases below the WELs, there are still health complaints from the workers which include the irritation of the eyes, nasal passages and throat. Another reason for the health impact could be due to the presence of aldehydes, as minor components of the diesel engine emissions, since these compounds also cause these types of symptoms on exposure. 4-Rail Services Ltd attempted to measure the concentration of these aldehydes using the DNPH method as recommended by the HSE. However, no results were obtained as the HPLC chromatogram contained no peaks of DNPH or the aldehyde-DNPH derivatives. Another method, colorimetric MBTH (2-methoxybenzothiazolin-2-one hydrazine), was used to measure the formaldehyde concentrations, however, no sensible result could be obtained from this analysis method either.

The University of Leeds was approached to investigate the limitations of the DNPH method in diesel engine emission environments in confined spaces, and thereafter develop a method for sampling and analysis of formaldehyde, acetaldehyde and acrolein in air to determine the personal exposure of workers, in these environments.

1.5 Research questions

The use of the DNPH method to measure the aldehydes in the London Underground maintenance sites failed to produce results. Previous research on the DNPH method found that ozone and NO_2 interfere with formaldehyde quantification through chromatographic interference[33-36] and destruction of the DNPH[37-39]. No research has quantified the destruction of the DNPH by NO_2 and ozone, or investigated whether any of the other DEEE gases interfere with the aldehyde quantification in the same way. Furthermore, very little information is available on the influence the DEEE gases, especially CO, an important pollutant, have on the capture and retention of the aldehydes during sampling.

Alternative derivatisation reagents have been evaluated for use in the measurement of aldehydes. A few of the derivatisation reagents react with NO_2 and ozone to form the same reaction product with both gases, thereby simplifying the chromatographic separation of the interference from the aldehyde-derivatives[40-42]. Similarly to the DNPH research, the destruction of the derivatisation reagents by NO_2 and O_3 has not been quantified, and very little information exists on the reaction of these derivatisation reagents with other DEEE gases. In addition, a few of the derivatisation reagents were chosen because of the formation of a stable derivative with acrolein.

The research questions that need to be answered are:

- What are the key parameters affecting the reliable and efficient measurement of aldehydes by DNPH in a polluted environment?
- How do these parameters affect the performance of the derivatisation reagents during the measurement of the aldehydes?
- Could alternative derivatisation reagents and analysis methods be used to develop a more reliable, robust and portable method for aldehyde monitoring?

1.6 Aims and objectives

The overall aim of this thesis is to identify the limitations of the existing DNPH method and develop a reliable, portable and cost effective method for the sampling and analysis of formaldehyde, acetaldehyde and acrolein in confined polluted spaces which can be widely used in any polluted environment.

To address the overall aim of the study, the following objectives were set:

- Identify the limitations and interferences on the DNPH method in a polluted environment, and determine the impact on the quantification of the aldehydes.
- Evaluate other derivatisation reagents available and how these are affected by the identified interferences of the DNPH method.
- Screen and choose a method, and develop the sampling and quantification methods.
- Test the robustness and accuracy of the newly developed method in simulated and real-world environments and compare the results with those obtained with the DNPH method.

The final method proposed should be easy to use in terms of cartridge preparation, sampling, sample preparation and analysis. The method should be robust, and have minimal interferences from the polluted environment. Lastly, the method should be affordable to implement, as compared to the DNPH method.

1.7 Thesis outline

Chapter 2 addresses the first two objectives in part by giving an overview of the DNPH method and the known limitations and how alternative derivatisation reagents were chosen to deal with some of these limitations. It also gives a brief overview of aldehyde measurements performed on tail-pipe emissions and DEEE environments.

The materials and standards used in this study are described in Chapter 3. The details of the instruments and the analysis methods are given along with a quick overview on the principles of the analysis techniques and validation process. The experimental methods used for this study is also described in this chapter.

In Chapter 4 the limitations of the DNPH method are evaluated. The first part of the chapter focusses on the chromatographic interferences and problems of the DNPH method with acrolein, ozone and NO_2, and identifies new interferences that have not been identified previously. The major DEEE gases (NO, NO_2 and CO) were investigated on how they affect the sampling of the aldehydes using a cartridge coated with DNPH. Finally, the destruction of the DNPH by NO, NO_2 and CO is quantified, and how this impacts on the capacity of the cartridge. The cost involved to increase the sampling capacity is calculated. This chapter focusses on the first objective of the thesis.

Chapter 5 addresses objective two by evaluating the alternative derivatisation reagents in the presence of NO, NO_2 and CO. The derivatisation reagents were chosen based on criteria set, and what is known from the literature, as will be described in Chapter 2. Also, the reaction of each of the derivatisation reagents with acrolein is examined. In addition, the oxidation of the aldehydes to the corresponding carboxylic acids is evaluated as an alternative to using a derivatisation reagent.

Chapter 6 describes the method development process undertaken, which addresses the third objective. The method development includes the assessment of various sorbents for the sampling of the aldehydes and a suitable derivatisation reagent is chosen. The final method's performance parameters are determined, as well as the storage stability of the cartridge, before and after sampling, is assessed.

Chapter 7 focusses on the final objective, testing the robustness and accuracy of the method in a polluted environment. A simulated polluted environment was generated in the laboratory for these tests. Finally, the method was applied to the sampling of the aldehydes in Neville Hill depot, a train maintenance site in Leeds. The results were compared to the results obtained from the DNPH method, which was sampled simultaneously with the new method.

Chapter 8 concludes the thesis, where it reviews whether research questions were answered and if the objectives were met. Further research into certain parts of the thesis is recommended, where further improvements of the method could be made.

Chapter 2
Literature Review

2.1 Introduction

The literature review starts with an overview of aldehydes in DEEE, with a summary of the type of aldehydes and typical concentrations found in tail-pipe emissions and diesel engines environments. Next, the problems encountered with the DNPH method will be reviewed, and their relevance to the current problem will be analysed. The focus will be on interferences from diesel engine emission components such as nitrogen dioxide, nitrogen oxide, and possibly other gases as well as carboxylic acids and VOCs and the levels at which these interferences may occur. Also, any remedies for these interferences will be assessed. Lastly, the development of various alternative derivatisation methods for the trace analysis of aldehydes will be reviewed. These alternative methods will be evaluated based on information on the method's susceptibility to the identified interferences from engine exhaust emission gases and any other compounds such as ozone, the reactivity of the reagent with the aldehydes of interest, as well as commercial availability and cost.

2.2 Aldehyde levels in diesel engine emissions

Aldehydes are components of DEEE along with carbon dioxide (CO_2), carbon monoxide (CO), and oxides of nitrogen (NO_x)[26]. Aldehydes are formed by partial oxidation of hydrocarbons during combustion in an engine[3]. The optimum diesel should have a high cetane number for an easy ignition (short ignition delay), an appropriate density and a low aromatic content, which will improve the completeness of combustion and thereby decreases the amount of aldehydes emitted from the engine[3]. The composition of engine emissions may also vary depending on the maintenance of the engine and the state of engine tuning, as well as the fuel pump setting[3, 26]. These factors affect the fuel to air ratio of the engine and therefore the level of combustion that takes place in the engine.

There are claims that there is a relationship between biodiesel content and aldehyde emissions[20, 21, 23, 24]. Table 2.1 shows the concentrations and emission factors from the tailpipe of vehicles and stationary industrial engines. Several biofuels at varying levels were used in the engines, however, no clear trend is seen. The use of Fischer-Tropsch fuels seem to result in lower aldehyde emissions[43]. The industrial engines and generators

gave results that are higher than the WELs set for formaldehyde and acrolein, however these concentrations are diluted after being emitted into the atmosphere. A study performed by Zarante et al.[44] showed acetaldehyde emission concentrations from a generator diesel engine that were considerably higher than other industrial engines. Although formaldehyde was detected in the sample, the levels were too low for quantification using gas chromatography with a flame-ionisation detector (GC-FID) as these detectors have a lower sensitivity for formaldehyde.

The results reported in literature on the concentrations of aldehydes present in ambient air in diesel engine operating environments are summarised in Table 2.1. The concentrations of the aldehydes reported in ambient air in diesel engine environments are well below the WELs for formaldehyde (2.5mg/m^3) and acetaldehyde (37 mg/m^3). In the instances where the concentration of acrolein was measured, these were also below the WEL (0.05 mg/m^3), though the measurements taken in a bus station in Salvador, Brazil, showed that the concentrations were almost three times the limit[45].

Table 2.1: Occurrence of aldehydes in diesel engine tailpipe emissions

Engine conditions	Fuel	Aftertreatment system	Method	Other concentrations	Units	Aldehyde			Ref.
						Formaldehyde	Acetaldehyde	Acrolein	
Naturally aspirated single-cylinder optical CI engine (Bore x Stroke: 92 x 100 mm)	n-heptane	None	GC-TCD[a] GC-FID		Mole fraction	0.017-0.018	0.01	0.003	46
8.9 L, turbocharged diesel engine, charge air cooled	BP no. 2 ULSD[b] fuel with 6 ppm sulphur	DOC, SCR, DPF	DNPH		mg/bhp.hr	<LOD[c] - 7.46	<LOD - 2.59	-	47
Mitsubishi pick-up truck, 2.84 L diesel engine	Diesel Waste cooking oil biodiesel (20 %)	None	DNPH		mg bhp/h	11.5 - 15.2 8.0 - 11.5	5.6 - 7.7 4.4 - 12.2	0.3 - 1.5 0.5 - 0.9	48
Tractor USEPA[d] 2010 emissions compliant diesel		TWC, DPF, SCR	DNPH	NH_3 0.04 - 2.20 g/mile	mg/mile	7.88 - 12.95	1.52 - 2.55	-	49
Euro 4 compliant vehicle	100 %Diesel 30 % UFOME[e] 30 % AFME[f] 30 % SMEP[g]	DOC	DNPH		mg/km	0.488 0.731 0.627 0.604	0.491 0.714 0.646 0.676	0.347[h] 0.588[h] 0.503[h] 0.490[h]	50
1.9 L Euro 3 passenger car diesel engine	Diesel Fischer-Tropsch A Fischer-Tropsch B	DOC	DNPH	CO (g/km) NO_x (g/km) 0.32 0.39 0.1 0.40 0.075 0.41	mg/km	8.4 2.7 1.2	4 0.8 0.6	-	43
Various gasoline and diesel fuelled cars, conformed to Euro 3		Various to comply with Euro 3	DNPH		mg/km	1.120 - 7.805	1.117 - 5.570	0.065 - 0.676	51
Commins-4B diesel engine	Diesel Ethanol with Biodiesel blend	TWC	DNPH	CO – 1 – 102 g/kW h NO_x – 0.1 – 2.3 g/kW h	mg/kW h	70 - 100 30 - 100	70 - 200 100 - 300	- -	24
5.3 L common rail, four-cylinder diesel engine	Diesel, tetralin, decalin, n-dodecane, iso-dodecane	None	MultiGas Analyzer		mg/m^3	2.5 - 125	1.8 - 155	-	52

Engine conditions	Fuel	Aftertreatment system	Method	Other concentrations	Units	Aldehyde			Ref.
						Formaldehyde	**Acetaldehyde**	**Acrolein**	
M790 Agrale diesel engine, DI[i]	Diesel	None	DNPH		mg/m^3	1.4 – 2.1	2.7 – 7.1	0.6 – 1.2	22
186FA diesel engine at 3600 rpm	BD0[j] BD50 BD100	None	DNPH		mg/m^3	16 - 34 12 - 33 10 - 19	0.2 - 0.45 0.1 - 0.55 0.05 - 0.9	1.0 - 2.7 0.55 - 1.5 0.2 - 0.5	53
Stationary, direct injection, CI engine (1800 rpm)	Diesel Castor oil biodiesel blend (35 %)	None	GC-FID		mg/m^3	-	155 149	-	44
Diesel engine Agrale model M85, 10 HP, 1800 rpm	B0 B2 B5 B10 B20 B50 B75 B100	None	DNPH		mg/m^3	5.1 7.8 6.9 7.6 6.3 4.8 5.4 6.3	22.5 20.7 27.5 21.2 14.8 7.3 16.5 14.6	0.07 0.28 0.44 0.33 0.47 0.33 0.58 0.51	21
Cummins-4B diesel engine, 1800 rpm	Diesel Biodiesel, ethanol, diesel blend	None	DNPH		mg/m^3	1.46 - 2.74 0.87 - 2.25	1.57 - 4.19 2.01 - 5.16	-	54
DI, heavy-duty diesel engine	Pure diesel 15 % Ethanol	Euro II compliant	DNPH	CO 1.67 – 1.82 g/kW h NO_x 6.04 – 6.55 g/kW h	mg/m^3	0.75 0.75	2.5 3.0	0.2 0.3	55
Diesel-fuelled car		None specified	MNBDH[k]		mg/m^3	2.6	0.5	-	41
Production vehicle with 5.8L V-8 diesel engine, cold start • Exhaust gas recirculation • Without recirculation		None	DNPH		mg/m^3	0.71 0.88	0.24 0.33	- -	56

[a] GC-TCD – Gas chromatography with thermal conductivity detector
[b] ULSD – Ultra-low sulphur diesel
[c] LOD – Limit of detection
[d] USEPA – United States Environmental Protection Agency
[e] UFOME – Used frying oil methyl ester
[f] AFME – Animal Fat Methyl Ester
[g] SMEP – Soy-bean oil Methyl Esters blended with Palm oil
[h] acetone included in result
[I] DI – Direct injection
[j] BD – Biodiesel
[k] MNBDH – N-Methyl-4-hydrazino-7-nitrobenzofuraz

Table 2.2: Occurrence of aldehydes in a diesel engine emission environment

Place	Environment	Pollution levels	Measurement Method	Aldehyde (μg/m^3)			Ref.
				Formaldehyde	Acetaldehyde	Acrolein	
Spain	Rural Urban Industrial	Refinery, chemical industry, power plants and coal mine (NO_2 - 1.0 - 29.3 μg/m^3)	DNPH	0.8 - 52.7 1.1 - 65.5 0.9 - 48.3	<LOD - 11.0 0.6 - 8.3 0.3 - 13.3	<LOD - 43.7[a] <LOD - 16.5[a] <LOD - 11.3[a]	57
North-western China	Restaurants	-	DNPH	11.0 - 66.5	15.9 - 78.3	-	58
Ningbo, China	Subway station		MBTH solution with LC-MS/MS[b]	0 - 55	-	-	59
Hong Kong	Rural and urban	None mentioned, higher in urban area than rural	DNPH	1.7 - 8.3	0.8 - 4.1	<LOD	60
Tehran, Iran	High traffic areas	Ozone - 10 - 55 ppb NO_2 - 25 - 75 ppb CO - 2.2 - 6 ppb	Chromotropic acid method	<LOD – 37.5 <LOD – 41.25	-	-	61
Metropolitan Area of Sao Paulo, Brazil	Traffic tunnel	LDVs[c] and HDVs[d]	DNPH	5 – 17.5	9.2 – 25.6	-	62
Kumamoto, Japan	City centre		2,4-pentanedione	1.3 – 40.6	-	-	63
Salvador, Brazil	Bus station	Mainly diesel busses	DNPH	115.0	150.6	148.7	45
Hong Kong - LPG[e] refilling station - University car park - Minibus station - Bus Depot station - Roadside monitoring station	Commercial Car park Residential Residential Roadside	LPG-fuelled taxi emission Gasoline-fuelled LDV emission Diesel-fuelled minibus emission Double-deck bus diesel emission Mixed vehicle types	DNPH	11.1 7.5 22.0 5.3 22.7	6.4 3.6 8.5 2.4 6.0	-	64
Chiba City, Japan	Air Monitoring Station	Ozone 11 - 61 μg/m^3	DNPH	2.4 - 3.8	2.1 - 3.9	-	65
Fluminense Federal University, Niterói City, Brazil	Commercial/ residential		DNPH	0.28 - 8.84	2.90 - 13.25	<LOD - 0.52	66
Kaohsiung city, Taiwan			DNPH	9.52 - 39.40	7.14 - 26.90	-	67

Place	Environment	Pollution levels	Measurement Method	Aldehyde (μg/m^3)			Ref.
				Formaldehyde	Acetaldehyde	Acrolein	
Guiyang city, China	Roadside		DNPH	1.5 - 35	1.6 - 15	-	[68]
Guangzhou, China	Roadside		DNPH	0.18 - 21.4	0.17 - 43.3	<LOD - 1.33	[69]
Shanghai China	Subway stations		PFPH[f]	13.5 - 35.6	6.64 - 24.7	<LOD - 1.27	[70]
Downtown Rio de Janeiro, Brazil	Roadside	CO - 0.87 - 1.30 ppm Ozone - 0.1 - 16.4 ppb	DNPH	12.4 - 190.2	6.7 - 60.2	-	[71]
Guangzhou, China	Roadside		DNPH	4.61 - 24.7	4.81 - 23.6	<LOD - 0.41	[72]
An San, South Korea	Urban area surrounding industrial complex		DNPH	2.7 – 52.8	10.9 – 85.6	3.4	[73]
Salvador, Brazil	Charcoal plants		DNPH	15 - 160	38 - 284	<LOD	[74]
Beijing, China	Ambient Roadside Subway		DNPH	10 40 5 - 15	20 30 10 - 20	-	[75]
Tijuca district, Rio de Janeiro, Brazil	Commercial		DNPH	95 - 270	12 - 55	-	[76]
Shin Mun Tunnel, Hong Kong	Traffic tunnel inlet Traffic tunnel outlet		DNPH	22.5 38.5	6.8 11.6	0.3 0.7	[77]
Gulf of Campeche, Mexico	Semi-urban		DNPH	2.5 – 32.5	11.0 – 45.8	-	[78]
Downtown Santiago, Chile	Urban		DNPH	1.5 – 6.5	1.3 – 5.9	-	[79]
Beijing, China	Urban		DNPH	4 - 26	6 - 17	-	[80]
Beirut, Lebanon	Urban	CO - 1.1 - 3.0 ppmv	DNPH	0.8 – 15.3	0.7 – 9.5	-	[81]
Hong Kong	Urban		DNPH	7 - 13	8 - 12.5	-	[82]
Salvador, Brazil	Bus station		DNPH	38.8 – 95.0	16.1 – 29.3	-	[83]

[a] acetone included in result
[b] LC-MS/MS – Liquid chromatography – tandem mass spectrometry
[c] LDV – Light duty vehicle
[d] HDV – Heavy duty vehicle
[e] LPG – Liquefied petroleum gas
[f] PFPH – 2,3,4,5,6-Pentafluorophenyl hydrazine

2.3 Measurement methods

There are various analytical techniques that could be used for the measurement of aldehydes in air, which include spectroscopic, wet chemical and derivatisation methods[84-86]. Spectroscopic methods have been used for the measurement of aldehydes, however, these methods usually require long optical paths, which make application in routine environment unsuitable[84]. These methods are also subject to interferences from water vapour, ozone and nitrogen dioxide[87]. Spectroscopic methods include Fourier-transform infrared spectroscopy (FTIR), tuneable diode laser spectroscopy (TDLS), differential optical absorption spectroscopy (DOAS), selected ion flow tube mass spectrometry (SIFT-MS), and laser-induced fluorescence spectroscopy (LIFS). Proton-transfer-reaction mass spectrometry (PTR-MS) has been applied to the analysis of indoor and outdoor aldehydes, with reported detection limits as low as 200 ppt[88]. However, the method was reported to be less sensitive to formaldehyde than other carbonyl compounds due to the loss of protonated formaldehyde from the reaction with water in a humid environment[88]. These spectroscopic methods cannot be used for personal monitoring, only for fixed place monitoring, because they are not portable instruments. Spectroscopic instrumentation is also expensive compared to other techniques, and require access to electricity, which is limited in places like the London Underground maintenance sites.

Wet chemical methods makes use of derivatisation reagents such as chromotropic acid, acetylacetone, pararosaniline, DNPH and MBTH in solution, which are placed in impingers, and the sample gas bubbled through the liquid where the aldehydes react with the derivatisation reagents. The UV active compounds in the solution are then analysed using UV. The chromotropic method is selective only for formaldehyde, and is subject to interferences from polyaromatic hydrocarbons (PAHs), phenols as well as strong oxidisers[3]. Pararosaniline reacts with formaldehyde to form a magenta colour in the presence of sodium sulphite. The intermediate product reacts with SO_2 to form the chromophore with a UV absorbance at 570 nm. However, a toxic mercury reagent is required to eliminate the sulphite formed from atmospheric SO_2. These methods require small impingers with liquids to be worn, which could break when a worker is performing a highly physical task. This introduces a risk of exposure to more chemicals, and makes the method less desirable for use for personal sampling.

Sampling using cartridges containing a sorbent material to capture and concentrate the analytes is a more practical approach for the personal monitoring environment. Sampling is made portable by making use of (plastic) cartridges, which are small and light-weight, and are clipped to the collar of the worker, close to the breathing space. A small sampling pump is clipped to the belt of the worker and connected to the cartridge using a pipe.

The incorporation of a derivatisation step in the sample preparation for analysis of an analyte is done for various reasons, including to increase the selectivity of the method for a particular analyte, enhancement of thermal stability of the analyte, or to attach a selective label for detection by a specific detector[89]. Derivatisation of an analyte can improve sensitivity of the analysis method for the particular analyte by several orders of magnitude. Drawbacks of using a derivatisation reagent is that it adds another step to the method, which increases the possibility of an analytical error, increasing the uncertainty of the result. A derivatisation reagent could also react with the matrix components, introducing new possible interferences.

A frequently used method using 2,4-dinitrophenylhydrazine (DNPH) is recommended by the Health and Safety Executive for the monitoring of formaldehyde acetaldehyde, propionaldehyde, acetone, butyraldehyde, valeraldehyde, isovaleraldehyde, hexanal, benzaldehyde, 2,5-dimethylbenzaldehyde, o-, m-, and p-tolualdehyde and glutaraldehyde[27]. Acrolein cannot be analysed using the DNPH method (discussed in Section 2.4.3), and another method using 2-HMP (Section 2.5.1) as a derivatisation reagent has been recommended[30, 31].

2.4 DNPH and its problems

The use of DNPH as a derivatisation reagent for the measurement of aldehydes was first standardised by the U.S. Environmental Protection Agency in 1984 (TO-5)[90]. The DNPH method is based on the principle that aldehydes react with DNPH to form an aldehyde-DNPH adduct as shown in Figure **2.1**. The reaction occurs via the nucleophilic addition of the amine group of the DNPH molecule to the carbonyl group of the aldehyde/ketone, followed by the elimination of a water molecule.

The method described in TO-5 made use of midget impingers containing a mixture of hydrochloric acid, DNPH and isooctane. A complicated solvent extraction process followed the sampling, after which the compounds were analysed by HPLC with UV

detection at 360 nm. The method included the quantification of unsaturated aldehydes, such as acrolein and crotonaldehyde. The only significant interferences reported in the method were from certain isomeric aldehydes and ketones such as acetone or propionaldehyde, which could not be resolved by HPLC. This method using impinger sampling was labour intensive, made use of acidic and hazardous reagents during sample preparation, lacked sensitivity, and gave poor reproducibility at ambient concentration levels[7]. Therefore, in 1990, the use of DNPH-coated cartridges was introduced as one of the standard methods (Method IP-6) to measure formaldehyde and other aldehydes in indoor air[91].

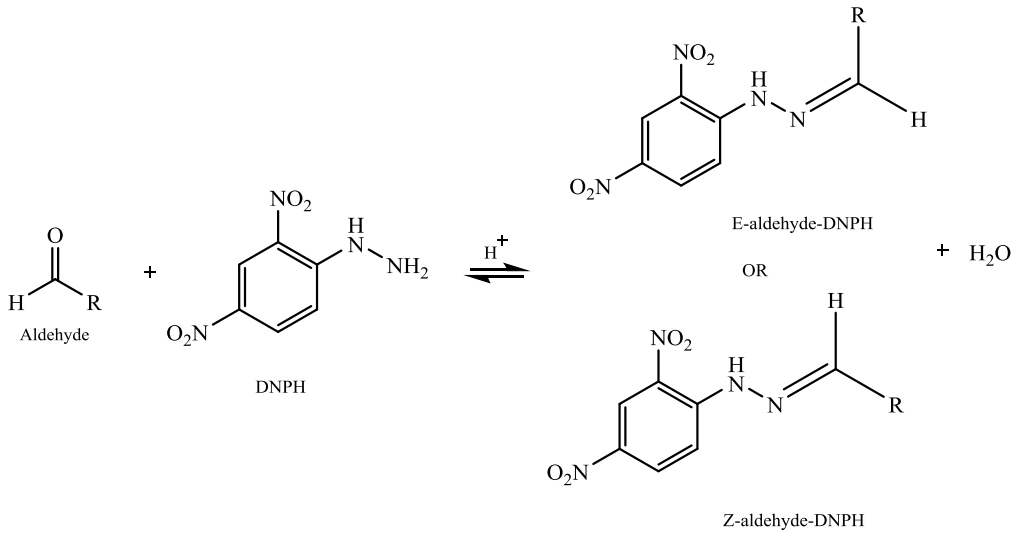

Figure 2.1: Reaction of aldehydes with DNPH[29]

The cartridge method stipulates that a known volume of air is passed through a DNPH-coated sorbent cartridge where the aldehydes are retained and react with DNPH. The DNPH derivatives are desorbed from the sorbent cartridge using acetonitrile, and then analysed using HPLC with UV detection at 360 nm, with the separation of the compounds achieved using a reversed phase (C18) column.

The method claimed a possible interference from organic compounds with similar retention times as the DNPH derivatives, if these compounds strongly absorbed at a wavelength of 360nm. Ozone was recognised as an interference on the method, and the use of an ozone removing cartridge was included in the method. However, the method still suffered from high formaldehyde background and required a clean room environment for the preparation of the cartridges. In an updated version, TO-11A[7], the use of

commercially prepared DNPH-coated cartridges was introduced. The document also mentioned the possible degradation of acrolein and crotonaldehyde during sampling, however the method was still recommended for the analysis of these compounds. The method was made an International Standard method in 2003, and in an update made in 2011[28] acrolein was removed from the list of aldehydes, due to its reactivity with itself and DNPH (Section 2.4.3). This method has subsequently been recommended for use by the UK HSE[27] for the analysis of formaldehyde acetaldehyde, propionaldehyde, acetone, butyraldehyde, valeraldehyde, isovaleraldehyde, hexanal, benzaldehyde, 2,5-dimethylbenzaldehyde, o-, m-, and p-tolualdehyde and glutaraldehyde[27] in air.

A few researchers using the DNPH method have encountered problems with the method, which have been reported in literature[35, 92, 93]. These are discussed along with the proposed solutions to the problems in the following sections.

2.4.1 Ozone

Ozone is a ubiquitous compound in the atmosphere and readily reacts with DNPH to form 2,4-dinitrophenol, 1,3-dinitrobenzene and 2,4-dinitroaniline, as shown in Figure **2.2**[37]. These degradation products may co-elute with formaldehyde-DNPH during HPLC analysis, which will contribute to an overestimation of the formaldehyde concentration. The interference from ozone is seen regardless of whether the sorbent is silica gel or C18, although the silica gel cartridges showed slightly better collection efficiencies[38].

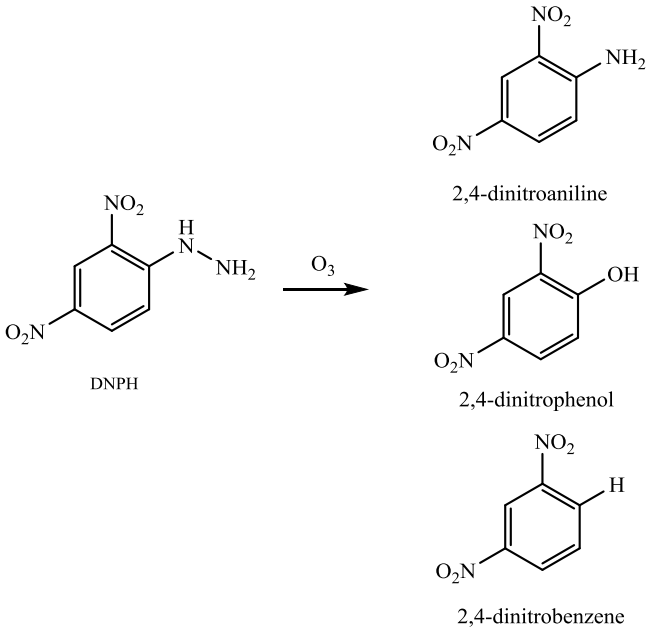

Figure 2.2: Ozone degradation products of DNPH[37]

When comparing the reaction of DNPH with ozone in the impinger and on the Si cartridge[39], it was noted that in both media, the DNPH reacted with ozone forming several of the same species. However, a decrease in the amount of formaldehyde quantified on the cartridge was observed, which was attributed to the formaldehyde-DNPH, which is immobilised on the Si-cartridge and therefore is exposed to further reaction with the incoming ozone. Due to the formaldehyde-DNPH being dispersed in the impinger solution, and with the large excess of DNPH, the formaldehyde-DNPH is spared from reaction with the ozone. Ozone also reacts with the other aldehyde-DNPH derivatives formed on the cartridge, which results in lower reported concentrations[35, 38]. The effect of the ozone interference on the aldehyde concentrations were seen at levels as low as 65 ppbv[33].

The use of a denuder or scrubber cartridge containing potassium iodide is recommended for the removal of ozone[27, 39]. For the KI to effectively remove the ozone, the scrubbers were found to require the presence of water vapour in the airstream (20 – 80 % Relative Humidity - RH)[38]. However, in very high humidity conditions (>90 % RH), the potassium iodide cartridge trapped water vapour during sampling, which resulted in the trapping of formaldehyde in the condensate on the KI cartridge, causing a reduction in the formaldehyde captured by the DNPH cartridge[38].

Several other denuder or scrubber cartridge options are available for the removal of ozone, many of which are not commercially available and need to be prepared in the laboratory. A graphitised carbon black thermal desorption cartridge was also used for the effective removal of ozone. The graphitised carbon black has the added advantage that it captures C5+ aldehydes, which could be analysed using gas chromatography mass spectrometry (GC-MS)[33]. Several other methods for the removal of ozone have been suggested, including the use of trans-1,2-bis(2-pyridyl)ethylene (2-BPE) or hydroquinone impregnated onto a silica gel cartridge, which is also placed before the DNPH cartridge in the sampling process[94].

2.4.2 Nitrogen dioxide

Nitrogen dioxide, either directly emitted or a secondary pollutant from diesel engines, reacts with DNPH in an acidic medium to form 2,4-dinitrophenyl azide (DNPA), as shown in Figure **2.3**. DNPA exhibits similar chromatographic properties to

formaldehyde-DNPH as shown in Figure **2.4**[34], therefore creating a challenge to separate it from formaldehyde-DNPH chromatographically.

The HPLC conditions have been modified to separate the DNPA from the formaldehyde-DNPH to an extent[35], but a dual-wavelength detection method was described to differentiate between the analyte and interferant[34]. Even though a separation of DNPA and formaldehyde was achieved, it was found that at NO_2 levels higher than 0.55 ppm, the DNPA interfered with the quantification of formaldehyde[36].

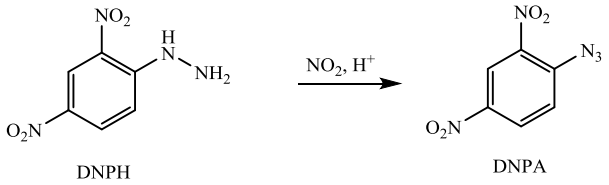

Figure 2.3: DNPH reacts with nitrogen dioxide to form DNPA[34]

The use of an ozone denuder cartridge, for the removal of ozone during sampling, was shown to compound the problem, as NO emissions were oxidised to NO_2[35].

The reaction of DNPH with NO_2 has been used to quantify NO_2 simultaneously with the aldehydes[95]. However, the reaction of NO_2 with DNPH decreases the amount of DNPH available for derivatisation, and therefore lowers the capacity of the cartridge for aldehyde quantification.

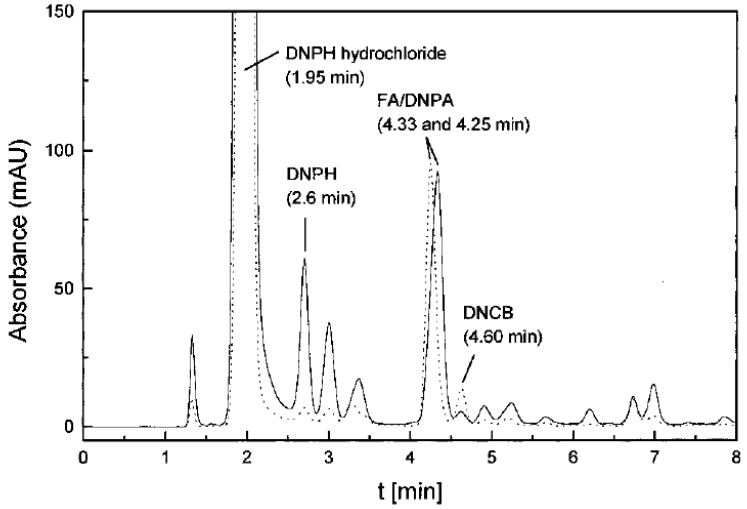

Figure 2.4: DNPA co-elutes with formaldehyde-DNPH (FA)[34]

2.4.3 Acrolein: Dimers and adduct formation

Acrolein was removed from the list of target analytes of the DNPH sampling method due to the appearance of several unknown peaks that were attributed to acrolein and its reaction products[27, 35] with DNPH.

Acrolein reacts with DNPH to form the DNPH derivative, ACR-D. The acrolein-DNPH derivative contains a double bond which reacts with another DNPH (AD1). This compound then reacts with another acrolein-DNPH molecule to form AD2 as shown in Figure **2.5**[96].

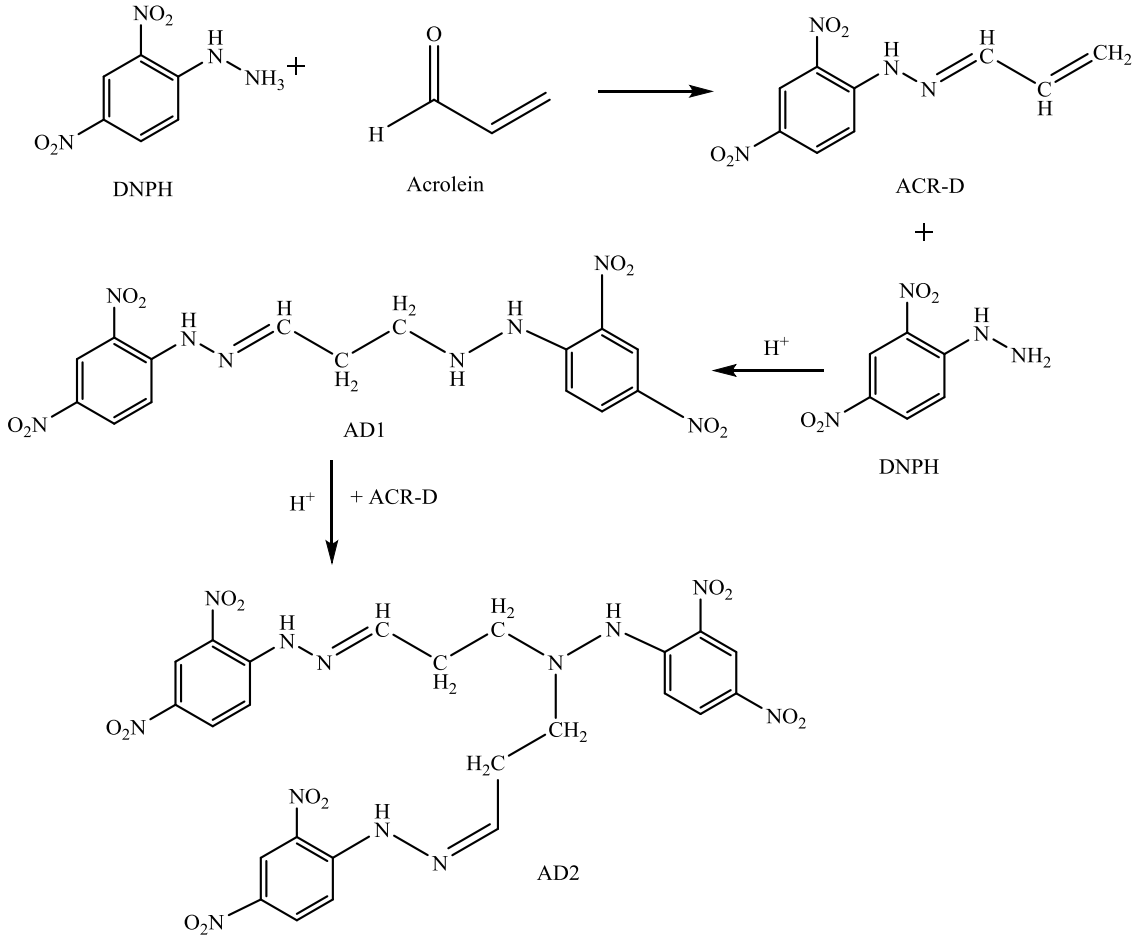

Figure 2.5: Adduct formation of ACR-D (Acrolein-DNPH) with DNPH[96]

Acrolein is a reactive compound which tends to dimerise to form a dimer (2-formyl-3,4-dihydro-2H-pyran, Figure **2.6**), which is another aldehyde, which also reacts with DNPH[97].

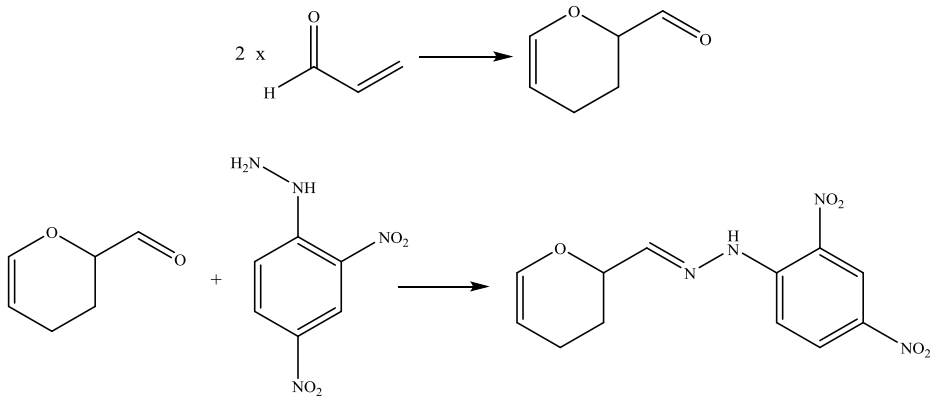

Figure 2.6: Acrolein dimerises to form 2-formyl-3,4-dihydro-2H-pyran[97] and reaction with DNPH to form the derivative

The chromatogram in Figure **2.7** shows the peak for acrolein-DNPH (ACR-D), and the peaks that were identified to be the acrolein-DNPH adducts that formed (AD1 and AD2). The acrolein-dimer-DNPH peak is possibly one of the peaks marked b or d. The summation of all these peaks was used to give an estimate of the acrolein concentration[98], however, there is a possibility that the peaks may co-elute with other aldehyde-DNPH derivatives, causing inaccurate results. The summation of the peaks is also not accurate since the UV response for each compound will differ. Liquid chromatography mass spectrometry (LC-MS) can be used to correctly identify the peaks and any co-elution of other compounds, however, this technique is expensive and not necessarily available in many laboratories.

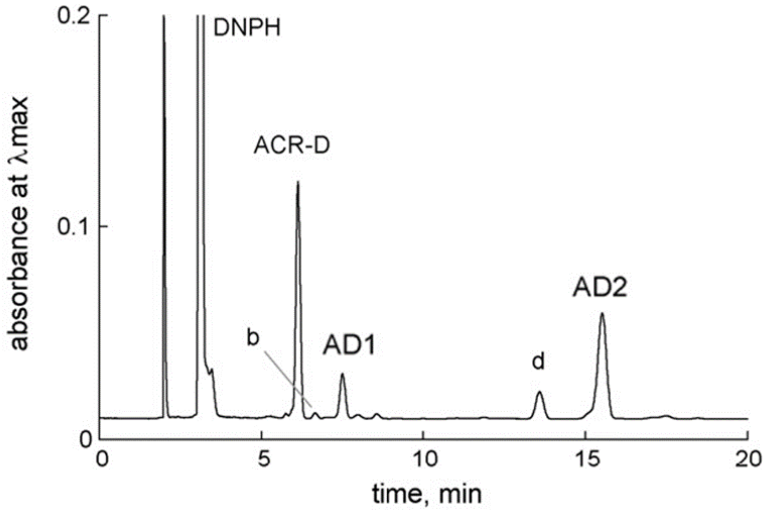

Figure 2.7: Chromatographic profile of acrolein-DNPH (ACR-D) and its decomposition products[96]

A suggested solution to prevent the decomposition of acrolein-DNPH is by using a hydroquinone-impregnated cartridge before the DNPH cartridge[96]. Hydroquinone is used to stabilise the pure acrolein compound when purchased commercially, as it prevents the dimerization of acrolein. The hydroquinone-impregnated cartridge captures the acrolein, preventing the dimerization of acrolein. The acrolein is only derivatised during the sample preparation step, when the cartridge is eluted at the same as the DNPH cartridge with the flow of the eluent through the DNPH cartridge and then through the hydroquinone cartridge. The reaction of acrolein with DNPH is accelerated by phosphoric acid in the acetonitrile eluent. Ethanol is added later, as the reaction of acrolein-DNPH with DNPH is inhibited by protic solvents such as ethanol. This makes the analysis of the sample time-sensitive.

An added advantage to using a hydroquinone-impregnated cartridge before the DNPH cartridge is that it could act as an ozone removal cartridge[99] as mentioned in Section 2.4.1, eliminating the need for a separate cartridge. However, it will be necessary to investigate the effect the ozone scavenging will have on the quantification of acrolein, as the ozone will reduce the capacity of the hydroquinone to stabilise the acrolein on the cartridge. The results may show that the KI cartridge for ozone may still be necessary.

2.4.4 Carbonyls and carboxylic acids

Many have reported the difficulty in separating the acrolein, acetone and propionaldehyde DNPH derivatives using HPLC[100-103]. With newer column technology available on the market with smaller particle size and adding tetrahydrofuran (THF) to the mobile phase[104], it should be possible to separate the C3 carbonyls. It has also been reported that LC-MS was used to differentiate between the carbonyl-DNPH derivative compounds[105, 106]. High concentrations of carbonyls will deplete the amount DNPH available to react with the aldehydes of interest. This depletion can be significant because acetone is commonly used in a laboratory.

Carboxylic acids contain a carbonyl functional group, however, due to a resonance stability of the molecule, which delocalises the electrons between the carbonyl- and hydroxyl group, a nucleophilic addition of DNPH is unlikely. This stability is seen in the presence of a base[107]. However, due to the presence of a strong acid, such as hydrochloric acid, the stabilising resonance may not occur, making it possible that the DNPH will react with the carboxylic acid.

Carboxylic acids were shown to react with DNPH, and that the acids could be simultaneously determined along with aldehydes[108]. The reaction was very slow, and was accelerated by heating the sample to 80°C for 4 hours. As the carboxylic acid derivatives elute before the DNPH peak, they do not interfere with aldehyde quantification, because the aldehyde derivatives all elute after the DNPH peak.

2.4.5 Humidity

Humidity affects the collection efficiency of DNPH for formaldehyde, acetaldehyde and propionaldehyde, due to the high solubility of the aldehydes in water. A humidity between 30 and 80 % RH did not affect the collection efficiency of formaldehyde[36], however the capacity of the cartridge increased for formaldehyde with humidity levels above 85 %[109]. The reverse effect was seen for acetaldehyde and propionaldehyde, where breakthrough of the aldehydes took place earlier in more humid air[110]. The effect that humidity has on the collection efficiency for acrolein is unknown.

2.4.6 Sorbent material

The performance of silica gel and C18 as sorbent materials for use in the measurement of formaldehyde using DNPH was evaluated[38]. The silica gel cartridge showed no breakthrough of the aldehyde whereas the C18 cartridge showed occasional breakthrough of 1-2 %. The breakthrough could be that the nonpolar C18 cartridge poorly retains formaldehyde, and the difference was attributed to the polar characteristic of the silica gel material, with OH groups available for hydrogen bonding, and therefore further opportunities for reaction, whereas the C18 cartridge is non-polar, with most of the OH groups on the silica gel sorbent derivatised with the C18 paraffinic chain.

A method was developed for the quantification of formaldehyde using Florisil as the sorbent material, coated with DNPH[36]. The collection efficiency was determined to be 97.3 %, and no interferences were observed from NO_2, SO_2, and humidity, although the levels of NO_2 and SO_2 were not specified in the tests.

2.4.7 Long-term sampling

The collection efficiency of various DNPH-coated solid sorbents for acetaldehyde decreases significantly when sampling over periods longer than 6 hours[111] while formaldehyde was unaffected. The discrepancy could not be explained by cartridge breakthrough and no other explanation could be found for the phenomenon. The study

was only carried out for formaldehyde and acetaldehyde and further investigation for other aldehydes should be carried out.

2.4.8 E/Z Isomers

Aldehyde derivatives of DNPH have E- and Z-isomers around the C=N double bond (Figure **2.1**), except for formaldehyde. The major isomer that forms is the E-isomer, however, under UV radiation and acidic conditions the Z-isomer is formed[29, 112]. Two peaks may therefore be observed for aldehydes during analysis, depending on the resolving power of the HPLC column. In these cases it is necessary to quantify the aldehyde by addition of the areas of both peaks.

Reductive amination has been used to reduce the double bond of the aldehyde-DNPH compounds to form the corresponding secondary amines using 2-picoline borane[29]. The secondary amines are analysed using HPLC, therefore resolving analytical errors due to the isomers.

2.4.9 Analysis technique

It is possible to analyse the DNPH derivatives by gas chromatography (GC) instead of HPLC, since GC could give better resolution and sensitivity than HPLC[113]. The improved resolution of GC results in the separation of the E- and Z-isomers of each aldehyde-DNPH derivative[114]. However, the low volatility of the aldehyde-DNPH compounds make GC analysis less ideal[40] and at higher injector temperatures these compounds decompose. The use of programmed temperature vaporisation (PTV) with solvent split injection has been a valuable injection technique for the analysis of real samples[114].

2.5 Alternative derivatisation methods

Various derivatisation methods using high performance liquid chromatography or gas chromatography have been developed as an alternative to the DNPH method as a result of some of the problems encountered.

Table **2.3** is a summary of alternative derivatisation reagents, along with the analysis method (GC/HPLC), reaction times with the aldehydes, as well as the cost of the reagent. An indication of reactivity with nitrogen dioxide and ozone is also given.

Very little information is available on the reactivity of the derivatisation reagents with nitrogen dioxide and ozone and the levels at which these compounds interfere with the

methods. A few of the derivatisation reagents that react with acrolein, require some extra effort to stabilise the acrolein derivative.

2.5.1 2-(Hydroxylmethyl)piperadine (2-HMP)

2-(Hydroxylmethyl)piperadine (2-HMP) forms only one reaction product with acrolein and therefore is the recommended method for measurement of acrolein in air[30]. The reaction time of 2-HMP with formaldehyde and acrolein is 12 hours[115] and 16 hours with acetaldehyde[116]. The derivatised sample is introduced into the GC using thermal desorption (TD), with several choices of detector available, mass spectrometry (MS)[117], flame-ionisation detector (FID)[116, 118], electron capture detector (ECD)[116], and nitrogen phosphorous detector (NPD) giving the most sensitive results[30, 31, 115]. The samples are stable on the sampling cartridge for at least 4 weeks at room temperature[31, 118].

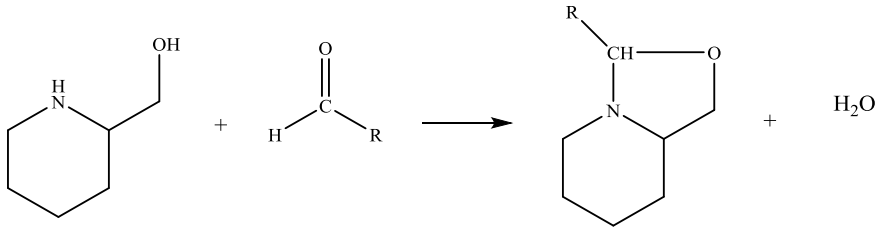

Figure 2.8: Derivatisation of aldehydes with 2-HMP

Derivatisation with 2-HMP (shown in Figure **2.8**) can be used for the quantification of formaldehyde[30, 117-119] and acetaldehyde[116] but these methods suffer from a few disadvantages. The method has high blank values for formaldehyde and acetaldehyde, requiring a blank subtraction in the quantification process[30, 116, 120]. Purification of the 2-HMP by crystallisation increases the levels of formaldehyde and acetaldehyde[115] which worsens the detection limits for these compounds. For this reason the DNPH method is preferred for the measurement of other aldehydes beside acrolein.

There is no information of the reaction of 2-HMP with nitrogen dioxide and ozone.

2.5.2 3-Methoxybenzothiazolin-2-one Hydrazine (MBTH)

3-Methoxybenzothiazolin-2-one hydrazine (MBTH) is used as a derivatisation reagent (shown in Figure **2.9**) in a spectrophotometric method which measures the total aldehyde concentration[87, 114, 121]. The reaction time of formaldehyde and acetaldehyde in solution is almost immediate, however acrolein only shows a 70 % reaction recovery after 1 hr at 95ºC[122]. The chromatographic separation of the aldehyde-MBTH derivatives is difficult

and not used[85], however, methods using micellar electro kinetic chromatography (MEKC)[121], GC-MS[123], HPLC-UV[122] and LC-MS/MS[59] have been reported.

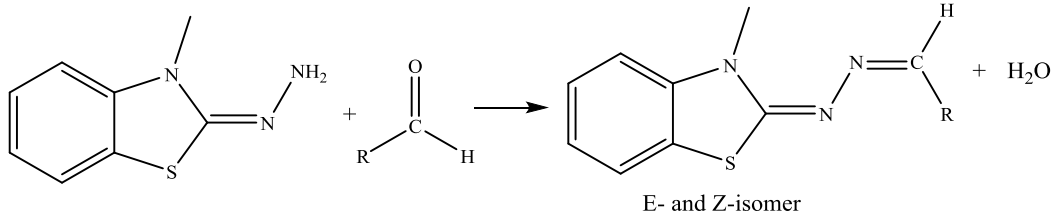

Figure 2.9: Derivatisation of aldehydes with MBTH

SO_2, a reducing reagent, at concentrations exceeding 30 mg/m^3 interferes with this method[3, 9]. This would indicate that other similar compounds such as NO_2 will probably react with MBTH, causing interference and a reduced capacity.

2.5.3 N-Methyl-2,4-Dinitrophenylhydrazine (MDNPH)

N-methyl-2,4-dinitrophenylhydrazine (MDNPH) is synthesised by alkylation of DNPH, and has a reduced reactivity towards aldehydes[40]. The aldehyde-MDNPH derivatives have slightly longer wavelength maxima, making the method more selective towards the aldehydes[124]. The method is not suitable for the quantification of acetaldehyde, as it has a low recovery during sampling for the compound, possibly due to the lower reactivity[125].

It can be used in high oxidant concentration matrices as it reacts with NO_2 and O_3 to form only one product, N-methyl-2,4-dinitroaniline (MDNA)[40], which is easily separated from the aldehyde-MDNPH derivatives during analysis with HPLC and therefore does not interfere with the quantification of the aldehydes. The reaction of the MDNPH with the oxidants, however, reduces the capacity of the sampling cartridge for aldehydes.

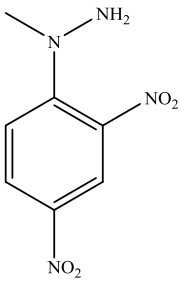

Figure 2.10: Structure of N-methyl-2,4-dinitrophenylhydrazine

2.5.4 N-Methyl-4-Hydrazino-7-Nitrobenzofurazan (MNBDH)

Similarly to MDNPH, N-methyl-4-hydrazino-7-nitrobenzofurazan (MNBDH) is used in environments with high ozone and nitrogen dioxide concentrations[41, 42, 126]. MNBDH forms only one reaction product, N-methyl-4-amino-7-nitrobenzofuran (MNBDA), with both oxidant gases, which is easily separated from the aldehyde derivatives using HPLC[40-42].

MNBDH, shown in Figure **2.11**, has a faster reaction rate with the aldehydes than both DNPH and MDNPH[41], with longer wavelength maxima (478 nm) and enhanced molar absorptivity, making the derivatisation method more selective and sensitive than the DNPH method[40]. The measurement of formaldehyde using this method compares well with the DNPH results, however, acetaldehyde shows a low recovery[125]. Another drawback of MNBDH is that it, and the aldehyde-MNBDH derivatives are unstable in air[127].

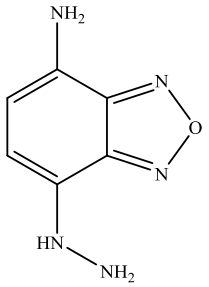

Figure 2.11: Structure of MNBDH

MNBDH can be used for the sampling of acrolein in air, if the pH of the eluent solution is adjusted to 9.5 immediately after the elution step[98]. The acrolein-MNBDH derivative is then stable in solution for at least 2 days at 4ºC.

2.5.5 1-Dimethylaminonaphthalene-5-Sulfonylhydrazide (DNSH)

1-Dimethylaminonaphthalene-5-sulfonylhydrazide (DNSH), shown in Figure **2.12**, is a fluorescent compound, making it possible to use a fluorescence detector (FLD) for analysis, which improves selectivity and sensitivity of the method[15]. DNSH along with hydroquinone can be used for the passive sampling and analysis of acrolein. The acrolein forms a di-derivatised compound, which is stable on the collection medium for 14 days at 4ºC[128]. However, the formaldehyde and acetaldehyde derivatives are prone to

hydrolysis as soon as 15 minutes after reaction takes place[40, 114, 129], and therefore the DNPH method is preferred for the analysis of the these aldehydes[130].

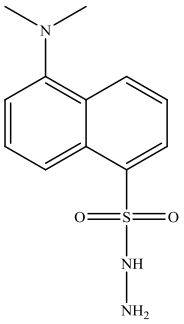

Figure 2.12: Chemical structure of DNSH

2.5.6 2,3,4,5,6-Pentafluorophenyl Hydrazine (PFPH)

Aldehydes react with 2,3,4,5,6-pentafluorophenyl hydrazine (PFPH) through a two-step reaction mechanism, shown in Figure **2.13**[131]. The reaction time is three days, and can be shortened to 24 hours by increasing the temperature of reaction to 60ºC[132]. Both the E- and Z-isomers form during the reaction and are separated during GC analysis, which are added together for quantification purposes[133, 134]. The PFPH-derivatives are thermally stable and volatile, and are therefore analysed using GC with thermal desorption for sample introduction.

Losses of the low molecular weight aldehyde derivatives (C1-3) were observed during prolonged sampling (> 1 hr), which is due to the volatility of these compounds[135], and therefore the DNPH method may be preferred in this instance[136].

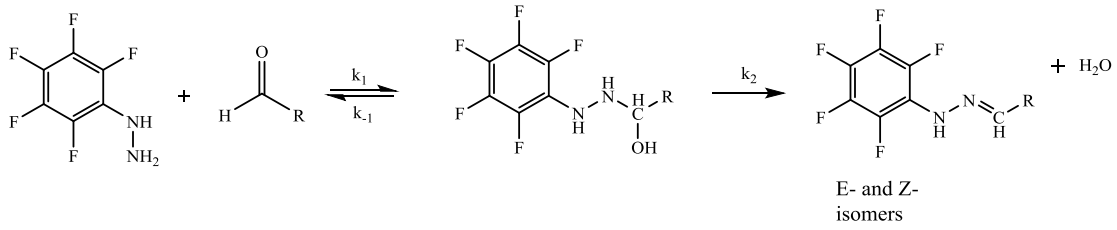

Figure 2.13: Two-step reaction of PFPH with an aldehyde[131]

Exposure of PFPH cartridges to ozone resulted in a greater destruction of the PFPH derivatives than DNPH derivatives[135]. No information is available on the reaction of PFPH with nitrogen dioxide.

2.5.7 *O*-(2,3,4,5,6-Pentafluorobenzyl)hydroxylamine (PFBHA)

Aldehydes react with *O*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine (PFBHA) in a slightly acidic environment (pH 4 - 6), according to the reaction shown in Figure **2.14** to form E- and Z- isomers of the derivative. The reaction time in aqueous solution is 24 hours[137] when using impingers for sampling, however, when sampling using TD cartridges or solid phase micro extraction (SPME) fibres coated with PFBHA, the reaction time is immediate[138].

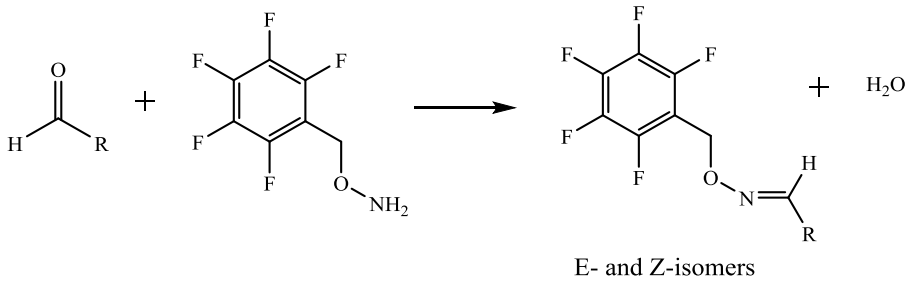

Figure 2.14: Reaction of an aldehyde with PFBHA[139]

The collection efficiency of the method is affected by the coating amount of the derivatisation reagent on the TD cartridge as well as the sampling flow rate. The unreacted PFBHA elutes between formaldehyde and acetaldehyde on a non-polar GC column, and therefore limits the amount of PFBHA that can be used on the sampling cartridge, and therefore the capacity for aldehydes. A low coating amount, requires a lower sample flow rate to increase residence time[131]. PFBHA reacts with acrolein to form a stable derivative, which is more stable than the acrolein-DNPH derivative[10].

2.5.8 2-Diphenylacetyl-1,3-Indandione-1-Hydrazine (DAIH)

2-Diphenylacetyl-1,3-indandione-1-hydrazine (DAIH), shown in Figure **2.15**, reacts with aldehydes to form E/Z isomers[129, 140], with a reaction time of about 60 minutes when sampling using impregnated silica gel cartridges[141]. The derivatives are analysed using HPLC with a fluorescence detector[129, 141, 142], making the method more selective and sensitive than the DNPH method. The concentration of acrolein can be determined using DAIH as derivatisation reagent and adjustment of the pH after elution to avoid the unknown peaks observed[142].

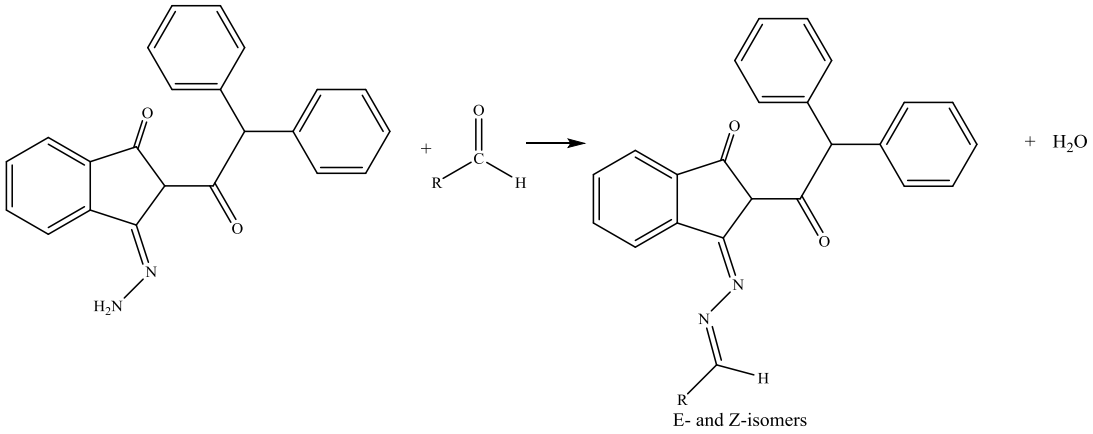

Figure 2.15: Reaction of DAIH with aldehydes

Ozone destroys DAIH and its aldehyde derivatives at levels of around 90 ppbv after only 1 hr, with the appearance of unidentified peaks[141].

2.5.9 4-Hydrazinobenzoic Acid (HBA)

The derivatives of 4-hydrazinobenzoic acid (HBA) have a maximum UV absorbance of 290 nm[143]. The reaction time of HBA with several aldehydes, as shown in Figure **2.16**, was determined to be between 15 min and 4 hrs[143]. The derivatives are analysed using capillary electrophoresis (CE)[143, 144] or HPLC[144], with relatively low detection limits, comparable to that of DNPH. No studies on the interference of NO_2 and O_3 have been performed for this method.

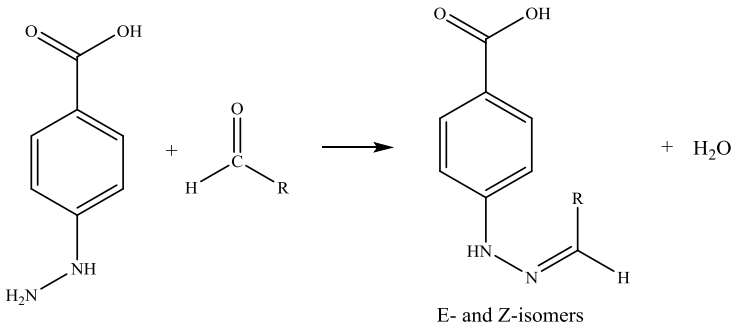

Figure 2.16: Derivatisation of aldehydes with HBA

2.5.10 Other derivatisation methods

Several other derivatisation reagents have been mentioned in literature for the sampling and analysis of various aldehydes. Due to steric hindrance from the methyl group on the hydrazine (Figure **2.17**), only one isomer is formed[145] from the reaction of N-methyl-4-

N',N'-dimethyl-amino-6-(4'-methoxy-1'-napthyl)-1,3,5-triazine-2-hydrazine (MDMNTH) with the aldehydes. MDMNTH[145] reacts with O_3 and NO_2 to form the same reaction product, which is easily separated from the aldehyde derivatives. The compound is not commercially available and needs to be synthesised in the laboratory.

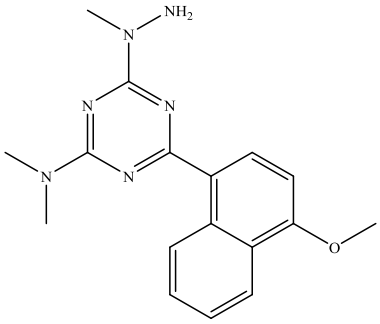

Figure 2.17: Structure of MDMNTH[145]

4-(2-((4-Bromophenethyl)-dimethylammonio)ethoxy)-benzenaminium dibromide (4-APEBA) reacts with aldehydes and carboxylic acids, with a reaction time of 3 hours at 10°C[146]. The method has only been used for the analysis C5 – C10 aldehydes in liquid biological samples, and has not been used for the analysis of aldehydes in gaseous samples. The compound is prohibitively expensive and is therefore not a feasible alternative to DNPH. N-benzyl ethanolamine (NBEA)[115, 147] and cysteamine[113] have been reported not to react with acrolein, and therefore are not suitable for the current application.

A final method, which involves hydrogen peroxide and sodium hydroxide to oxidise the aldehydes to their corresponding carboxylic acid, which are analysed using anion chromatography. This method is subject to interference from the already present carboxylic acids in the sample[148].

Table 2.3: Alternative derivatisation reagents

Derivatisation reagent	Cost (£/g)*	Analysis method	Reactivity with aldehydes			Reaction products with NO_2 and O_3	Other comments	Ref.
			Formaldehyde	Acetaldehyde	Acrolein			
DNPH	3.19	HPLC GC	< 5 min reaction time	Sampling >6hrs leads to low recoveries	Adduct formation	Several reaction products	• Recommended method by HSE, OSHA, SCOEL	40, 41, 74, 102, 113, 114, 149
2-HMP	8.98	TD-GC-MS GC-FID GC-NPD	16 hrs	16 hrs	16 hrs	Unknown	• Recommended method for acrolein • High blank values for formaldehyde and acetaldehyde. • Interference from acids in air	30, 115-118, 120, 150
MBTH	6.62	UV GC-MS HPLC-UV LC-MS/MS	50 minutes	50 minutes	Unknown	Possible interference observed	• Colorimetric method • Limited chromatography applications	3, 59, 87, 114, 121-123
MDNPH	-	HPLC-UV	20 min	Low sampling recovery	Unknown	One reaction product MDNA	• Reduced reactivity with aldehydes • Not commercially available	40, 87, 124, 151, 152
MNBDH	3220	HPLC-UV LC-MS	150 s	Low sampling recovery	Possible if pH adjusted after elution	One reaction product MNBDA	• Expensive • Derivatives unstable in air	40, 41, 87, 98, 114, 125, 127, 145, 153
DNSH	264	HPLC-FLD CE-UV CE-FLD	10 min	Isomers formed	Reacts with acrolein	Unknown	• Prone to hydrolysis • Decomposition of derivatives after 15 min • Fluorescent compound improves sensitivity and selectivity	15, 35, 40, 114, 128, 130, 154, 155

Derivatisation reagent	Cost (£/g)	Analysis method	Reactivity with aldehydes			Reaction products with NO_2 and O_3	Other comments	Ref.
			Formaldehyde	Acetaldehyde	Acrolein			
PFPH	6.89	GC-MS GC-NPD	3 days (24 hrs at 60ºC)	E/Z isomers formed	Reacts with acrolein	Reacts with ozone	• Kinetically limited sampling • No sample prep time when using TD-GC	70, 114, 131, 133, 134, 156-158
PFBHA	57.40	GC-MS GC-ECD HPLC-UV/MS	15 min	E/Z isomers formed	Stable derivative formed	Unknown – Ozone interference on acrolein quantification	• Quantification of carboxylic acids possible	10, 35, 87, 131, 139, 159-163
DAIH	131.50	HPLC-FLD	60 min	60 min	Possible with pH adjustment	Ozone destroys DAIH and aldehyde derivatives		129, 140-142
HBA	3.19	CE-UV HPLC-UV/MS	15 min – 4 hrs	15 min – 4 hrs	Unknown	Unknown		143, 144
4-APEBA	16480	HPLC-UV	Unknown	Unknown	Unknown	Unknown	• Only tested for C5 – C10 carbonyls • Expensive	146
MDMNTH	-	HPLC-UV	30 min at room temperature in water	30 min	Unknown	One reaction product	• No isomers formed due to steric hindrance • Synthesis required	40, 87, 145, 164
UDMH[a]	0.41	HPLC	20 min	Unknown	Unknown	Unknown	• Reacts with O_2 and CO_2 to form dimethyl nitrosamine which is toxic	165
NBEA	1.53	GC-MS	Fast	Fast	No reaction	Unknown		115, 147
Cysteamine	7.12	GC-MS	Fast	Fast	No reaction	Unknown		113

[a] UDMH – Unsymmetrical Dimethyl Hydrazine
* Costs obtained from Sigma Aldrich (www.sigmaaldrich.com) 27/07/2019

2.6 Conclusion

Aldehydes are part of combustion products, such as diesel engine emissions without proper emission treatment and other combustion sources such as open fires, and therefore it is necessary to analyse for aldehydes in these environments. The recommended methods using DNPH as derivatisation reagent for the sampling and analysis of the aldehydes suffers from several problems, which makes the method cumbersome and necessitates another analysis method, using 2-HMP. There is information on how ozone and NO_2 interfere chromatographically with the quantification of formaldehyde and other aldehydes because of co-elution, and destruction of the DNPH. The full impact that ozone and NO_2 have on the method has not been investigated. Furthermore, the impact of other DEEE gases (carbon monoxide, NO, PAHs, VOCs) on the DNPH method has not been mentioned and is therefore unknown. This will be investigated in Chapter 4.

An overview of other derivatisation methods for personal sampling purposes have highlighted several other methods for the analysis of aldehydes, none of which have been successfully applied for the simultaneous quantification of formaldehyde, acetaldehyde and acrolein. Several of the derivatisation reagents are not suitable for the current application due to their expense (MNBDH, 4-APEBA) or synthesis requirements (MDNPH, MDMNTH), low stability (DNSH), toxicity (UDMH) and low reactivity with acrolein (NBEA and cysteamine).

Some of the derivatisation reagents have been identified to suffer from interference from nitrogen dioxide and ozone, but, similarly to the DNPH method, the impact on the quantification has not been fully evaluated. The levels of NO_2 and O_3 at which interference and destruction of the derivatisation reagent is seen is mostly unknown, which will be studied in Chapter 5. Also, any other DEEE gases that were identified to also interfere with the DNPH method, will also need to be evaluated with the alternative derivatisation reagents.

Several further questions are raised from the literature review:

- Are the interferences described for the DNPH method, also interferences on the other derivatisation reagents? Are there any other interferences, such as CO, which is an important air pollutant, and which has not been reported on?

- How do these interfering compounds impact the sampling of the aldehydes? Is there competitive adsorption on the sorbent, or displacement of the aldehyde-derivatives?
- How does the reaction of the interfering compounds with the derivatisation reagents impact on the capacity of the sampling cartridge for the aldehydes.

Chapter 3
Materials and methods

3.1 Introduction

The following chapter describes all the materials and equipment that was used during this study. Full details of the experiments conducted are given in this chapter, and are referred to throughout the thesis. All experiments were performed in triplicate, and in some cases more replicates were added. The analytical techniques used were chromatographically based (HPLC, IC and GC), thus a short overview of the principles of chromatography is included. The overall aim of the thesis is to develop an analytical method for the sampling and analysis of aldehydes in a polluted environment, and therefore the method will need to be validated. The validation parameters are then described along with the equations used to calculate the parameter values. A description of the on-site sampling campaign is also included at the end of this chapter.

3.2 Chemicals and materials

The aldehyde-DNPH standard was purchased from Sigma-Aldrich (CRM4M7285, TO11/IP6A Aldehyde/Ketone-DNPH Mix, Supelco). A series of standards was prepared by diluting the standard using acetonitrile. The resulting concentrations are shown in Table 3.1. This series of standards was used for the calibration of the DNPH method.

A PAH standard, purchased form Restek (610 PAH Calibration Mix A, Catalogue no.: 31264, 125 - 250 μg/mL in methylene chloride), diluted with acetonitrile (1:4), was used for aromatic interference determination on the DNPH method. The names and concentrations of the PAHs are listed in Table 3.2.

The cartridges and sorbents (Table 3.3), aldehydes (Table 3.4), solvents (Table 3.5), derivatisation reagents (Table 3.6), gases (Table 3.7) and other chemicals that were used for all the experiments described later in this chapter are given in the tables below.

Table 3.1: Aldehyde-DNPH standard concentrations

Aldehyde	Molecular formula	Standard concentration (μg/mL)						
		1	2	3	4	5	6	7
Formaldehyde	CH_2O	14.2	9.47	4.73	2.84	0.95	0.47	0.095
Acetaldehyde	C_2H_4O	14.7	9.80	4.90	2.94	0.98	0.49	0.098
Acrolein	C_3H_4O	14.5	9.67	4.83	2.90	0.97	0.48	0.097
Acetone	C_3H_6O	14.8	9.87	4.93	2.96	0.99	0.49	0.099
Propionaldehyde	C_3H_6O	14.9	9.94	4.96	2.98	0.99	0.50	0.099
Crotonaldehyde	C_4H_6O	15.0	10.00	5.00	3.00	1.00	0.50	0.100
Butyraldehyde	C_4H_8O	14.8	9.87	4.93	2.96	0.99	0.49	0.099
Benzaldehyde	C_7H_6O	14.7	9.80	4.90	2.94	0.98	0.49	0.098
Isovaleraldehyde	$C_5H_{10}O$	14.7	9.80	4.90	2.94	0.98	0.49	0.098
Valeraldehyde	$C_5H_{10}O$	14.4	9.60	4.80	2.88	0.96	0.48	0.096
o-Tolualdehyde	C_8H_8O	14.9	9.94	4.96	2.98	0.99	0.50	0.099
m-Tolualdehyde	C_8H_8O	15.3	10.21	5.09	3.06	1.02	0.51	0.102
p-Tolualdehyde	C_8H_8O	14.6	9.74	4.86	2.92	0.97	0.49	0.097
Hexaldehyde	$C_6H_{12}O$	14.6	9.74	4.86	2.92	0.97	0.49	0.097
2,5-Dimethylbenz-aldehyde	$C_9H_{10}O$	14.8	9.87	4.93	2.96	0.99	0.49	0.099

Table 3.2: PAH calibration mixture

Compounds	Concentration (μg/mL)
Acenaphthene	250
Acenaphthylene	250
Anthracene	250
Benz(a)anthracene	125
Benzo(a)pyrene	125
Benzo(b)fluoranthene	125
Benzo(k)fluoranthene	125
Benzo(g,h,i)perylene	125
Chrysene	125
Dibenz(a,h)anthracene	125
Fluoranthene	125
Fluorene	250
Indeno(1,2,3,-cd)pyrene	125
Naphthalene	250
Phenanthrene	125
Pyrene	125

Table 3.3: Cartridges and sorbents

Cartridge/sorbent	Supplier	Catalogue number	Other information
LpDNPH S10	Supelco	21014	350 mg silica gel, 1 mg DNPH, volume of 3 mL
LpDNPH Ozone Scrubbers	Supelco	505285	KI cartridge
Carbograph 4TD	Markes International Ltd	C-CG420	20/40 mesh
Carbograph 5TD	Markes International Ltd	C-CG540	40/60 mesh
Carboxen 1003	Markes International Ltd	C-C1003	
Molecular Sieve 5Å	Markes International Ltd	C-MSV5A	
Tenax TA	Markes International Ltd	C-TNXTA	35/60 mesh

Table 3.4: Aldehydes

Aldehyde	Supplier	Catalogue number	Information
Formaldehyde	Sigma-Aldrich	252549-25ML	ACS Reagent, 37wt % in H_2O, 10 – 15 % methanol
Acetaldehyde	Sigma-Aldrich	00070-100ML	Puriss p.a. ≥ 99.5 % (GC) anhydrous
Acrolein	Sigma-Aldrich	110221-25ML	90 % contains hydroquinone as stabiliser

Table 3.5: Solvents

Solvent	Supplier	Catalogue number	Information
Acetonitrile	Fisher Scientific	10407440	99.99 % (HPLC grade)
Hexane	Fisher Scientific	10703611	98.18 %
Dichloromethane	Sigma-Aldrich	L090000-2.5L	Contains amylene as stabiliser
Deionised water	Laboratory prepared		18MΩ

Table 3.6: Derivatisation reagents

Derivatisation reagent	Supplier	Catalogue number	Information
PFBHA	Sigma- Aldrich	76735-1G	for GC derivatisation ≥99.0 % (AT)
PFPH	Sigma-Aldrich	93742-10G	for HPLC derivatisation ≥98.0 % (GC)
DAIH	Sigma-Aldrich	D204838-1G	98 %
HBA	Sigma-Aldrich	246395-5G	97 %
MBTH	Sigma-Aldrich	65875-2.5G	≥99.0 % (HPLC)

Table 3.7: Gases

Gas	Supplier	Catalogue number	Information
NO	BOC Limited	2654163	20.8 ppm balance nitrogen
NO_2	BOC Limited	2613983	20.1 ppm balance nitrogen
CO	BOC Limited	2654162	40 ppm balance nitrogen
N_2	BOC Limited		N5.5

Table 3.8: Other chemicals and materials

Chemical name	Supplier	Catalogue number	Information
Acetic acid (glacial)	Supelco	R475165	Neat
Formic acid	Supelco	R412236	Neat
Phosphoric acid	Sigma-Aldrich	79617-250ML	BioUltra ≥85 % (T)
Hydroquinone	Sigma-Aldrich	H17902-100G	ReagentPlus® ≥99.5 %
Hydrogen peroxide	Fisher Chemical	10121810	30 % w/v extra pure SLR
NaOH	Honeywell	58045-500G	Anhydrous ≥98 %
Tedlar bag	Supelco	24634	10 L, Thermogreen® LB-2 Septa
Gas sampling bulb	Sigma-Aldrich	22162-U	Glass, 125 mL with Teflon stopcock
Gauze, spring, caps and tubes for thermal desorption	Markes International Ltd	C-GZ020	Sorbent retaining, stainless steel, ¼ inch and PTFE ferrule, brass

3.3 Method Validation

Method validation results show the quality and consistency of the analytical results that can be expected in real samples. It verifies the suitability of a method to be used as a tool for quality control and research support[166]. The statistical parameters include selectivity, calibration curve, linearity, calibration range, accuracy, precision, recovery, limit of detection, limit of quantification, and stability. The data acquired for the method validation was done in triplicate, with the acceptance criteria at 95 %. The guidelines given by OSHA for air sampling along with chromatographic analysis[167] were also followed.

The validation results for the DNPH method, the IC analysis of the carboxylic acids, and the final PFBHA method were calculated and reported.

3.3.1 Compound selectivity

Selectivity refers to the capability of an analytical method to produce a signal unambiguously due to the analyte, in the presence of other compounds, which is measured by resolution (R) using the equation given below. Any possible interferences should also be tested.

$$R = \frac{t_{R2} - t_{R1}}{(w_1 + w_2)/2} \quad [1]$$

t_{R1} and t_{R2} are the retention times of the analytes peaks, and w_1 and w_2 are the widths of the analyte peaks of the chromatogram. Chapter 4 and Chapter 5 are dedicated to the study of how NO, NO_2 and CO interfere with the derivatisation methods for the sampling and analysis of formaldehyde, acetaldehyde and acrolein.

3.3.2 Calibration curve, linearity and range

A calibration was set up by plotting the peak area of the analyte against its concentration in the standard, and it was assumed that there was a linear relationship. Least-square linear regression was used to calculate the slope (m), y-intercept (c) and determination coefficient (R^2) of the calibration curve. Data analysis was performed using the Analysis Toolpak in Excel at the 95 % confidence level.

$$y = mx + c \quad [2]$$

At least three calibration standards were analysed in triplicate to confirm the linearity. An R^2 close to 1 indicates a linear relationship, with a value higher than 0.990 needed for acceptance of the calibration curve. The range should be linear and span 50 – 150 % of the expected concentration.

3.3.3 Limit of detection (LOD) and quantification (LOQ)

The limit of detection is the minimum concentration value at which the signal can be reliably differentiated from the background noise, at a specified confidence level. The limit of detection, for this study, was calculated as 3.3 times the standard deviation of the y-intercept (σ) of the calibration curve, divided by the slope of the calibration curve (S). As mentioned previously, the confidence level of 95 % was used.

$$LOD = \frac{3.3\sigma}{S} \quad [3]$$

The limit of quantification is the lowest concentration quantitatively determined that is accurate and precise within the acceptance criteria. Quantification below the LOQ and above the LOD is possible, but has a high uncertainty. The LOQ was calculated as ten times the standard deviation of the y-intercept divided by the slope of the calibration at the 95 % confidence level.

$$LOQ = \frac{10\sigma}{S} \quad [4]$$

3.3.4 Sensitivity

Sensitivity is a measure of the response related to a change in concentration. It is given by the slop of the calibration curve (m).

3.3.5 Accuracy and precision

The accuracy of the method is how close the measured value is to the "true value". In this work it is described by the method recovery.

$$Method\ recovery = \frac{Mass\ on\ cartridges\ (front + back)}{Mass\ loaded\ into\ bulb} \times 100\ \% \quad [5]$$

The acceptable recovery range of an analyte is between 70 and 110 %[168]. The precision of the method describes how close the replicate measurements are to each other and is given by the relative standard deviation (RSD). An RSD close to 0 indicates an excellent precision.

3.3.6 Collection efficiency

The effectiveness of the capture of the aldehydes on the cartridges was measured by the collection efficiency, as calculated in the equation below.

$$Collection\ efficiency = \frac{Mass\ on\ the\ front\ cartridge}{Mass\ on\ front + back\ cartridge} \times 100\ \% \quad [6]$$

Acceptable recovery and collection efficiency results are >75 %, preferable if >90 %[167].

3.4 Preparation of standards, solutions and cartridges

3.4.1 Aldehyde standard solution

The solution used for preparing aldehyde-derivative standards, in the gas bulb, and direct spiking onto the cartridges was prepared by weighing the aldehydes into a 100 mL volumetric flask, half-filled with acetonitrile. Hydroquinone was added to the solution to stabilise the acrolein in the solution. The volumetric flask was kept capped as much as possible to avoid losses of the aldehydes. The mass of each compound in the solution was ca. 200 mg formaldehyde, 60 mg acetaldehyde, 50 mg acrolein and 50 mg hydroquinone. The solution was stored in the fridge, and freshly prepared every week.

3.4.2 Carboxylic acid standard solution

A ca. 1000 mg/L stock solution of formic and acetic acid, respectively, was prepared by weighing ca. 25 mg of each acid into a 25 mL volumetric flask, and filled up to the mark with deionised water. A series of standards was prepared by diluting the stock solution using a micropipette into 25 mL volumetric flasks. The volumes pipetted into the flasks to prepare the calibration standards for IC are given in Table 3.9.

Table 3.9: Volumes used to prepare calibration standards for IC

Standard no.	Dilution volume (μL)	Stock or standard solution used	Final concentration of each of the acids (mg/L)
1	500	Stock	20.0
2	375	Stock	15.0
3	313	Stock	12.5
4	250	Stock	10.0
5	125	Stock	5.0
6	1250	1	1.0
7	625	1	0.5

3.4.3 Derivatisation reagent solutions

The derivatisation reagent solutions were prepared by weighing the amounts indicated in Table 3.10 into 10 mL volumetric flasks and filled to the mark with the appropriate solvent. These solutions were used to prepare the cartridges, as well as for the post-sampling derivatisation procedure.

Table 3.10: Solvents used for the derivatisation reagents

Derivatisation reagent	Mass (mg)	Solvent
PFBHA	26.89	0.1 % H_3PO_4 H_2O and acetonitrile (1:1)
PFPH	24.99	Dichloromethane
DAIH	44.75	Acetonitrile
HBA	19.19	H_2O and acetonitrile (1:1)
MBTH	22.60	H_2O
H_2O_2	(0.1 mL)	0.1 % H_3PO_4
Hydroquinone	37.50	Acetonitrile
DNPH	-	Acetonitrile
Hydroquinone and PFBHA	60 75	0.1 % H_3PO_4 H_2O and acetonitrile (1:1)

3.4.4 Preparation of aldehyde derivatives

The aldehyde derivatives were prepared by mixing the aldehyde standard solution with an excess amount of the derivatisation reagent in the solvent as in indicated in Table 3.10. The solution mixtures were left overnight to ensure a complete reaction[131, 157]. These solutions were used for the analytical method development on GC or HPLC for each derivatisation reagent.

3.4.5 Preparation of sampling cartridges containing the derivatisation reagents, hydroquinone or hydrogen peroxide.

The used DNPH cartridges containing only silica gel (after elution of the DNPH and the derivatives from the cartridge) were used to prepare the cartridges containing the various derivatisation reagents (or hydroquinone or H_2O_2) for the sampling experiments. A volume of 400 μL of the derivatisation reagent solution (Section 3.4.3) was injected onto the cartridge (the approximate dead volume in the silica gel portion of the cartridge). The final molar amount of the derivatisation reagents (or hydroquinone or H_2O_2) on the cartridges was equivalent to the molar amount of the commercial DNPH cartridge loading (5.05 μmol). All the cartridges, except for the H_2O_2 cartridges, were dried overnight in a fan oven at 50°C.

The cartridges for the final PFBHA method were prepared by preparing a solution containing both the PFBHA and hydroquinone at the concentrations specified as before,

and injecting 400 μL of this solution onto the silica gel cartridges. The cartridges were dried overnight in the fan oven at 50°C.

This procedure resulted in cartridges containing consistent concentrations of the various reagents for analytical purposes (RSD of 3.74 %, calculated from the responses of the derivatisation reagent of blank cartridges containing only the derivatisation reagents).

3.4.5.1 Shelf-life of cartridge after preparation

Cartridges containing derivatisation reagents were prepared as described previously in this section. The cartridges were capped and stored at room temperature, in a dark cupboard until analysed. Each day, one of the cartridges was analysed and the peak response of the derivatisation reagent was monitored over 8 days.

3.4.6 Preparation of the sorbent cartridges for the sorbent tests

Ca. 300 mg of each of the sorbent materials listed in Table 3.3 was packed into empty stainless steel thermal desorption cartridges. These were capped and stored until used in the sorbent tests.

3.4.7 Spiking of cartridges

For spiking tests, the aldehyde standard solution was directly introduced onto the cartridge by injecting a 100 μl of the aldehyde solution onto the cartridge using a micropipette.

3.5 Analysis methods

The analysis methods used in this study, namely HPLC, IC and GC are all chromatographic techniques. Chromatography is the separation of compounds based on the partition or distribution of the compounds between two immiscible phases[169]. The two phases are generally a solid stationary phase, and a liquid or gas mobile phase. The type of the mobile phase determines whether a technique is classified as liquid or gas chromatography. The HPLC technique that is referred to and used in thesis is based on partition chromatography, and specifically used is the reversed phase chromatography. Ion exchange chromatography (IC) is also classified as liquid chromatography.

3.5.1 General Principles of Chromatography[169-171]

The analytes in a sample are separated on a GC or LC column due to the difference in the distribution coefficients of the analytes between the stationary and mobile phases. A

chromatogram showing the parameters used to describe the chromatography is given in Figure 3.1. Each peak on the chromatogram represents an analyte in the sample.

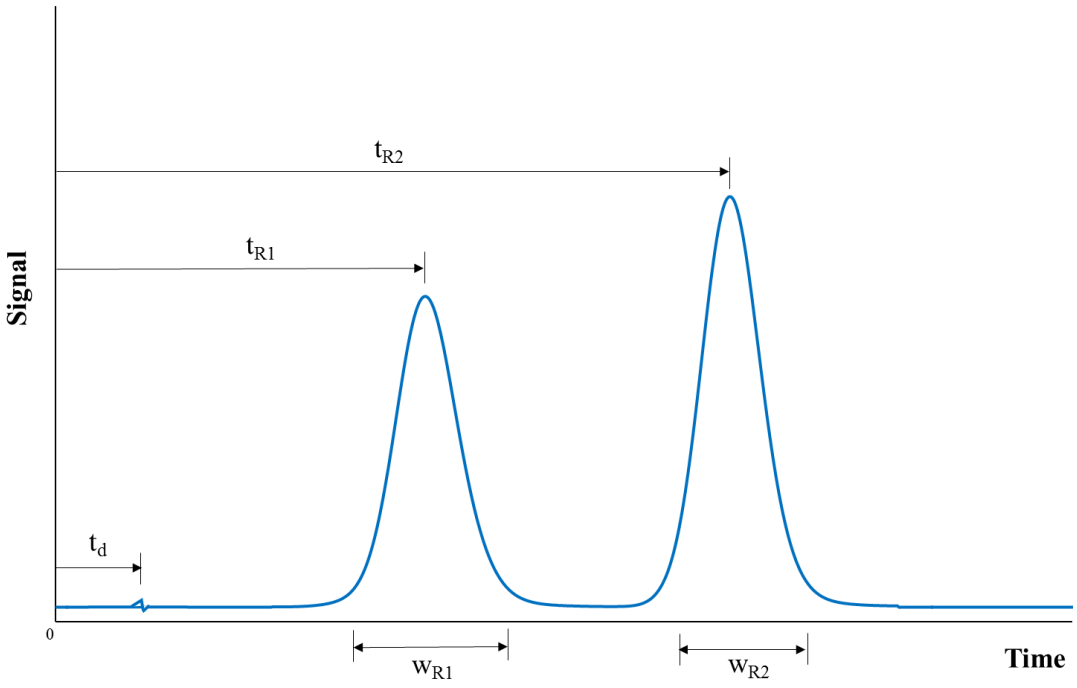

Figure 3.1: Chromatogram showing parameters used for the description of the chromatography

The dead time (t_d) is the time it takes for an analyte that is not retained by the column, to reach the detector. The retention time of an analyte is therefore the time it takes to move through the column and reach the detector. The dead time, retention times of the analytes (t_{R1}, t_{R2}) and peak widths (w_{R1}, w_{R2}), as indicated in Figure 3.1 are used to calculate the descriptive parameters in chromatography.

3.5.1.1 Resolution

The resolution (R) is a quantitative measure of how well two peaks are separated or resolved. The resolution of peaks is essential for accurate results, as discussed in the case of acrolein and the co-elution of the other C3-carbonyl compounds with it, in Chapter 2.

Resolution is calculated from the chromatographic data by the following equation:

$$R = \frac{t_{R2} - t_{R1}}{(w_1 + w_2)/2} \qquad [7]$$

Two peaks are recognised as separated at a resolution value of 0.5 and a resolution of 1.5 or more is necessary for the accurate quantitative determination of the separated analytes.

Resolution is also calculated by taking into account the selectivity, capacity and number of theoretical plates, as given in equation [8][172]. These factors are therefore levers that can be changed to achieve a full separation of peaks. These factors are discussed in the following sections.

$$R = \frac{\sqrt{N}}{4}\left(\frac{\alpha - 1}{\alpha}\right)\left(\frac{k'}{k' + 1}\right) \quad [8]$$

N = Number of theoretical plates
k' = Capacity factor
α = Selectivity

3.5.1.2 Partition coefficient and capacity factor

As already mentioned, all separations of analytes are based upon the difference in which analytes are partitioned between the mobile and stationary phase of a chromatographic system with the partitioning occurring due to the affinity of the analyte for the mobile phase and the stationary phase. The partition coefficient, K, is defined as

$$K = \frac{C_s}{C_m} \quad [9]$$

C_s is the analyte concentration in the stationary phase and C_m is the analyte concentration in the mobile phase[173].

The partition coefficient is related to the capacity factor of the column. The capacity factor is a description of the ability of the column to retain an analyte or the migration rate of the analytes through a column. Equation [10][174] shows how the capacity factor (k') is calculated.

$$k' = K\left(\frac{V_s}{V_m}\right) = \frac{t_R - t_d}{t_d} \quad [10]$$

V_s and V_m are the volumes of the stationary and mobile phases respectively. The capacity factor can also be calculated from the chromatographic data using the retention time of the analyte (t_R) and the column dead time (t_d).

A small k' value (< 1) indicates the poor retention of an analyte by the column, therefore it will elute near the void volume. A larger k' value (1 – 5) implies that the column retains the analyte, which results in a longer retention time. A very large k' value (> 10) is associated with peak broadening and, as a result, a decrease in the sensitivity for the analyte. Good separations of peaks are achieved with a capacity factor of between 1 and 5 for gradient separations, and for isocratic separations the capacity factor can be increased to 10.

As the capacity factor is determined by the stationary and mobile phase, it can be improved by changing the type of column used or changing the mobile phase composition.

3.5.1.3 Column Selectivity

The column selectivity (α) is a measure of the ability to discriminate between structurally related compounds. The selectivity is influenced by the mobile phase composition and choice of stationary phase of the column. Selectivity is calculated from the ratio of the retention times of two analyte peaks.

$$\alpha = \frac{t_{R2} - t_d}{t_{R1} - t_d} \qquad [11]$$

3.5.1.4 Theoretical plates and column efficiency

A column is divided into N theoretical plates, where the thermodynamic equilibrium of the analytes occurs between the mobile and stationary phase within each plate. The number of theoretical plates is proportional to the column length, L. The plate height, H, is also known as the height equivalent to a theoretical plate (HETP), and given in the equation below.

$$H = \frac{L}{N} \qquad [12]$$

The column efficiency increases as the number of plates becomes greater and the plate height becomes smaller. The number of plates is determined from the chromatographic data using the following equation:

$$N = 16\left(\frac{t_R}{w}\right)^2 \qquad [13]$$

The number of theoretical plates required to achieve a desired resolution on a column with a specific stationary phase, can be calculated by rearranging the resolution equation [172].

$$N = 16R^2 \left(\frac{k' + 1}{k'}\right)^2 \left(\frac{\alpha}{\alpha - 1}\right)^2 \quad [14]$$

A summary of the analysis methods developed and used in this thesis is given in Figure 3.2, showing the derivatisation reagent used for each aldehyde, and the accompanying analysis technique for each derivatisation reagent.

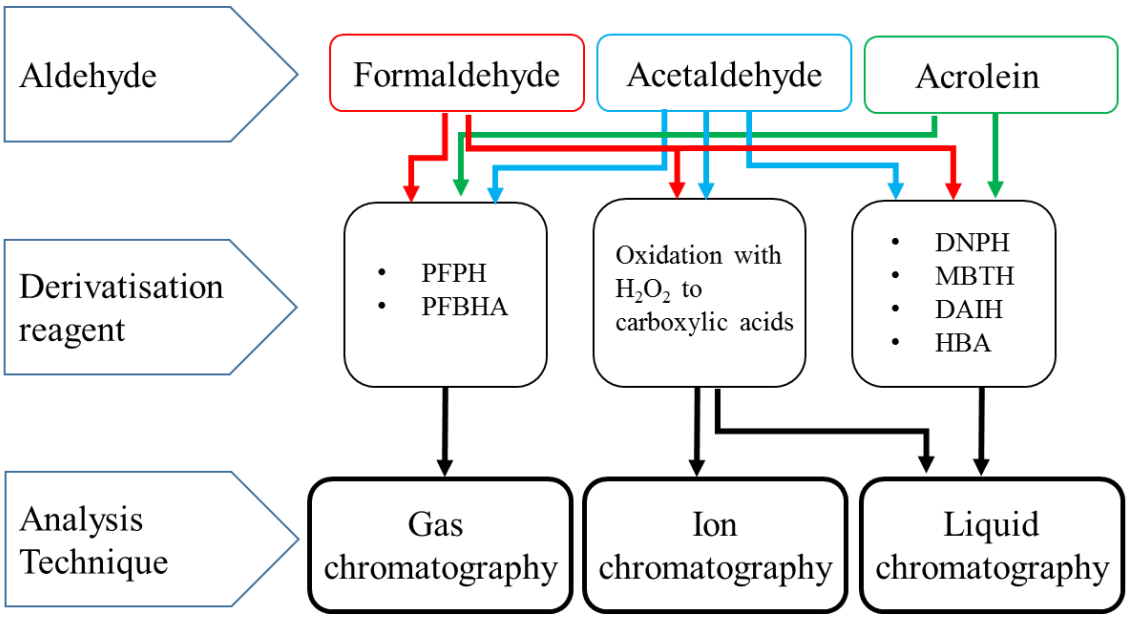

Figure 3.2: Summary of analysis methods for the determination of aldehydes

3.5.2 HPLC methods

A high performance liquid chromatography (HPLC) system, equipped with a photodiode array detector (PDA) (Ultimate 3000, Thermo Scientific, Waltham, MA, USA) (Figure 3.3) was used for all HPLC analysis methods. An Ascentis Express RP-Amide (2.7 µm, 10 cm x 4.6 mm) column fitted with a guard cartridge was used to separate the analytes in all HPLC analysis methods. The flow rate was set at 1.0 mL/min and the column oven was set at 30°C. An injection volume of 10 µL was used, unless otherwise specified.

Figure 3.3: Ultimate 3000 HPLC system, Thermo Scientific, with PDA detector

3.5.2.1 DNPH derivatives analysis

The HPLC method used for the analysis of the aldehyde-DNPH derivatives was adapted from the method as described in US EPA Method 8315 on Ascentis RP Amide[175]. The gradient for the mobile phase composition is described in Table 3.11.

Table 3.11: DNPH method mobile phase composition

Time (min)	% H_2O	% Acetonitrile
0	60	40
2	60	40
15	15	85
15.5	60	40

The UV detector was set at a wavelength of 360 nm, with the reference wavelength set at 320 nm, both with bandwidths of 4 nm. The chromatogram of the aldehyde/ketone-DNPH mixture is shown in Figure 3.4.

Table 3.12: HPLC regression and recovery data for the aldehydes and acetone

Aldehyde	Regression equation	Correlation coefficient (R^2)	Recovery data (n = 5)	
			Recovery (%)	RSD (%)
Formaldehyde	y = 1.74x + 0.03	0.9990	98.5	3.57
Acetaldehyde	y = 1.52x + 0.04	0.9988	98.8	3.00
Acrolein	y = 1.27x - 0.01	0.9989	98.4	2.57
Acetone	y = 1.57x + 0.23	0.9970	98.9	1.75

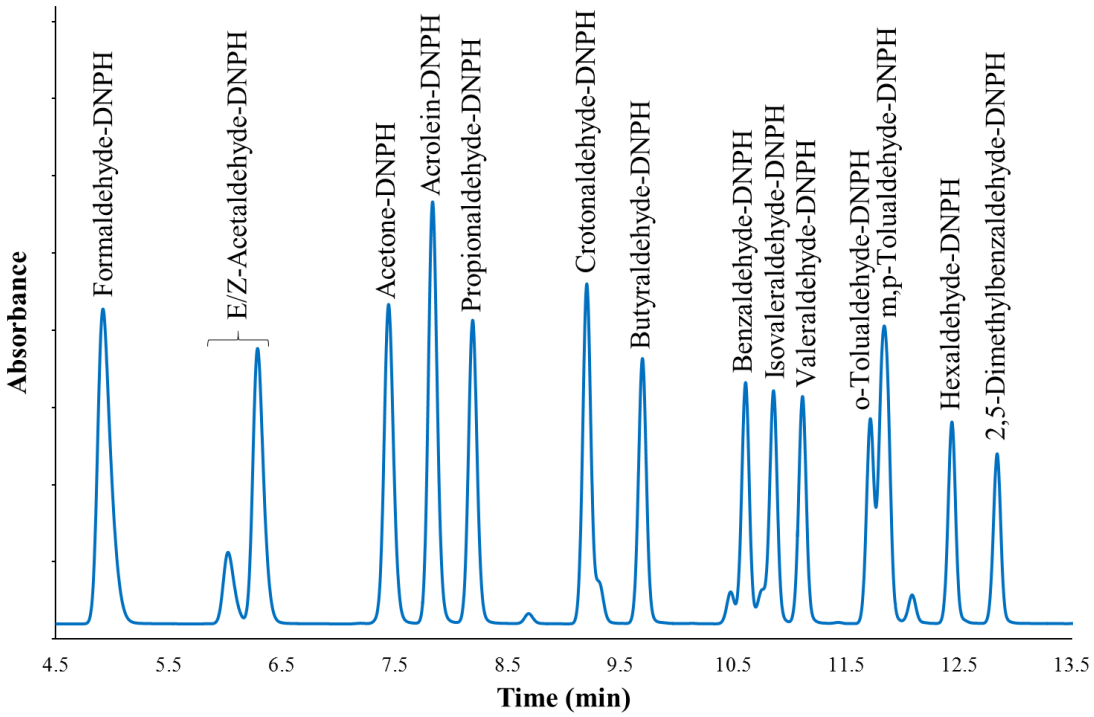

Figure 3.4: HPLC chromatogram of aldehyde-DNPH derivatives

To determine the recovery of the aldehydes from the method was determined by injecting Standard 4 as a sample, and quantifying the aldehydes and ketones using the calibration curve. The analysis was repeated five times. The results are shown in Table 3.12.

3.5.2.2 MBTH derivatives analysis

MBTH is soluble in water, and has a good UV response, therefore the best analysis method would be using HPLC. The HPLC method for the analysis of the aldehyde-MBTH derivatives was similar to the DNPH method, only the mobile phase composition gradient, shown in Table 3.13 and the UV wavelength was set at 310 nm. The chromatogram of the aldehyde-MBTH derivatives are shown in Figure 3.5.

Table 3.13: MBTH method mobile phase composition

Time (min)	% H_2O	% Acetonitrile
0	80	20
2	80	20
15	30	70
15.5	80	20

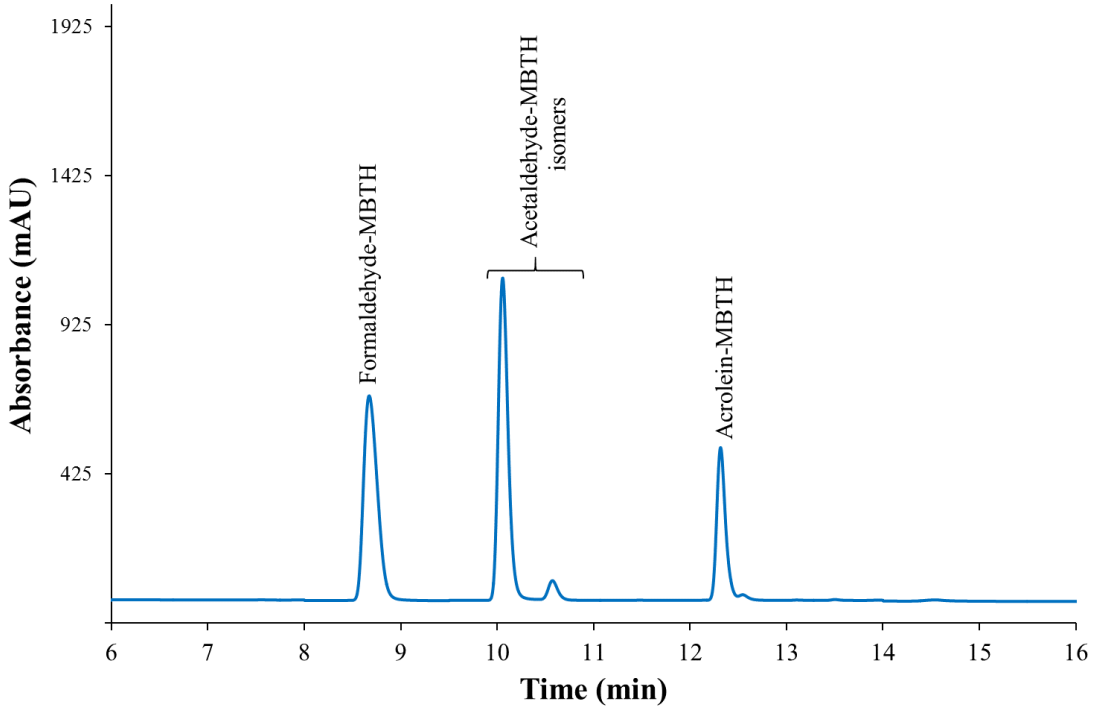

Figure 3.5: HPLC chromatogram of the aldehyde-MBTH derivatives

3.5.2.3 DAIH derivatives analysis

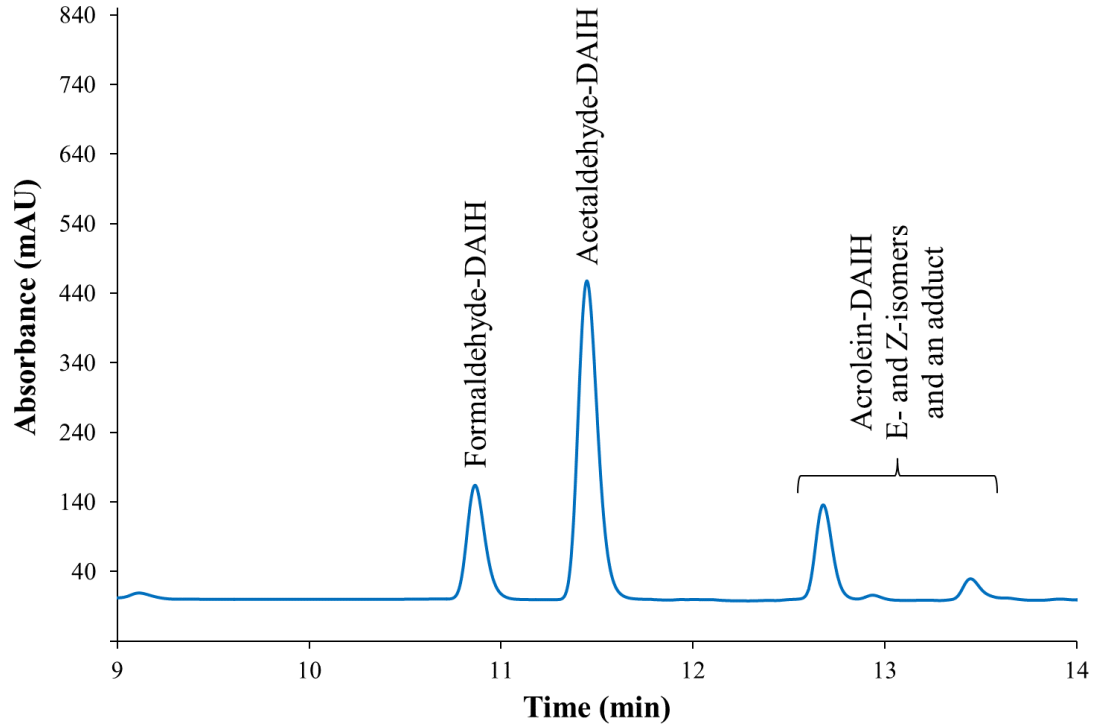

Figure 3.6: HPLC chromatogram of the aldehyde-DAIH derivatives

DAIH is not volatile, and is soluble in water. Therefore HPLC was chosen as the method of analysis for the DAIH derivatives. The analysis method for DAIH is the same as the DNPH method, except that the detector was set at the optimum UV response at a wavelength of 240 nm. The chromatogram of the aldehyde-DAIH derivatives are shown in Figure 3.6.

3.5.2.4 HBA derivatives analysis

HBA is thermally unstable, but soluble in water. The analysis method therefore was HPLC using an acidic mobile phase. The gradient mobile composition is described in Table 3.14. The monitoring wavelength of the UV was set at 310 nm. Figure 3.7 is the chromatogram of the aldehyde-HBA derivatives.

Table 3.14: HBA method mobile phase composition

Time (min)	% H_2O with 0.1 % H_3PO_4	% Acetonitrile
0	90	10
2	90	10
15	40	60
15.5	90	10

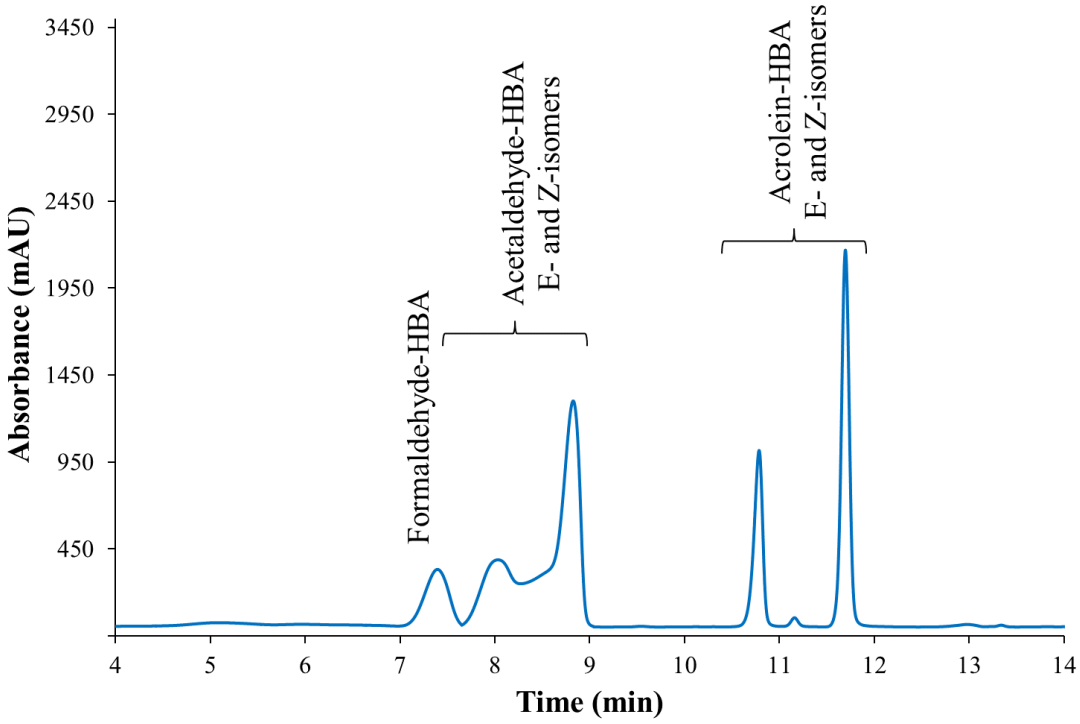

Figure 3.7: HPLC chromatogram of the aldehyde-HBA derivatives

3.5.2.5 Hydrogen peroxide

Two methods were used for the analysis of the carboxylic acids. The HPLC method was used initially for the analysis of the samples, requiring the use of an acidic solution for desorption of the carboxylic acids from the cartridge. An acidic pH below the pK_a of formic acid (3.7)[170] is needed to keep both the formic and acetic acids in their neutral acidic forms for analysis on the amide modified C18 HPLC column. The solution for desorption for analysis using IC needed to be above the pK_a of acetic acid (4.8)[170] to ensure that all the acids were present as formate and acetate in solution for anion exchange chromatography to take place.

HPLC method

Two methods were used to analyse the carboxylic acids after oxidation of the aldehydes by hydrogen peroxide (Chapter 5), namely IC and HPLC methods. The HPLC method made use of the Ascentis Express RP-Amide column, with the column temperature set at 30°C, and a mobile phase composition as described in Table 3.15. The flow rate was set at 1.0 mL/min and the UV wavelength was set at 210 nm.

Table 3.15: Mobile phase composition for HPLC analysis of the carboxylic acids

Time (min)	% H_2O with 0.1 % H_3PO_4	% Acetonitrile
0	95	5
2	95	5
10	5	95
12	5	95
13	95	5

IC method

A Dionex ICS-900 Ion Chromatography equipped with a Thermo Scientific AG11 guard column (50 mm x 4 mm) and AS11 (250 mm x 4 mm) analytical column was used for the analysis of the carboxylic acids in their ionic form. The mobile phase was 0.5 mM KOH in deionised water, at a flow rate of 0.35 mL/min. The conductivity detector has a suppressor (AMMS 300 MicroMembrane Suppressor) to reduce the conductivity of the mobile phase and the regeneration solution was 1.0 mM H_2SO_4 in deionised water. The injection volume of the sample is 10 μL and the analysis time was set at 20 minutes.

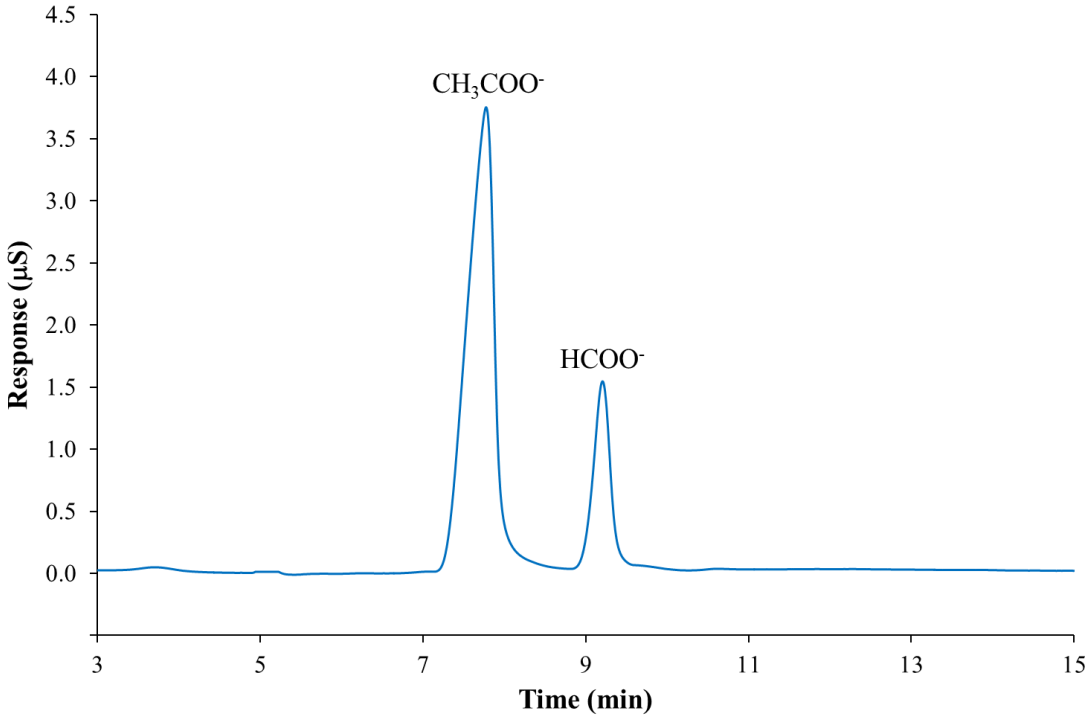

Figure 3.8: Ion chromatogram of the acetate and formate ions

The ion chromatographic method was validated and the performance parameters are shown in Table **3.16**. A chromatogram of the separation of the formate and acetate using this method is shown in Figure **3.8**. The chromatogram shows the acetate and formate ions at a concentration of around 5 mg/L. The peak of the formate ion is fronting, indicating an overloading of the column. This could be easily rectified by reducing the injection volume, but unfortunately the instrument used has a set sample loop volume which is not variable.

The validation parameter values are similar to those for the DNPH method (Section 4.2), although slightly higher limits of detection and quantification were obtained. This is due to choice of the range of standards used. To obtain lower limits, standards with lower concentrations could be included in the calibration. However the LOD and LOQ obtained are still acceptable for the measurement of formaldehyde and acetaldehyde.

Table 3.16: IC analytical performance parameters

	Anion	
Parameter	**Formaldehyde as formate**	**Acetaldehyde as acetate**
Linearity (R^2)	0.999	0.997
Repeatability (RSD)	4.43	1.57
Sensitivity (μS/(mg/L))	0.0298	0.0925
Retention time Precision (RSD)	0.22	0.58
Range (mg/L)	0.38 - 20	0.5 - 20
LOD ($\mu g/m^3$)[a]	1.89	3.23
LOQ ($\mu g/m^3$)[a]	5.72	9.78

[a] The limits of detection and quantification are expressed as the aldehyde before oxidation per volume (m^3) of air sampled at 1 L/min.

3.5.3 GC methods

For all GC analysis methods a Shimadzu GC-2010 Plus with GCMS-QP2010SE mass spectrometer (Figure 3.9) equipped with an Agilent DB5-MS column (5% Phenyl arylene polymer, with dimensions 25 m x 0.25 mm I.D. x 0.25 μm) was used.

Figure 3.9: Shimadzu GC-2010 Plus with GCMS-QP2010SE

3.5.3.1 DNPH reaction products identification method by GC-MS

The injector temperature was set at 280°C, and a volume of 1μL of the sample was injected splitless onto the column. The initial oven temperature was set at 150° and held for 2 min. The temperature was ramped at 10°C/min until a final temperature of 280°C was reached, and held for 10 minutes. The ion source, at 260°C, of the mass spectrometer was operated in electron ionisation (EI, 70 eV) mode, with the interface temperature to

the MS at 280°C. A total ion current (TIC) mass range of m/z 35-500 was scanned. The identification of the compounds was done based on their match with those listed on the NIST11 library search as well as matching retention times to the aldehyde-DNPH standard injected.

3.5.3.2 PFPH and PFBHA derivatives analysis on GC-MS

The PFPH and PFBHA aldehyde-derivatives were analysed on the same GC-MS analysis method, as the derivatives of both reagents were similar.

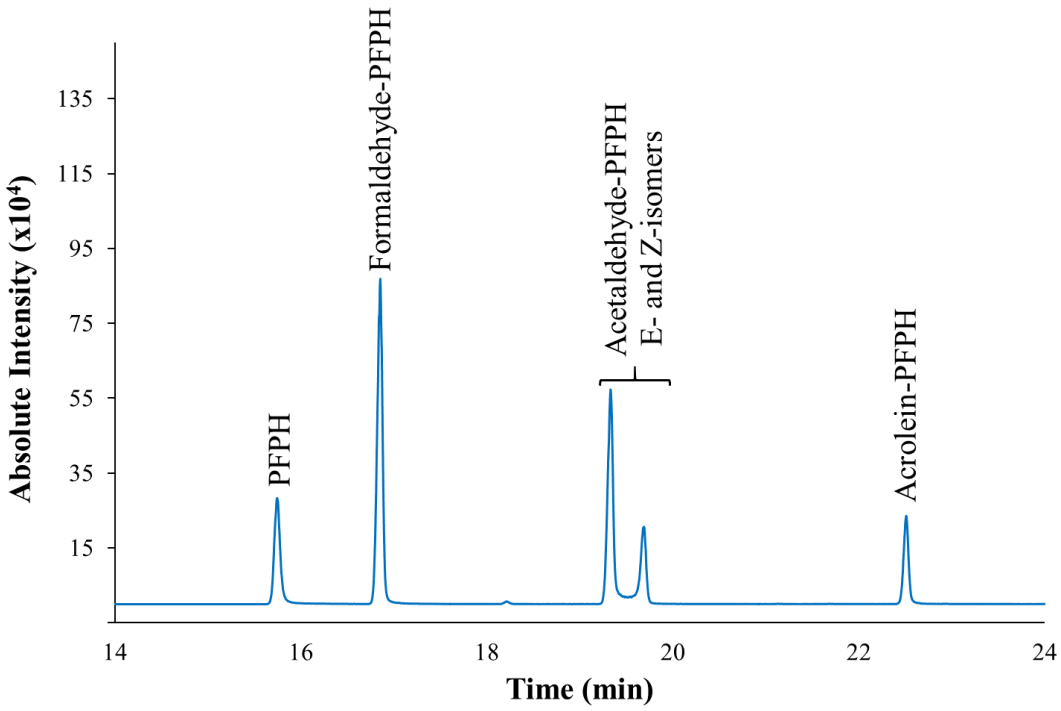

Figure 3.10: GC-MS chromatogram of the aldehyde-PFPH derivatives

A sample volume of 1 µl with a 1.0 split was injected onto the GC column. The oven temperature was initially held at 45°C for 2 minutes after injection, thereafter the oven temperature was increased to a final temperature of 250°C at a rate of 5°C/min. The mass spectrometer was operated in electron ionization (EI) mode at 70 eV and the GC/MS interface temperature was set at 280 °C. The ion source temperature was set at 260°C, and a total ion current mass range of m/z 35 – 500 was scanned. Selective ion monitoring (SIM) of the PFPH derivatives at m/z of 155, and of the PFBHA derivatives at m/z at 181 was also performed for quantification purposes. The areas of both *E*- and *Z*-isomers of each aldehyde-PFPH or aldehyde-PFBHA derivative were utilized for quantification of

the aldehydes. The chromatograms of the PFPH- and PFBHA-derivatives are shown in Figure 3.10 and Figure 3.11, respectively.

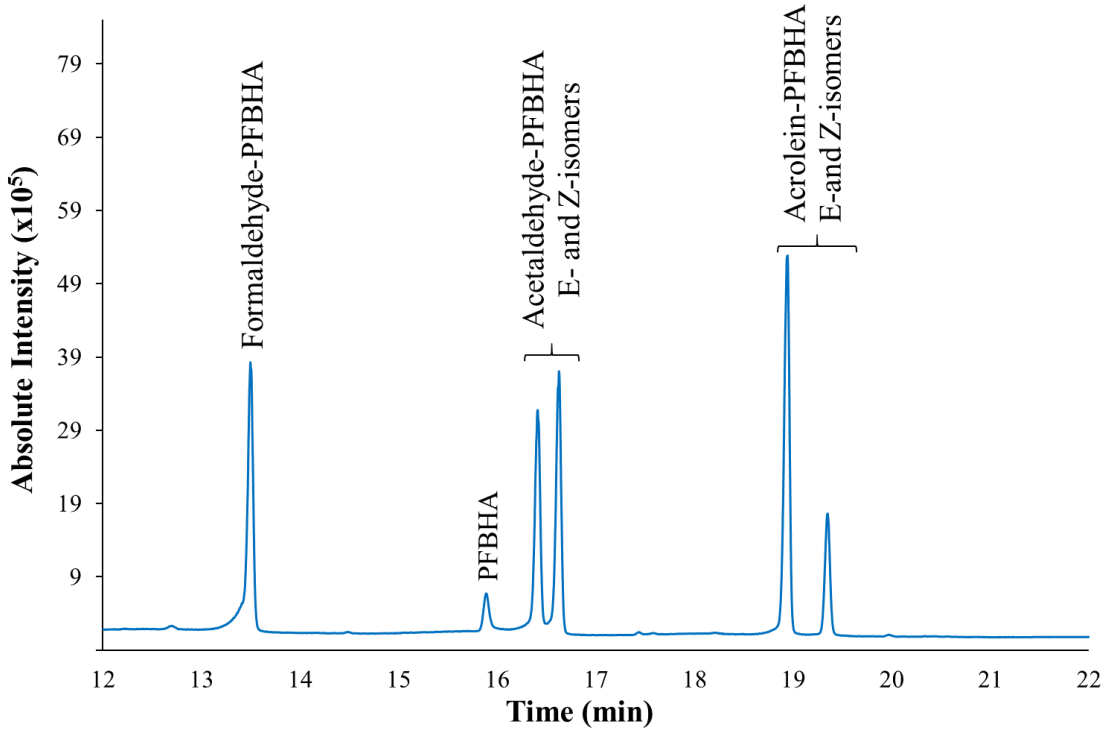

Figure 3.11: GC-MS chromatogram of the aldehyde-PFBHA derivatives

3.6 Elution of cartridges

Each cartridge was eluted using 5 mL of the solvent (see Table 3.10) into a 5 mL volumetric flask, which was then filled to the mark with the solvent. The cartridge retains some of the solvent and therefore the volumetric flask was filled to the mark with solvent, after elution. The solution was then transferred to a 2 mL vial for analysis with HPLC, GC or IC, as required. The volume was enough to completely remove all the aldehyde-derivatives from the cartridges, as a subsequent elution of the cartridge showed no traces of the aldehyde-derivatives.

3.6.1 Stability of the aldehydes on the cartridge during storage

The new PFBHA method cartridges were spiked (Section 3.4.7) with the aldehyde standard solution, after which the cartridge was capped and placed in a zip seal bag, and stored in a refrigerator at 5°C. Each subsequent day a cartridge was taken from the bag, eluted (Section 3.6) and analysed (Section 3.5.3.2). This test was performed over 9 days.

3.6.2 Stability of the aldehydes in solution after elution

A PFBHA cartridge was spiked with the aldehyde standard solution, capped and left for 30 minutes for derivatisation to take place. The cartridge was eluted with acetonitrile into a 5 mL volumetric flask. The eluent was stored in the fridge at 5°C, and analysed each day for 9 days.

3.7 Experimental setup with the simple gas simulation chamber

A 125 mL glass gas sampling bulb, with Teflon stopcocks, was used to set up a simple simulation chamber, as shown in Figure 3.12. The glass was silanised before use to avoid absorption of the compounds onto the walls of the bulb. The gas flow is introduced through the inlet, either from a gas line or a Tedlar bag (Table 3.17) filled with a gas mixture. The concentrations were chosen based on concentrations in a polluted workplace[176]. When needed, the aldehydes were introduced to the bulb using a pipette to inject 100 μL of the prepared aldehyde solution, via the septum inlet. The sampling cartridge set was connected to the outlet and the flow of gas out of the bulb, containing a mixture of the gas with the volatilised aldehydes, moved through the cartridge at a specified flow rate between 0.5 – 1 L/min. The flow rate was controlled using the personal sampling pump (ESCORT Elf® Air sampling pump, Zefon International), which was connected to the end of the cartridge. After the experiment, the cartridge was removed, capped and stored in the refrigerator until elution.

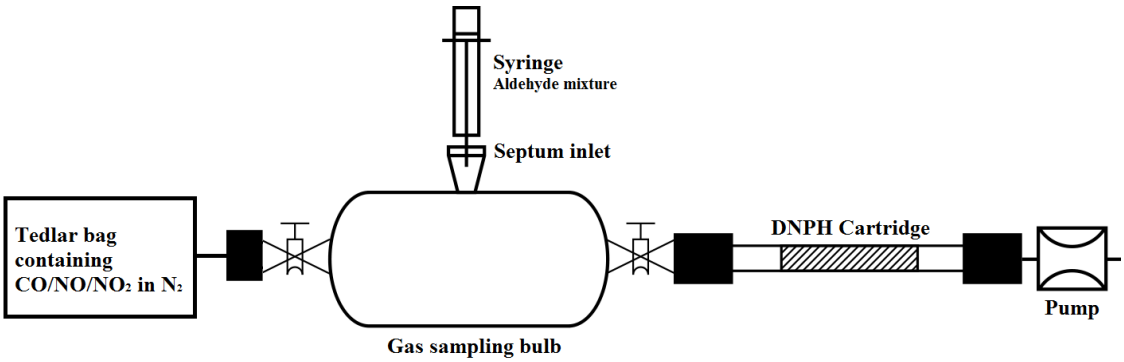

Figure 3.12: Simple simulation chamber for the study of individual interferences

Table 3.17: Mass of gas introduced to cartridges[176]

Gas	Mass through cartridge (mg)	Equivalent 8 hour concentration (mg/m^3)
NO	0.123	0.26
NO_2	0.188	0.39
CO	0.230	0.48
Ozone	0.055	0.11

3.7.1 Gas evaluation tests

3.7.1.1 Reaction of NO, NO_2 and CO with the derivatisation reagents and hydroquinone

A Tedlar gas bag was filled with the specific gas (either NO, NO_2 or CO) and connected to the inlet of the gas sampling bulb. The experimental procedure described previously was followed. No aldehydes were introduced into the gas sampling bulb. The cartridges used each contained one of the derivatisation reagents that was tested.

3.7.1.2 NO, NO_2 and CO effect on aldehyde capture

The gas sampling bulb was injected with 100 μL of the aldehyde standard solution, and the procedure described in Section 3.7.1.1 was followed.

3.7.1.3 NO, NO_2 and CO effect on aldehyde retention

A volume of 100 μL of the aldehyde standard solution was spiked onto cartridge (Section 3.4.7) and left for 10 minutes to react, and afterwards connected to the outlet of the gas bulb. The experimental procedure, as described previously, was followed.

3.7.1.4 Ozone exposure tests

An UVP SOG-1 Stable Ozone Generator, with a Pen-Ray lamp and compressed air was used to generate ozone for the exposure tests. The ozone generator produces a continuous flow of ozone using the photochemical reaction of oxygen under shortwave UV. The compressed air flow was controlled by a needle valve, and the amount of ozone generated was controlled through the choice of flow rate and the length of the Pen-Ray lamp was that was uncovered. The generator was calibrated by the manufacturer for ozone generation with pure O_2, however recalibration was required as compressed air was being used as the oxygen source in this study. The ozone concentration in the output flow was measured using a 49C O_3 Analyser (Thermo Environmental Instruments Inc.), and the calibration curves for each flow was obtained, shown in Figure 3.13.

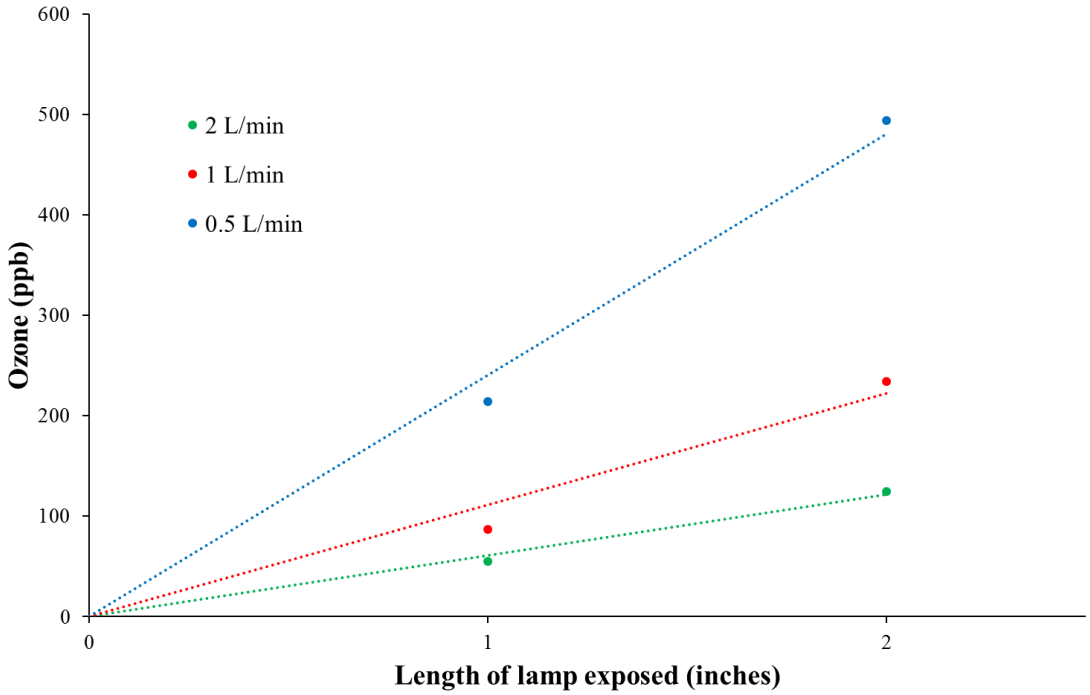

Figure 3.13: Calibration of the ozone generator when using compressed air

The cartridges were connected to the outlet of the ozone generator, which was set to generate a specific amounts of ozone, as specified later in the chapters.

3.7.1.5 Simulated polluted environments

The DNPH and final PFBHA methods were tested in a simulated polluted environment. The polluted environment was created using the Environics Series 4000 Gas Mixing System with 4 mass flow controllers (MFC) with sulfinert (pictured in Figure 3.14), which mixed the gases (NO, NO_2 and CO) with a balance of nitrogen, to the required concentrations (Table 3.18). A Tedlar bag was filled with the mixture of gases and connected to the inlet of the gas bulb. Increasing volumes of the aldehyde standard solution was injected into the sample bulb for each test, as shown in Table 3.18. The experimental procedure as described in 3.7.1.1 was followed.

Figure 3.14: Environics Series 4000 gas mixing system

Table 3.18: Concentrations of the gases and aldehydes in the simulated polluted environment

Concentration (mg/m³)[a]					
NO	**NO_2**	**CO**	**Formaldehyde**	**Acetaldehyde**	**Acrolein**
0.62	0.47	2.16	0.03	0.03[b]	0.02
			0.08	0.06	0.05
			0.16	0.13	0.10
			0.24	0.19	0.16
			0.32	0.26	0.21
			0.47	0.38	0.31
			1.26	1.02	0.84

[a] TWA of 8 hours
[b] Below LOD of acetaldehyde

3.7.2 NO_2 quantification using the new PFBHA method

The various NO_2 gas standards were prepared using the gas mixing system to dilute the NO_2 gas using nitrogen. Tedlar bags were filled with 78, 196, 392 and 588 μg/m^3 of NO_2 gas, and connected to the gas bulb inlet. The PFBHA cartridges (Section 3.4.5) were connected to the outlet of the gas bulb, and the experimental procedure described in Section 3.7.1.1 was followed. The cartridges were eluted (Section 3.6) and analysed (Section 3.5.3.2).

A calibration curve for the quantification of NO_2 using the new PFBHA method was plotted using the peak responses of the p-benzoquinone against the NO_2 concentrations.

3.7.3 Sorbent tests

Each cartridge was connected to a PFBHA cartridge, which was used as a breakthrough cartridge. The cartridge set was connected to the gas sampling bulb (as described in

Section 3.5), which contained 100 μL of the aldehyde standard solution. The sorbent capturing efficiency was calculated as follows:

$$Aldehyde\ capture\ efficiency = \left[1 - \frac{Mass\ \ on\ PFBHA\ cartridge}{Mass\ loaded\ in\ bulb}\right] \times 100\% \qquad [15]$$

3.8 Post-sampling derivatisation procedure for reaction time determination

A set of the hydroquinone cartridges after sampling (Section 3.7.1) was injected with 400 μL of the individual derivatisation reagent solutions (Section 3.4.3). The cartridges were capped and allowed to react for 3 hours. Thereafter, the cartridge was eluted with the appropriate solvent and analysed.

3.9 Method Recovery

The gas bulb was spiked with 100 μL of the aldehyde standard solution. Nitrogen gas was connected to the inlet of the bulb with the test cartridge system connected to the outlet of the bulb. The solution spiked into the bulb would volatilise in this time and be swept onto the cartridge by the gas flow. Each experiment lasted at least 20 minutes, if not specified. The method recovery was calculated using equation [5].

3.10 Conclusion

This chapter gives a detailed description of the procedures followed to develop the analytical methods for the determination of formaldehyde, acetaldehyde and acrolein in air using various derivatisation reagents. General chromatography principles were described as the main analysis techniques used were gas-, liquid-, and ion chromatography. Several tests are described which were performed to ensure the robustness of the final analytical method for the sampling and analysis of aldehydes in air. Details of the validation parameters have also been included, which will be used to determine whether the final method developed is fit for purpose.

Chapter 4
Investigation of the limitations of the DNPH method

4.1 Introduction

The recommended method for the measurement of formaldehyde in air is by capturing the aldehydes on a silica gel or C18 cartridge, which is coated with DNPH for derivatisation of the aldehydes, and then followed by HPLC analysis of the derivatives[27]. It is important to understand the DNPH method's shortcomings, as described in literature, and why it fails to measure the aldehydes in a polluted environments such as diesel engine exhaust emission (DEEE) environments. An understanding of the shortcomings will aid in adjusting the method to be able to analyse for the aldehyde using the DNPH method, or in the development of a new method using an alternative derivatisation agent.

Validation of a method includes the determination of the selectivity of the method, the capability of a method to produce a signal unambiguously due to the analyte, in the presence of other compounds. The accuracy of the method determines how close the measured value is to the true value. The accuracy of a method is affected by the matrix of the sample and consequently, a study into the interferences and how they affect the sampling and analysis of the aldehydes is required.

Two types of interferences can occur in a method that includes sampling and analysis steps. The sample matrix can interfere during the sampling process with the capture and retention of the aldehydes. The matrix gases may also interfere by being retained on the cartridge and then possibly also reacting with the derivatisation agent. These matrix gases and the reaction products with DNPH can appear on the chromatogram if it has a UV response, and may possibly co-elute with the analyte peaks.

In a combustion environment such as a diesel engine environment the major emission gases include NO_x, and CO, with minor amounts of PAH, carboxylic acids and aldehydes. Literature (Chapter 2) has already identified the chromatographic interferences on the DNPH method from the reaction of DNPH with nitrogen dioxide (NO_2), ozone (O_3), nitrogen oxide (NO), and carboxylic acids. The resulting reaction products could co-elute with the aldehyde-DNPH derivatives and therefore cause error in quantification of the

aldehydes. Acetone- and propionaldehyde-DNPH derivatives co-elute with acrolein-DNPH and therefore make it difficult to analyse for acrolein.

Several strategies have been followed to improve the chromatographic separation of the NO_x and ozone reaction products from the DNPH derivatives, which also include the use of the UV spectra to deconvolute peaks that are co-eluting[34]. However, the impact of the gases on the capture and retention of the aldehydes by the DNPH cartridges have not been assessed. Also, the amount of DNPH consumed by the DEEE gases has not been quantified. The consumption of DNPH reduces the capacity of the DNPH cartridges for the derivatisation of aldehydes, and therefore is an important factor to consider.

Furthermore there is no record of how CO reacts with DNPH, and thus the impact this gas has on the sampling and analysis of the aldehydes, especially in diesel engine environments has not been assessed.

The major gases (CO and NO_x) have concentrations a great deal higher than the aldehydes (CO ~ 1.5 g/kWh, NO_x ~ 0.4 g/kWh, aldehydes a fraction of the HC content ~ 0.13 g/kWh)[16] in diesel engine environments and may therefore impact the sampling process, by competing with the aldehydes for adsorption sites, reacting with the DNPH and thereby decreasing the availability of DNPH during long-term sampling, or displace the aldehyde-DNPH derivatives from the cartridge.

Polyaromatic hydrocarbons (PAHs) are also present in diesel engine environments as a minor component of DEEE gases. During sampling, PAHs may be adsorbed onto the cartridge, but should not react with the DNPH, as they do not contain the carbonyl functional group for reaction with DNPH. The PAHs may be then desorbed along with the aldehyde-DNPH derivatives and therefore be present in the solution that is injected into the HPLC. These UV active compounds may therefore interfere on the HPLC chromatogram.

The aim of this chapter is to assess the effect each of the DEEE gases have on both the sampling and analysis of aldehydes using the DNPH method. The objectives are listed below:

- Setup of the DNPH method and determination of method performance parameters for the analysis of formaldehyde and acetaldehyde in a clean environment.

- Determination of the effect DEEE gases have on the chromatography during analysis with DNPH, whether the DEEE gases react with DNPH, or are captured by the cartridge and present in the solution injected into the HPLC.
- Establish the mechanism of interference of the major DEEE gases and how these gases affect the quantification of the aldehydes, i.e. by competing for adsorption sites, displacing the aldehyde-DNPH derivatives, or reducing the availability of DNPH for the derivatisation of the aldehydes i.e. consumption of the DNPH.

4.2 Implementation and validation

A method for the analysis of 21 carbonyl-DNPH derivatives[175] was used as a starting point in the implementation of the method. The method separates and analyses 21 carbonyl-DNPH compounds and is 60 minutes long. Using a column with a smaller particle size, slight difference in functionality, and shorter length, the method was shortened to suite this application, to 15 minutes (Figure **4.1**).

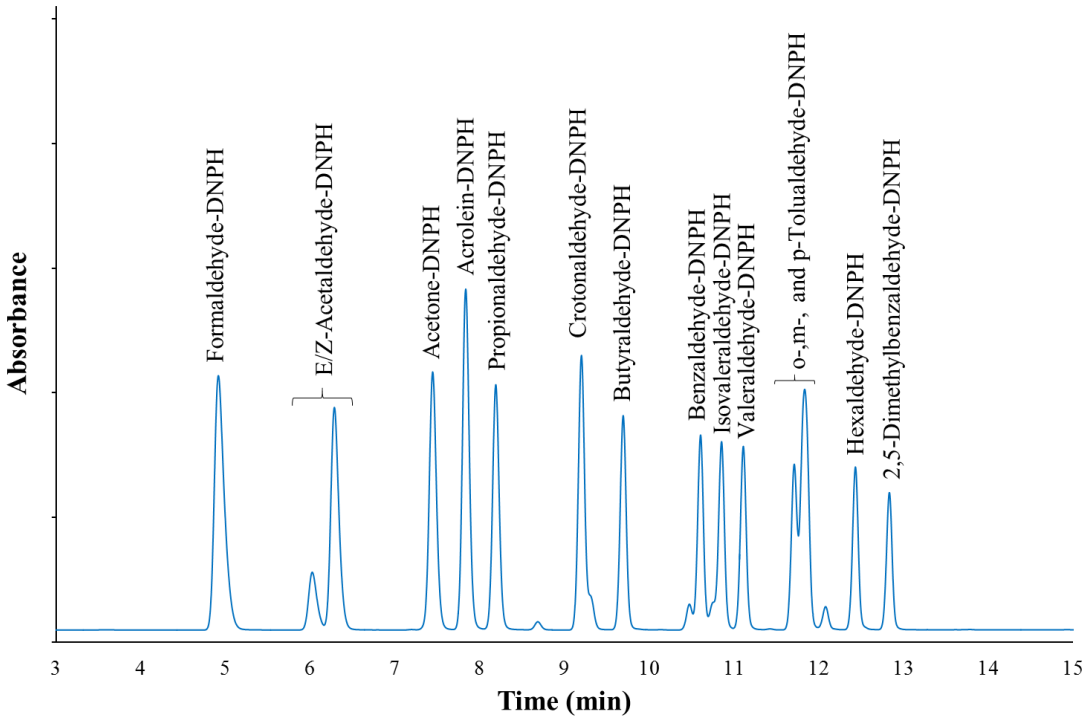

Figure 4.1: Chromatogram of carbonyl-DNPH compounds

The smaller particle size in the column (2.7 µm) increases the number of theoretical plates due to the increase of adsorption sites on the column. The length of the column can therefore be shortened, as the column efficiency would still be similar, using the same

mobile phase flow rate. The shorter column means that the analysis time is shortened, with the same separation achieved. The smaller particle size would normally increase the pressure at which the HPLC will operate, however the column contains Fused-Core particles lowers the pressure. The column used in this application contains an amide group in the C18 chain attached to the silica backbone, which makes the column more selective for polar compounds.

A certified reference material standard (CRM) with 15 carbonyl-DNPH derivatives was used to determine the retention times of the each DNPH derivative, as shown in Figure **4.1**.

The HPLC instrument performance data was obtained to determine if the instrument meets the performance criteria for the DNPH method. The HPLC performance data was determined as described in Section 3.3, and the results are reported in Table **4.1**. The required performance criteria specified for formaldehyde in MDHS 102 is also listed in Table **4.1**. The newly implemented DNPH analysis method satisfies all the requirements for formaldehyde and acetaldehyde.

Table 4.1: HPLC performance data for the DNPH method

Parameter	Linearity (R^2)	Repeatability (RSD)	Sensitivity (mAU/(μg/mL))	Retention time Precision (RSD)
Requirement	>0.999	<10 %	-	<2 %
Formaldehyde	0.9993	3.52	1.74	0.25
Acetaldehyde	0.9993	2.97	1.52	0.17

The combined sampling and analysis performance data was acquired next and tabulated in Table **4.2**. The LOQ, which is the lowest concentration that is quantitatively determined, that is accurate and precise, needs to be less than 10 % of the WEL. The required LOQ for formaldehyde and acetaldehyde is 0.25 and 3.7 mg/m^3, respectively, and the method fulfils this requirement. The accuracy of the method, which is measured by the method recovery, is shown as higher than 99 % for both formaldehyde and acetaldehyde in a clean air environment. The impact of a combustion pollutant matrix on the accuracy of the method will be studied in Section 4.4.1. The precision of the method for acetaldehyde quantification is slightly higher than requirement for formaldehyde.

Table 4.2: Sampling and analytical performance of the DNPH method

Parameter	LOD (μg/m^3)	LOQ (μg/m^3)	Method recovery (%)	Precision (RSD)
Requirement for formaldehyde[27]	-	10 % of WEL[a]	>99	<5
Formaldehyde	1.38	4.19	99	4.9
Acetaldehyde	1.48	4.49	99	6.5

[a] Formaldehyde WEL – 2.5 mg/m^3
Acetaldehyde WEL – 37 mg/m^3

The selectivity of the sampling and analysis method will be verified in Section 4.3, where the chromatographic interferences are investigated.

4.3 Chromatographic interferences

Interferences seen on an HPLC chromatogram in the DNPH method will result from the co-elution of the reaction products of the DEEE gases with DNPH, as well as any other UV active compound that may be retained on the cartridge and desorbed with the aldehyde-DNPH derivatives. These interferences will result in the inaccurate quantification of the aldehydes.

In the following sections the possible chromatographic interferences are explored, both those described in literature and any other possible sources identified in the DEEE gases. The separation of the C3-carbonyl-DNPH compounds will be investigated along with the stability of the acrolein-DNPH derivative. Chromatographic interferences have already been identified from the reaction products of ozone, NO_2, NO and carboxylic acids with DNPH, and will be studied. Possible interference from PAHs and CO, the remaining DEEE gas components, will also be examined.

4.3.1 Acrolein

4.3.1.1 Separation of C3 aldehyde derivatives

Part of establishing an analysis method is to ensure a good separation of the all compounds in the sample. The C3-carbonyl-DNPH compounds, which include acetone, acrolein and propionaldehyde, are not separated easily, as discussed in Section 2.4.4. Most applications make use of tetrahydrofuran (THF) added to the mobile phase to obtain a reasonable separation of the C3-carbonyl-DNPH compounds. However, this separation

is often overlooked since in most environments it is not expected to find acrolein, and acetone is more often found.

As it was important to understand the problems with the reactivity of the acrolein-DNPH derivative it was necessary to optimise the method so that separation of the C3-carbonyl-DNPH compounds was achieved.

The column used in this study, Ascentis Express RP-Amide, contains a smaller stationary phase particle size of 2.7 μm, which improves the separation efficiency of the column. This attribute, along with amide functionality included in the C18 carbon chain, which improves the column's selectivity for polar compounds, made the separation of the C3-carbonyl-DNPH derivatives possible. Acrolein-DNPH elutes between acetone-DNPH and propionaldehyde-DNPH, as seen in Figure **4.2**. The resolution between the acetone-DNPH and acrolein-DNPH is 2.5 and between acrolein-DNPH and propionaldehyde-DNPH is 2.4. A resolution larger than 1.5 is required for accurate quantification using peak areas.

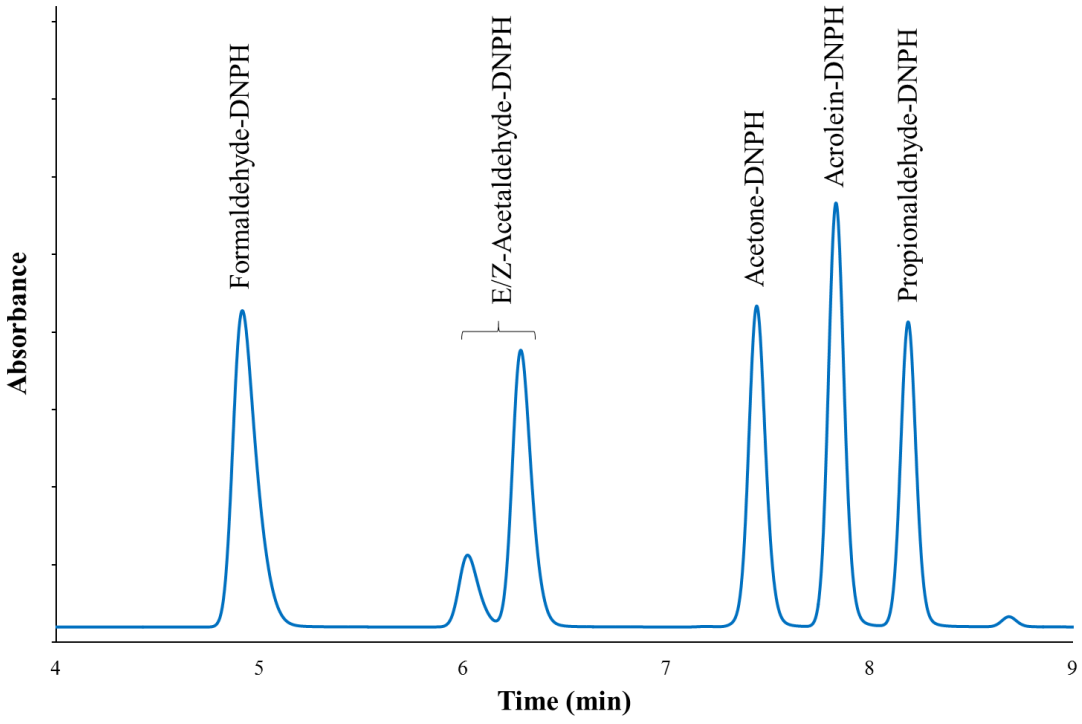

Figure 4.2: Separation of the C3-aldehyde-DNPH compounds

The CRM standard that was used, contained acrolein-DNPH with no excess DNPH for adduct formation, therefore no reaction products were seen as would normally be

expected when acrolein is present. However, on the sample cartridges and the desorption solution, an excess of DNPH will be present. Acrolein is reactive, dimerising and forming adducts with DNPH and therefore the resulting compounds and their possible interference on the method is examined in the next section.

4.3.1.2 Dimers and adduct formation

Acrolein was not included in the method validation carried out in Section 4.2 as the method recovery for acrolein was only 2.8 %. This is due to the formation of the acrolein dimer, 2-formyl-3,4-dihydro-2H-pyran, which also reacts with the DNPH, as well as the adduct formation as described in Section 2.4.3.

The chromatogram obtained for the method recovery experiment for acrolein is shown in Figure **4.3**. Four unidentified peaks were observed with retention times of 8.9, 9.5, 11.7 and 12.1 minutes. This chromatogram looks almost identical to the chromatogram obtained by Uchiyama et al. (2010)[96], as discussed in Section 2.4.3. The retention times differ as different chromatographic conditions were used for the separations. The difference in the peak heights may be due to the differences in the time taken between the sampling of the acrolein and the analysis of the sample. The peaks therefore are assigned to AD1 and AD2 according to the assignment by Uchiyama et al.

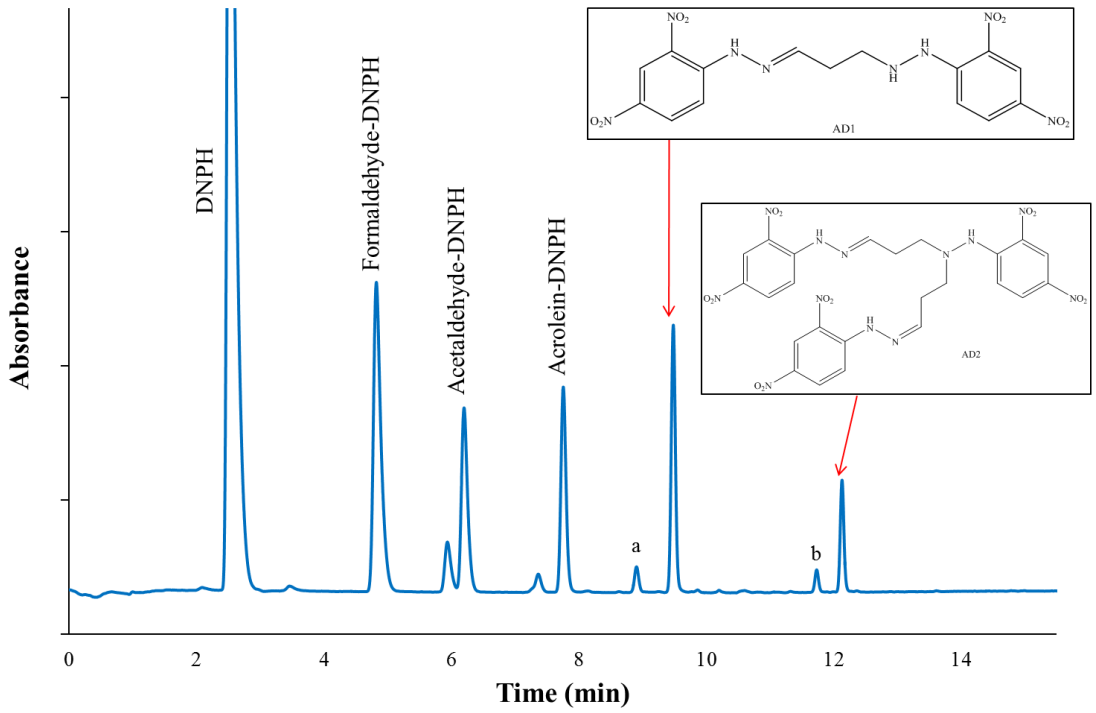

Figure 4.3: Chromatogram showing Acrolein-DNPH and the adducts formed

The peak with retention time of 11.7 minutes, labelled b, has the same retention time as the o,m,p-tolualdehyde-DNPH compounds (Figure 4.1), and would thus be incorrectly identified as tolualdehyde-DNPH by the HPLC software.

The sum of the all 5 of the acrolein-related peaks (Acrolein-DNPH, AD1, AD2, a and b) was used to determine whether this was a better estimate of the acrolein recovery as described by Schulte-Ladbeck et al.(2001)[98]. The method recovery improved, but still not to an acceptable level (<75 %, Section 3.9). This is due to the difference in the UV responses that each of these compounds have, and the summation of the peaks would assume that all the peaks would have the same UV response at 360 nm. Furthermore, the co-elution of one of the peaks with another aldehyde-DNPH compound would occur in real samples where the aldehyde composition is unknown, and would give rise to inaccurate acrolein results.

The sample was analysed using GC-MS to possibly identify the compounds, however, the compounds were not seen on the GC chromatogram, as the compounds are very large and therefore probably not volatile enough for GC analysis.

4.3.2 Ozone

According to work done by Achatz et al.(1999)[37], ozone reacts with DNPH to form 8 products, three of which were identified to be 2,4-dinitrophenol, 2,4-dinitroanaline, and 1,3-dinitrobenzene.

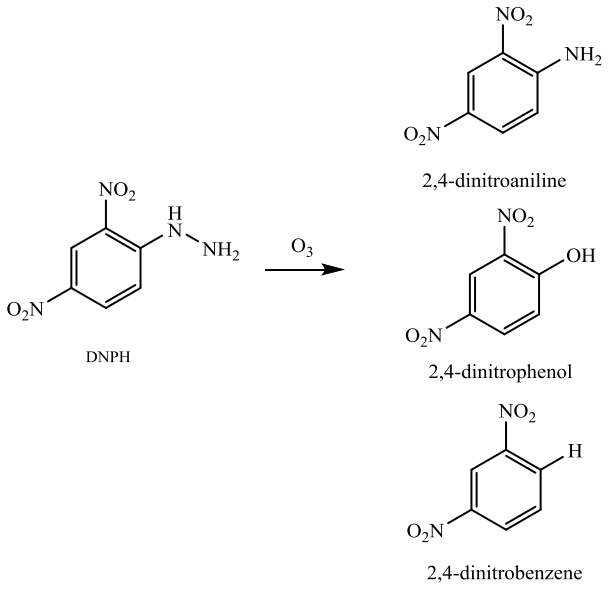

Figure 4.4: Ozone degradation products of DNPH[37]

In this study, the DNPH cartridge was analysed after it was exposed to ozone (56.1 μg ozone, equivalent to 116.8 μg/m^3 8 hours TWA), revealing the presence of eight peaks, with various UV maxima. The peaks were identified according to the compound's UV maximum and relating to those found by the Achatz et al[37], the peak allocation is shown in Table **4.3**. The comparison shows that similar DNPH degradation products have been observed, although the compounds may have exchanged positions on the chromatogram, due to the difference in chromatographic conditions.

The sample was analysed by GC-MS and the presence of the three degradation products, 2,4-dinitroaniline, 2,4-dinitrophenol and 2,4-dinitrobenzene were confirmed. Several siloxane compounds were also seen, indicating that the ozone is possibly also degrading the silica gel sorbent of the cartridge.

The reaction of the ozone with DNPH results in the 8 products, and it was observed that the DNPH peak decreased in size to about 28.6 % of the available DNPH. This severely reduces the capacity of the cartridge for the analysis of carbonyls, and a sampling period of 8 hours will not be achievable in the presence of ozone, as all the DNPH will have reacted with ozone.

Table 4.3: Chromatographic data of DNPH degradation products and comparison with results obtained by Achatz et al.[37]

Current experimental results			Results from Achatz et al.		
R_t (min)	**UV maximum (nm)**	**Peak identification**	**R_t (min)**	**UV maximum (nm)**	**Peak identification**
0.94	363	2,4-Dinitrophenol	1.2	338	
1.48	335	2,4-Dinitroaniline	1.6	360	2,4-Dinitrophenol
2.93	263	1,3-Dinitrobenzene	2.0	342	2,4-Dinitroaniline
3.16	245		2.2	260	
3.31	342		2.4	238	1,3-Dinitrobenzene
3.94	311		2.7	347	
4.53	259		3	308	
9.67	430		9.3	430	

The use of a KI-cartridge is recommended in MDHS 102[27] for the removal of ozone from the sampled air before reaching the DNPH cartridge. The cartridge is placed before the

DNPH cartridge during sampling. The KI cartridge requires a relative humidity of between 20 and 80 % for the effective removal of the ozone from the sampled air[38]. The KI reacts with ozone, in the presence of water, to form oxygen, potassium hydroxide and iodine as shown in reaction equation [16] below:

$$O_3 + KI + H_2O \rightarrow O_2 + KOH + I_2 \qquad [16]$$

4.3.3 Nitrogen oxides

Nitrogen dioxide is a major component of DEEE gases either as a primary or secondary pollutant, especially when the engine does not have an after treatment system, to remove the NO_x. The DNPH cartridge was exposed to 0.188 mg of NO_2 (equivalent to 0.39 mg/m^3 over 8 hours, representing typical NO_2 concentrations in a polluted workplace[176]), after which the cartridge was desorbed with acetonitrile, and the eluent was analysed on HPLC and GC.

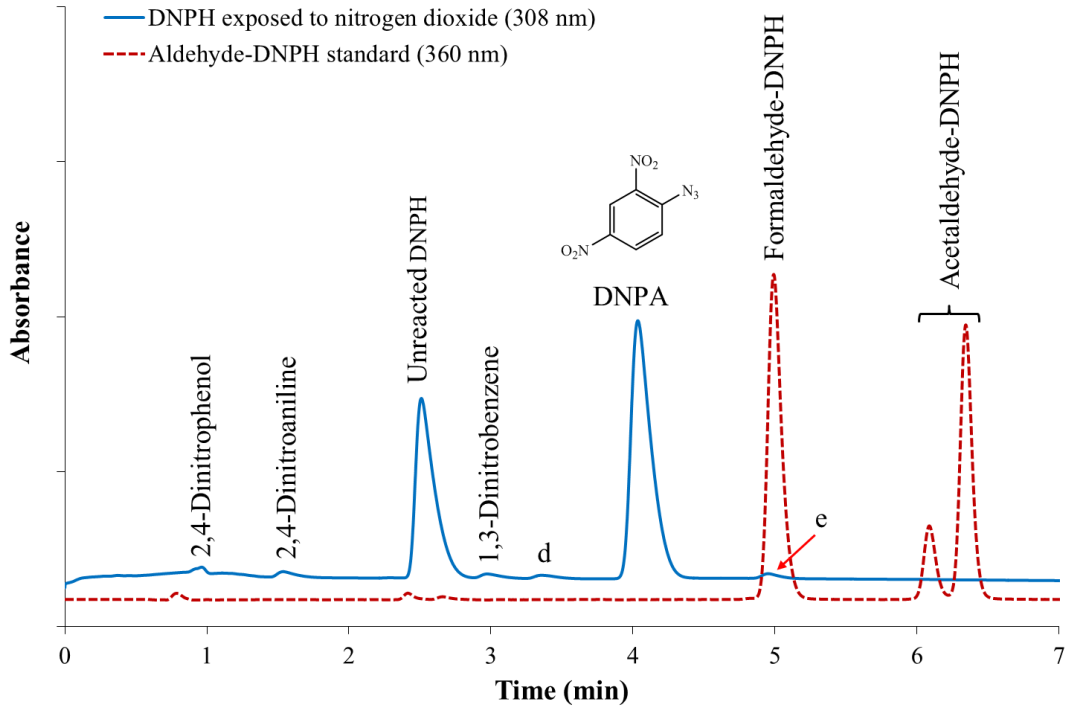

Figure 4.5: Reaction products of NO_2 with DNPH

As previously reported by Pötter and Karst (1996)[34], DNPA was the major product that had formed on the cartridge, and observed on the HPLC chromatogram (Figure **4.5**), at a retention time of 4.1 min. The identity of the peak was confirmed to be DNPA with GC-MS analysis. Using this HPLC method there is a baseline separation of the DNPA from

the formaldehyde-DNPH peak, which ensures that the compound poses no chromatographic interference on the quantification of formaldehyde.

The GC-MS analysis also identified 4-nitrobenzoic acid and 1,3-dinitrobenzene (also a reaction product of ozone with DNPH) in the sample, as reaction products of NO_2 with DNPH, but at much lower levels than the DNPA in the sample. Two peaks were observed on the chromatogram at 308 nm (Figure **4.5**), which were identified to be 2,4-dinitrophenol, 2,4-dinitroaniline and 1,3-dinitrobenzene according to their retention times, as assigned in Section 4.3.2. Therefore these are also reaction products of NO_2 with DNPH, similarly to the reaction products of ozone. These compounds are not visible on the chromatogram at 360 nm (Figure **4.6**). Either one of the peaks labelled 'd' or 'e' in Figure **4.5** and Figure **4.6** could be assigned to the 4-nitrobenzoic acid. These peaks are visible on the chromatogram at 360 nm, and therefore the peak labelled 'e' will interfere with the quantification of formaldehyde, which would result in the overestimation of the formaldehyde concentration in the sample.

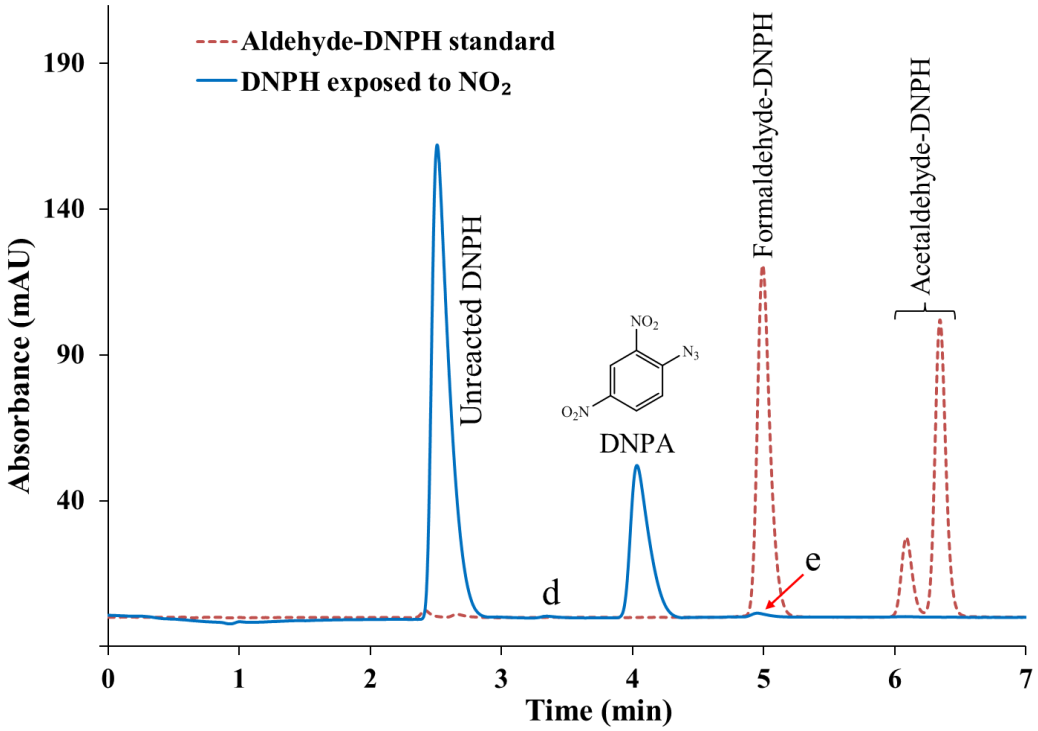

Figure 4.6: HPLC chromatogram of the reaction products of NO_2 with DNPH, DNPA

A DNPH cartridge was exposed to 0.123 mg of NO gas (equivalent to 0.26 mg/m^3 of NO over 8 hours) and eluted afterwards with acetonitrile, which was analysed by HPLC and

GC-MS. Both the HPLC and GC-MS analysis methods did not detect any reaction products of the NO with the DNPH. The concentration of the unreacted DNPH did not decrease after exposure to NO, therefore no reaction with DNPH occurred. This contradicts the literature that reports that NO does form reaction products with DNPH. However, the reasoning required the conversion of NO to NO_2 before the reaction would take place.

4.3.4 Carboxylic acids

Carboxylic acids contain a carbonyl group that may react with the DNPH, although the stability of the carboxylic acid, makes the reaction less likely. Carboxylic acids are a minor component of DEEE gases, and therefore will probably be captured by the silica gel cartridge. It is therefore necessary to determine whether the carboxylic acids will react with the DNPH during sample transport to the laboratory and storage.

A solution containing ca. 50 mg/L of formic and acetic acid in water (equivalent to 104 mg/m^3 formic or acetic acid in air), respectively, was spiked onto a DNPH cartridge and left to react with the DNPH for 72 hours. The cartridge was stored in a fridge at 5°C during this time, which is the storage condition for the cartridge before analysis. The cartridge was desorbed using acetonitrile and the eluent analysed on HPLC and GC. No reaction products of the carboxylic acids with the DNPH were observed. According to the literature report the carboxylic acids did react with DNPH at 80°C after 5 hours, and therefore could be quantified in this way[108]. The reaction of the carboxylic acid with the DNPH also requires the presence of a strong acid, which is present on the cartridge. However, under normal (ambient and refrigerated storage) conditions, it is unlikely that the carboxylic acids would react with the DNPH, as has been confirmed with this experiment.

4.3.5 Polyaromatic hydrocarbons (PAHs)

PAHs form a minor part of the exhaust emissions, however, as they could possibly be trapped by the DNPH cartridge, they may be present in the acetonitrile eluent that is injected for analysis. PAHs have a strong UV response due to the delocalised electrons around the aromatic rings[1], and therefore may be detected during the analysis of the aldehyde-DNPH sample solution.

A diluted PAH standard (Section 3.2) was injected onto the HPLC using the DNPH method conditions, to determine whether these compounds will interfere chromatographically.

The chromatogram obtained at 360 nm for the PAH standard is given in Figure **4.7**, shows that anthracene elutes between propionaldehyde-DNPH and crotonaldehyde-DNPH. However, benz(a)anthracene co-elutes with butyraldehyde. The interference is not on the main aldehydes of interest, formaldehyde, acetaldehyde and acrolein, and therefore, for now there is no major concern.

The PAHs do not react with DNPH, and therefore no other form of interference is expected.

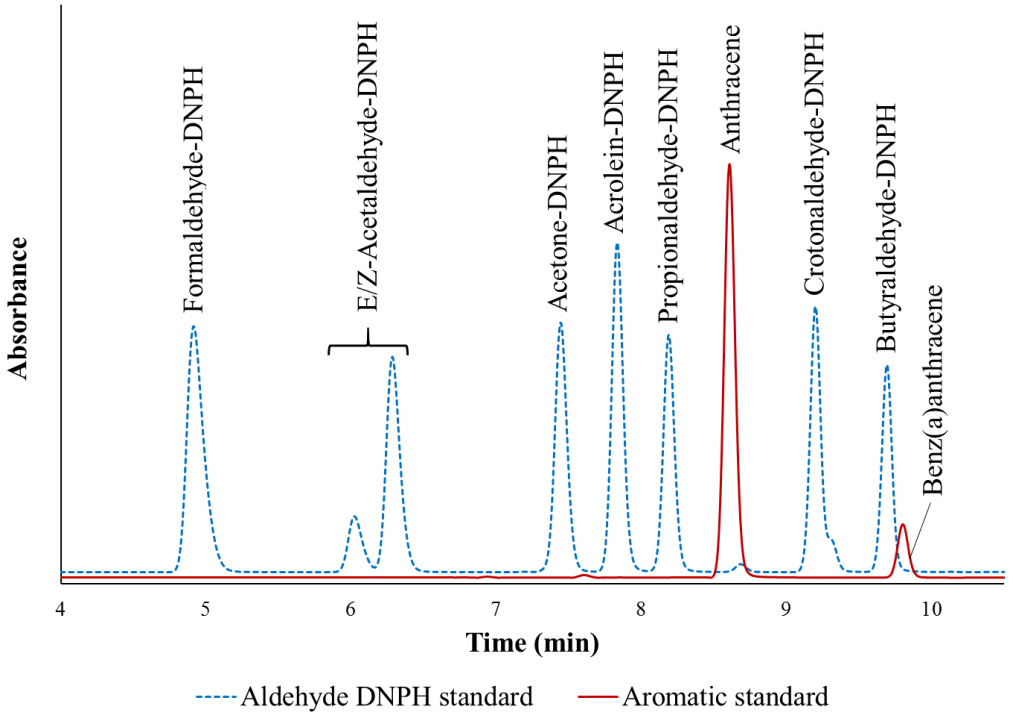

Figure 4.7: Chromatogram of the PAH standard and aldehyde-DNPH standard

4.3.6 Carbon monoxide

Carbon monoxide is present in the DEEE mixture and other combustion processes because of incomplete combustion. Carbon monoxide is a reactive compound as it contains a carbon oxygen double bond, and therefore could have an effect on the sampling of aldehydes using the DNPH method, by reacting with the DNPH.

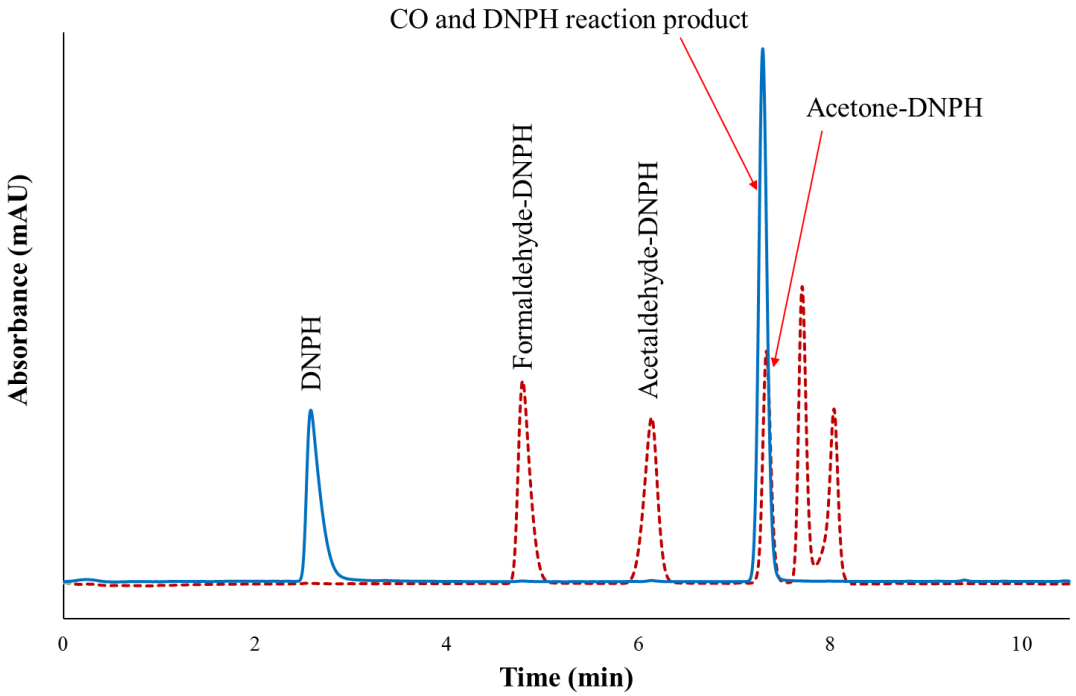

Figure 4.8: Chromatogram of CO and DNPH reaction product

On exposure of a DNPH cartridge to 0.23 mg of carbon monoxide gas (equivalent to 0.48 mg/m^3 over 8 hours), it was observed that the cartridge turned from yellow to white, indicating that a reaction occurred. The acetonitrile eluent was analysed on HPLC and a peak with the same retention time (7.26 min) as acetone-DNPH was observed as shown in Figure **4.8**. Acetone was not present in the gas mixture that was pumped through the DNPH cartridge, therefore the reaction product of CO and DNPH co-elutes with acetone-DNPH. The reaction product of CO and DNPH will therefore interfere with the quantification of acetone in the sample. No other peaks, besides the DNPH peak were detected in the sample. The UV spectra of the acetone-DNPH and the CO-DNPH reaction product were compared (Figure **4.9**) and are also almost identical.

The eluent containing the reaction product was then injected onto GC-MS to identify the compound. Only one compound, besides the unreacted DNPH was identified on the GC chromatogram. The mass spectrum obtained for the compound is shown in Figure **4.10**, and the fragmentation pattern compares well with the fragmentation pattern of acetone-DNPH.

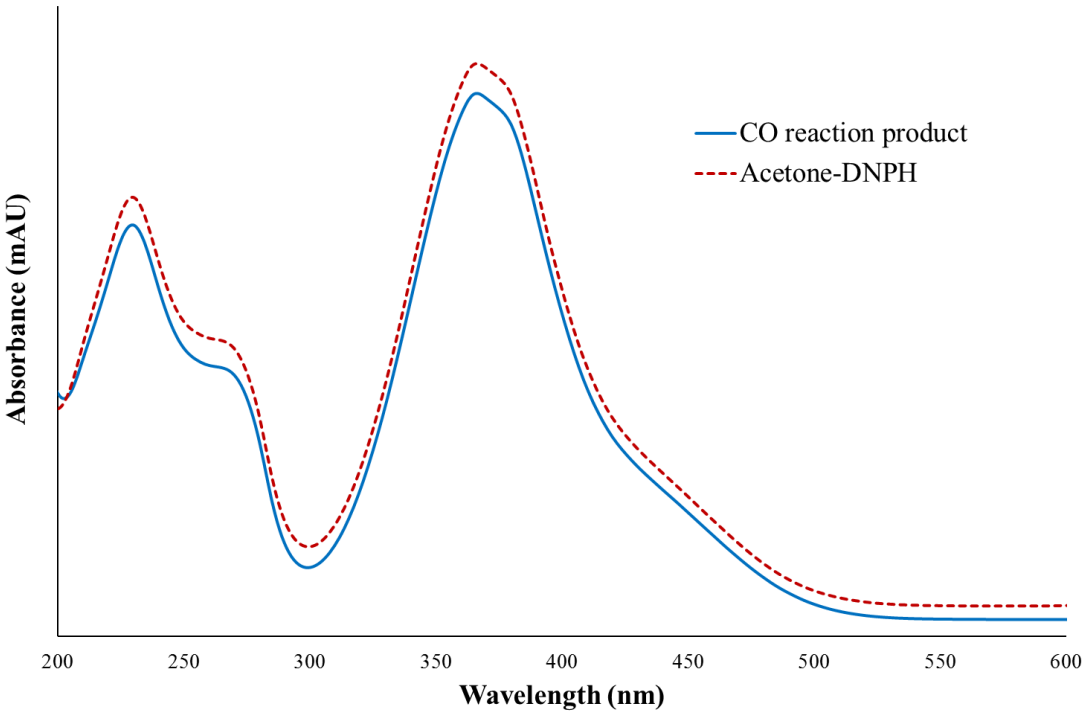

Figure 4.9: UV spectra comparison of acetone-DNPH with the CO and DNPH reaction products

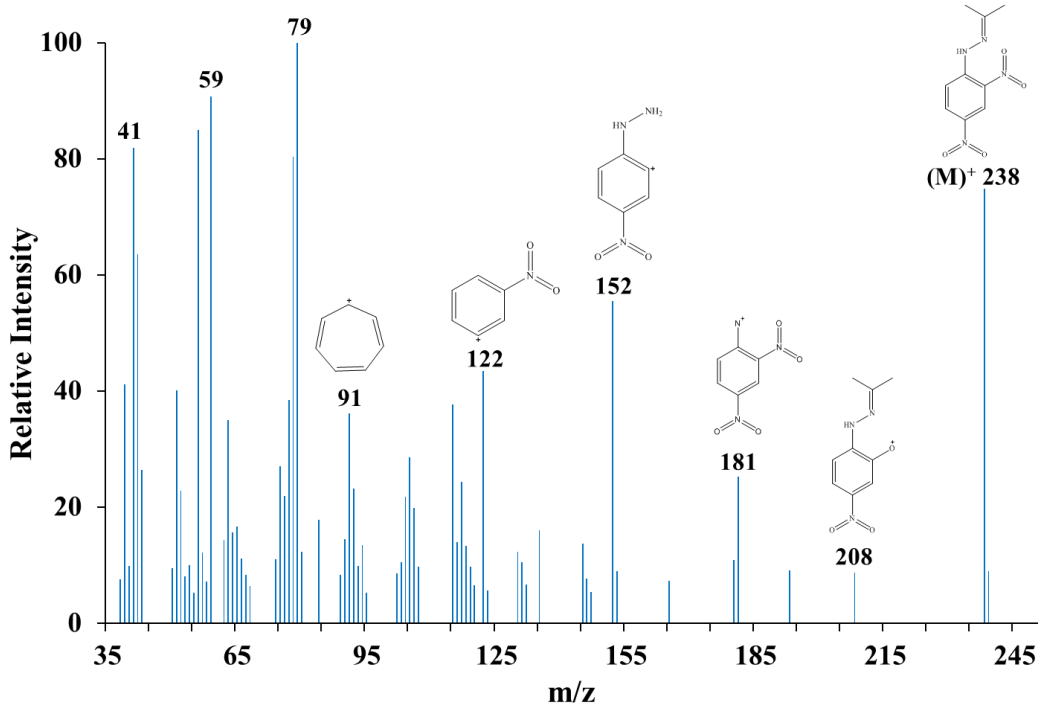

Figure 4.10: MS spectrum for the reaction product of CO and DNPH

Consequently, the reaction product of CO and DNPH would result in a peak that would be mistaken for acetone-DNPH, and therefore result in an overestimation of the acetone concentration in the sample, if acetone is one of the compounds to be quantified.

4.4 Interferences during sampling

It has been established that there is no co-elution of the reaction products of NO, NO_2 and CO and DNPH with the formaldehyde- and acetaldehyde-DNPH peaks on the chromatogram. However, NO, NO_2 and CO can possibly affect the measurement of aldehydes by the DNPH method in the following ways:

- Competing for adsorption sites during sampling
- Consumption of the DNPH, reducing the capacity for the aldehydes
- Displacing the aldehyde-DNPH from the cartridge
- Reversible reaction of DNPH with the carbonyls.

The aldehydes are captured by the silica gel substrate due to their affinity through polarity. The aldehydes then react rapidly with the DNPH, which is present as a coating on the cartridge. In the case of sampling in a polluted environment, NO, NO_2, CO and aldehydes will be drawn simultaneously into the DNPH cartridge. NO, NO_2 and CO could compete with the aldehydes for adsorption sites on the silica during the sampling, and trigger the release of the aldehyde before reaction with DNPH, or already formed aldehyde-DNPH from the cartridge. The gases could react with the DNPH or the aldehyde-DNPH, the former reaction resulting in a decrease of the capacity of the cartridge, and both reactions causing the method recovery to be poorer. In the following sections, the effect of NO, NO_2 and CO on the measurement of aldehydes by the DNPH method will be evaluated for their effect on the sampling of aldehydes with the DNPH method.

Ozone was not included in the experiments as the effect will not be seen as a KI cartridge is used to remove the ozone from the sample matrix. The KI cartridge does not have any effect on the other gases, which pass through the cartridge unchanged.

4.4.1 Effect of gases on aldehyde capture and retention on the cartridge

To determine the effect that each individual gas has on the capture of the aldehydes, the simple simulation chamber was used (Section 3.7.1), and each gas (NO, NO_2 and CO, respectively) was introduced through to the bulb and pumped through the cartridge, along with the volatilised aldehydes through to the DNPH cartridge that was connected to the

bulb. The cartridge was eluted with acetonitrile and the eluent analysed with HPLC. The method recovery was used to determine the accuracy of the DNPH method in the presence of each gas, using the equation for method recovery (Section 3.9). The results are presented in Figure **4.11**. In the absence of any NO, NO_2 and CO gases, the aldehyde recovery was >99 % for each aldehyde.

Formaldehyde capture was affected by the presence of all three gases, however in different ways. Nitrogen oxide reduced the amount of formaldehyde recovered by the DNPH method significantly ($p < 0.00001$). As nitrogen oxide does not react with DNPH (Section 4.3.3) it is not due to a lack of the DNPH capacity, and therefore NO is competing with formaldehyde for adsorption sites on the silica gel sorbent during sampling[177]. The NO may also be displacing the formaldehyde-DNPH from the cartridge, although this is less likely as formaldehyde-DNPH is not very volatile.

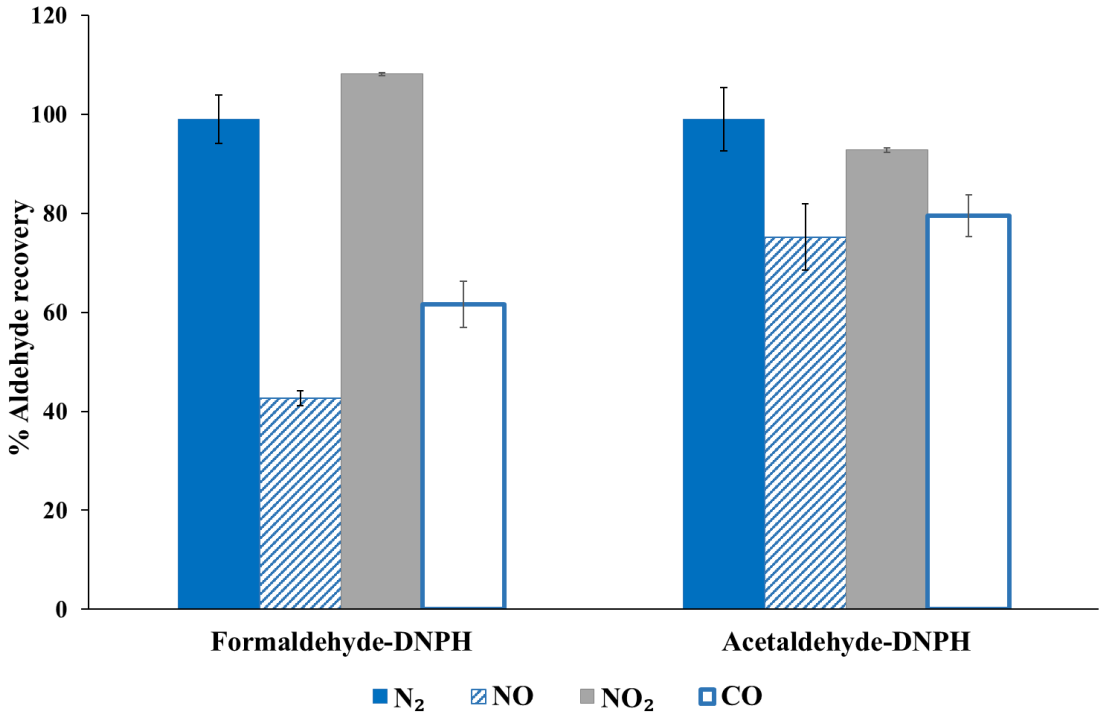

Figure 4.11: Effect of NO, NO_2 and CO on aldehyde capture

Carbon monoxide also reduced the amount of formaldehyde recovered, for similar reasons as stated for nitrogen oxide. However, carbon monoxide does react with DNPH (4.3.6), and therefore it reduces the amount of DNPH available to react with the aldehydes. As the reduction effect was seen only for formaldehyde, it appears that the CO competing for adsorption sites on the cartridge is the major cause for the lower recovery.

The reaction product of the CO with the DNPH may also be displacing the formaldehyde and formaldehyde-DNPH from the cartridge.

A slightly overestimated result for formaldehyde recovery was seen in the presence of NO_2. This is possibly due to the formation of the 4-nitrobenzoic acid (Section 4.3.3) as a result of the reaction of NO_2 with DNPH, which possibly co-elutes with the formaldehyde-DNPH peak. The overestimation is unexpected as the molar absorptivity of the compound is low at the analysis wavelength of 360 nm.

The acetaldehyde recovery was less affected by the presence of NO, CO and NO_2, but still gave an underestimated value for acetaldehyde concentration in the sample. The NO, NO_2 and CO gases are also competing with the adsorption of acetaldehyde and the reaction products are also probably displacing the acetaldehyde-DNPH from the cartridge during sampling.

To determine the whether the NO, NO_2 and CO gases displace the already formed aldehyde-DNPH compounds on the cartridge, the aldehyde solution was directly spiked onto unused DNPH cartridges and given time to react with the DNPH (30 minutes). Each gas (NO, NO_2 and CO) was pumped through a cartridge containing aldehyde-DNPH derivatives respectively. The cartridges were eluted with acetonitrile and prepared for HPLC analysis. Figure **4.12** shows the results for the experiment.

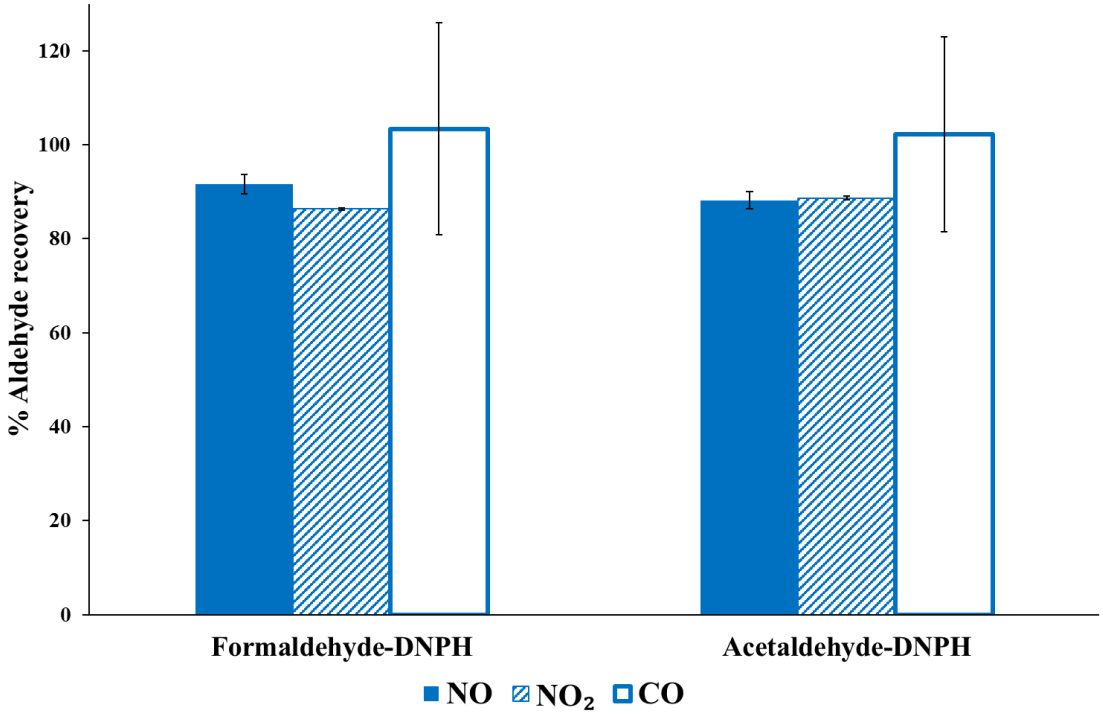

Figure 4.12: Effect of gas on aldehyde derivatives displacement from the cartridge

The results show that the three gases have an effect on the retention of the aldehyde-DNPH derivatives on the DNPH cartridge. The decreased recovery of formaldehyde and acetaldehyde in the presence of NO and NO_2 indicated a mechanism of the gases displacing the DNPH derivatives from the cartridge is possible. In this experiment, the aldehydes had already reacted with the DNPH to form the derivative, which is not very volatile. However, the derivatisation reaction is reversible, as is seen in Figure **2.1**. The forward reaction is catalysed by the presence of the acid on the cartridge. It is probable that the gases are causing the reverse reaction to occur, by reacting with the acid, thereby reducing the acid present. Therefore the aldehyde-DNPH is following the reverse reaction and breaking up into the original gas and DNPH compounds, and consequently the aldehydes could be lost from the cartridge. The aldehyde recovery results in the presence of CO show a complete average recovery of formaldehyde and acetaldehyde (Figure **4.12**), however the large variance in the recovery results indicates that the CO is interfering with the recovery of the formaldehyde and acetaldehyde thereby reducing the robustness factor of the adsorption.

4.4.2 Consumption of DNPH by diesel engine exhaust gases

One of the identified mechanisms for interference of the DNPH method, is the reaction of NO, NO_2 and CO gases with the DNPH, thereby consuming the DNPH and decreasing the capacity of the cartridge. To quantify this impact, the consumption of the DNPH was calculated by determining the amount of moles of DNPH consumed for every mole of gas the cartridge is exposed to.

The results from the experiments performed in Section 4.3.3 and 4.3.6 were used to calculate the amount of DNPH consumed. The results are presented in Figure **4.13**, and shows that the most reactive compound, ozone, consumes the most DNPH per mole of the gas. As NO does not react with DNPH, it does not consume any of the DNPH.

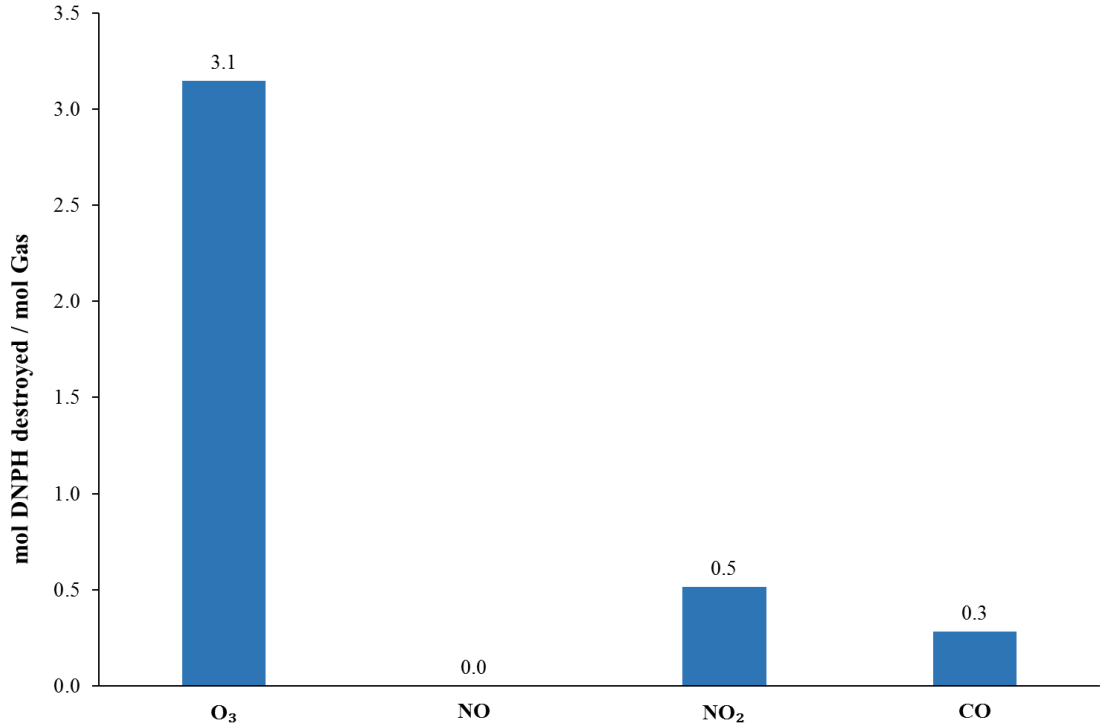

Figure 4.13: DNPH consumed per mole gas

From these results it seems that the ozone would have the largest impact on the DNPH cartridge during an 8 hour sampling period. The use of an ozone removal cartridge, such as the KI cartridge, therefore becomes essential and is included in the method description[28]. The amount of DNPH consumed by the interfering gases, which are based on the scenario of the gas concentrations at the upper limit of the workplace exposure limit, has been calculated from this data (Table **4.4**).

Table 4.4: DNPH consumed by DEEE gases

Gas	NO	CO	NO_2
mol DNPH / mol gas	0	0.28	0.52
WEL (mg/m^3)	2.5	23	0.9
DNPH consumed (mg)	0	21.8	1.01

It is clear that although NO_2 consumes the most DNPH per mole of the gas, due to the higher concentrations of CO in the WEL limit in diesel engine exhaust environments, the CO requirement for DNPH is the highest. The high CO concentrations in off-road diesel engine environments are anticipated, where very often no exhaust aftertreatment devices are fitted. The popular choice of DNPH cartridge, contains 1 mg DNPH per 350 mg of

silica gel on the cartridge. The NO_2 requires this amount of DNPH alone, and therefore this cartridge is inadequate for sampling in a diesel engine exhaust environment.

An equation to calculate the minimum capacity required of the DNPH cartridge for the sampling of the aldehydes in a polluted environment is given in Equation 17 below.

$$m_{DNPH} = 396V_{sample}\left[\left(\frac{C_{CO}}{Mr_{CO}} \times a\right) + \left(\frac{C_{NO_2}}{Mr_{NO_2}} \times b\right) + \left(\frac{C_{Form}}{Mr_{Form}}\right) + \left(\frac{C_{Acet}}{Mr_{Acet}}\right)\right] \quad [17]$$

Where:

m_{DNPH} = mass DNPH required (mg)
V_{sample} = Total volume of the sample (m^3) (Flow rate (m^3/min) x time (min))
C_x = Expected concentration of the relevant (x) gas (mg/m^3)
Mr_x = Molar mass of the relevant gas (g/mol)
a, b = Moles of DNPH consumed per mole of the relevant gas

This equation can be used to determine the amount of DNPH required for sampling aldehydes in a polluted environment. The constant of 396 is made up of the molecular weight of DNPH (198 g/mol), and a factor of 2, to ensure adequate capacity for unknowns, such as other carbonyls that may be present. By increasing the capacity of the DNPH cartridge, the recovery of the aldehydes will be improved. However, this will not compensate for the effect that the gases have on the quantification of the aldehydes, due to competition for absorption sites on the cartridge, and the reversing of the DNPH derivatisation reaction with the aldehydes.

4.5 Cost of increasing capacity

The capacity of the cartridge appears to be a major contribution to the failure of the DNPH method, and therefore needs to be taken into consideration. As mentioned previously, the popular DNPH cartridge choice has 1 mg of DNPH on 350 mg of chromatographic grade silica gel, which equates to 0.29 % (m/m) DNPH loading. The capacity of the cartridge for formaldehyde is specified by Supelco as approximately 75 μg, which would therefore reacted with half of the DNPH on the cartridge (0.5 mg). The stoichiometric ratio of DNPH to formaldehyde is 1:1, therefore the capacity of the cartridge for formaldehyde is calculated to be 50 % of the DNPH available on the cartridge for reaction.

There are several strategies that can be used to increase the capacity of the sampling method, including the following:

- Using more cartridges
- Increasing the size of the cartridge
- Increasing the DNPH loading on the cartridge
- Decreasing the sampling flow rate

An environment where diesel engines are being used in an confined space with the average concentrations of NO, NO_2 and CO are 1.5, 0.56, and 5.75 mg/m^3 respectively, is used as an example for illustrative purposes (typical concentrations of the London Underground[178]). The concentrations of formaldehyde and acrolein of 2.5 and 0.05 mg/m^3 (UK HSE WEL), and acetaldehyde at 2.0 mg/m^3 have been estimated. The calculated amount of DNPH required for sampling, as shown in Table **4.5**, at a sampling flow rate of 1.0 L/min for 8 hours, will be 18.4 mg of DNPH. When taking into account that a capacity of 50 % of the available DNPH may be required, the total amount of DNPH required on the cartridge is 36.8 mg (Table **4.5**).

Table 4.5: Calculation of DNPH requirement in diesel engine environment

Gas	Average concentration (mg/m^3)	Mass DNPH required at 1.0 L/min (mg)	Mass DNPH required at 0.1 L/min (mg)
NO_2	0.56	0.6	0.06
NO	1.5	0	0
CO	5.75	5.5	0.55
Formaldehyde	2.5	7.9	0.79
Acetaldehyde	2.0	4.3	0.43
Acrolein	0.05	0.1	0.01
Total		18.4	1.84

The number of cartridges required to obtain the necessary DNPH capacity is calculated by taking the required amount of DNPH, 36.8 mg, and dividing it by the amount of DNPH on the cartridge. The number is rounded up, and then one cartridge is added as the breakthrough cartridge.

The sampling flow rate can be up to 2.0 L/min. The higher the flow rate, the larger the sample volume and the faster the cartridge DNPH will be depleted. Hence, lowering the

flow rate requires less capacity. However, most personal sampling pumps have a flow range of 0.5 L/min to 5 L/min and special attachments are required to lower the flow rate to 0.1 L/min. By lowering the flow rate, and therefore the sample volume, the sample becomes less representative of the air.

The first option is to add enough cartridges to manage the capacity requirement. In this example, a total of 38 cartridges is needed. The cartridges are connected in series, and therefore would make the sampling setup impractical for personal sampling. Increasing the size (silica gel content with the same DNPH loading) or the DNPH loading, decreases the number of cartridges required, which makes the sampling setup more manageable.

Table 4.6: Amount of cartridges needed and cost of increasing capacity

Option	1.0 L/min		0.5 L/min		0.1 L/min	
(Cartridge, DNPH loading %, mass Si)	Amount	Cost (£)	Amount	Cost (£)	Amount	Cost (£)
Cartridge with breakthrough (standard)	2	14.36	2	14.36	2	14.36
Increase number of cartridges (S10, 0.29 %, 350 mg)	38	265.66	20	143.60	5	35.90
Increase DNPH loading (H10, 0.86 %, 350 mg)	14	161.56	8	92.32	3	34.62
Increase size of the cartridge (H30, 0.86 %, 1 g)	6	147.00	4	98.00	2	49.00
Increasing the size of the cartridge (H300, 0.86 %, 10 g)	1	56.90	1	56.90	1	56.90

Increasing the cartridge size or using more cartridges also increases the amount of solvent required for desorption of the aldehyde-DNPH derivatives from the cartridge. The waste generated also increases and consequently increases the cost of analysis. More importantly, the amount of hours required for the sample preparation in the laboratory will increase. When having to elute more than 10 cartridges, the time spent on sample preparation doubles, increasing the cost of analysis considerably. The larger cartridges (1g, and 10g) also require more time for elution of the derivatives from the cartridge,

making the analysis more expensive. This cost could easily overshadow the cost of the cartridge, and therefore also needs to be taken into consideration.

The strategies for increasing capacity by increasing the number of cartridges, increasing DNPH loading or cartridge size, and lowering the sampling flow rate have been illustrated in Table **4.6**. The increase in the cost of each option is shown. The cost shown in the table only takes into account the cost of the cartridges. Solvent and waste handling were not included, as these would proportionally increase as well.

The use of impingers for personal sampling were considered. The impingers would contain solvent, which could introduce another hazard to the worker's environment in the event of breakage. However, the DNPH capacity can be easily be increased by increasing the concentration of DNPH in solution, without having to increase the sampling train size.

The last alternative is to replace the derivatisation agent with one that is less reactive with NO, NO_2 and CO. This alternative will be investigated in the following chapter.

4.6 Conclusion

The DNPH method has been shown to be subject to chromatographic interference from the reaction products from ozone, NO_2 and CO. Using newer column technology, the resolution of the interfering peaks from the aldehyde-DNPH peaks is improved, and therefore eliminates the chromatographic interference. Therefore, the reaction product of NO_2 with DNPH, DNPA, does not interfere with formaldehyde-DNPH, and the C3 carbonyl-DNPH peaks are completely resolved, without the use of THF.

Although the problem of chromatographic interference from the reaction products of the DEEE gases with DNPH on the aldehyde-DNPH peaks has been resolved, these gases also interfere during the sampling process by competing for adsorption sites on the cartridge. Also, the gases displace the aldehyde-DNPH derivatives by possibly reacting with the acid catalyst on the cartridge, and subsequently allowing the reversal of the derivatisation reaction.

Evaluation of the acrolein quantification showed very similar results to previously reported work. For that reason, it will be necessary to further investigate the stabilisation of acrolein during sampling, or to find an alternative derivatisation agent that is not prone to adduct formation, as is seen with DNPH.

The reaction product of CO with DNPH resembles acetone-DNPH in all aspects investigated (retention time, UV spectra and MS fragmentation patterns). Further characterisation, using Nuclear Magnetic Resonance (NMR), is required to positively identify the compound. It was also established that PAHs captured on the cartridge would not interfere with analysis, and that it was unlikely that any carboxylic acids present would react with DNPH.

The reaction of NO_2 and CO with DNPH reduces the available amount of DNPH (capacity) on the cartridge for derivatisation of the aldehydes. Due to the probable higher concentrations of CO in a DEEE environment with no aftertreatment systems in place, the capacity of the cartridge is severely affected by CO, although the reactivity with DNPH is lower than for NO_2. In combustion environments it is therefore necessary to take into account the concentration levels of NO_2 and CO, along with the expected concentrations for formaldehyde and acetaldehyde, when the required capacity for the sampling cartridge is calculated. Any alternative derivatisation reagents considered, should have a low reactivity with NO, NO_2, and especially CO, for use in polluted environments.

Several strategies for increasing the capacity for sampling with the DNPH method were explored, and is possible, but these increase the cost of the cartridge, solvent for desorption and waste handling. Yet, addressing the capacity of the sampling method does not solve the reactivity of acrolein and the subsequent adduct formation.

The first objective, to identify the limitations and interferences of the DNPH method was met in this chapter. It was confirmed that ozone and NO_2 could cause chromatographic interference on the aldehyde-DNPH chromatogram. For the first time, CO was shown to react with DNPH and interfere with the determination of acetone. One of the major mechanisms of interference with the quantification of the aldehydes is the destruction of the DNPH by NO_2 and CO. These findings reveal a potential risk of the underestimation of formaldehyde and acetaldehyde measurements in a polluted workspace such as a diesel engine operated environment where NO_x and CO concentration levels could be high.

Chapter 5
Evaluation of alternative derivatisation reagents for the derivatisation of aldehydes

5.1 Introduction

The DNPH method is able to measure the aldehydes to the required workplace exposure limits, however, the method has problems in polluted environments that contain NO_2 and CO, as shown in the previous chapter. The gases, i.e. NO_2 and CO, react with the DNPH to form products that interfere with the chromatographic analysis of the aldehydes. The reaction of these gases with DNPH also destroys the DNPH thereby reducing the capacity of the DNPH cartridge for the aldehydes. Along with NO, these gases also compete with the aldehyde adsorption onto the cartridge during sampling. CO plays a major role in the DNPH measurement discrepancy, which has previously not been taken into account. It is therefore necessary to investigate alternative methods of measurement of the aldehydes in polluted environments.

The use of spectroscopic methods are not practical for personal sampling and quantification of aldehydes in a workplace environment, as the instruments are not portable. Spectroscopic methods are a less ideal alternative as the instrumentation is expensive, and need access to a dedicated space with electricity. This makes the use of sampling cartridges preferable for personal sampling, especially in mobile work environments, such as underground train track maintenance sites.

It is therefore necessary to study alternative derivatisation reagents taking into account the knowledge gained on the DNPH method, i.e. reactivity of the derivatisation reagent with pollution gases, which subsequently interfere with sampling and analysis. The criteria for choosing an alternative derivatisation reagent for the measurement of the aldehydes would include a low reactivity with NO, NO_2 and CO, as well as the reaction with acrolein and the stability of the derivative that is formed.

The major reason for using a derivatisation reagent for HPLC analysis, is to add a compound that is detectable by the detectors used for HPLC, making the method more sensitive for the aldehydes. The derivatisation of the aldehydes for GC analysis, is to

ensure the stability of the compounds while keeping the compounds volatile enough for analysis.

Various derivatisation reagents have previously been evaluated for the analysis of aldehydes, as discussed in Chapter 2. Each study evaluated the derivatisation for reasons such as the improvement of the analysis of acrolein, the low reaction rate of the derivatisation reagent with ozone and nitrogen dioxide, or the reaction of NO, NO_2 and ozone with the derivatisation reagent and the subsequent interference the resulting compounds have on the quantification of the aldehydes. However, the derivatisation reagents have not been evaluated for their performance in polluted environments with CO present. The reactivity of the derivatisation reagents with NO, NO_2 and CO has also not been quantified, and therefore it is not known to what extent the gases destroy the derivatisation reagent.

A possible alternative to the derivatisation of the aldehydes is to oxidise the aldehydes to their corresponding carboxylic acids. Oxidation of the aldehydes to the corresponding carboxylic acids will achieve a similar goal as the derivatisation of the aldehydes. The carboxylic acids are easily analysed in their ionic form on ion chromatography (IC) using an anion exchange column and is a sensitive method for the analysis of formate and acetate[179]. The carboxylic acids are also less volatile than the aldehydes, and therefore make the samples more manageable. The IC method also only uses aqueous buffers, which are easily disposed of or the water could be cleaned up using ion exchange resins and distillation.

The oxidation of the aldehydes to carboxylic acids could be achieved using a substrate coated with an oxidising agent. An oxidising agent is a compound that oxidises another compound, while itself is reduced[180]. Several chemical compounds were considered as options, namely H_2O_2, $K_2Cr_2O_7$, $CuCl_2$ and $KMnO_4$. The compound's reduction half-reactions are shown in Table **5.1**, along with their standard potentials. Standard potentials indicate the strength of the oxidising agent, with a higher positive potential indicating a stronger oxidising agent. A few other compounds are also included in the table for illustrative purposes.

The strongest oxidising agent is ozone, however, this is also one of the gases that is expected to present in a polluted environment. It also cannot be used to coat a solid sorbent for a cartridge. All of the oxidising agents considered, except the $CuCl_2$ requires

the presence of hydrogen ions for the oxidation of the aldehydes to take place, and therefore an acid should be present as well. Some of the oxidising agents also undergo a colour change during the oxidation process. The dichromate ion ($Cr_2O_7^{2-}$) starts out as an orange compound, and after being reduced, the chromium will be in 3+ oxidation state, which has a green colour. The purple permanganate becomes a pale pink when reduced. The $CuCl_2$ crystals are blue in colour, and after being reduced, solid copper is formed, which is a dark red colour. The colour change may be useful in the use of cartridges, however, it isn't an essential property of the oxidising agent.

Table 5.1: Standard Reduction Potentials in aqueous solutions at 25°C[180]

Reduction Half-Reaction	Standard Potential E° (V)
$O_3(g) + 2H^+(aq) + 2e^- \rightleftharpoons O_2(g) + H_2O(l)$	2.07
${S_2O_8}^{2-}(aq) + 2e^- \rightleftharpoons 2{SO_4}^{2-}(aq)$	2.01
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	1.78
${MnO_4}^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	1.49
$Cr_2O_7(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	1.33
${NO_3}^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	0.96
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	0.34

The use of dichromate is not ideal because it is highly toxic, although Cr^{3+} is an essential element needed for life, and involved in glucose metabolism in humans[181], therefore it will not be tested. Permanganate is unstable in the presence of an acid[181], and decomposes to form MnO_2. This property will need to be taken into consideration when the stability of a cartridge coated with permanganate is determined, if $KMnO_4$ is used as an oxidising agent.

Hydrogen peroxide is a strong oxidising agent in both acid and basic solution environments. Oxidation with H_2O_2 in a basic environment is faster than when the environment is acidic, and therefore decomposition of the compound occurs rapidly in basic solution[181]. H_2O_2 is reduced to water, and therefore was chosen as the oxidising agent to be used for the oxidation of the aldehydes to carboxylic acids for analysis using IC.

The oxidation of the aldehydes by hydrogen peroxide proceed as follows:

$$HCHO + H_2O_2 \rightleftharpoons HCOOH + H_2O \quad [18]$$

$$CH_3CHO + H_2O_2 \rightleftharpoons CH_3COOH + H_2O \quad [19]$$

Acrolein is oxidised to acrylic acid. Similarly to acrolein, acrylic acid has a tendency to polymerise, making this oxidation method less than ideal for the analysis of acrolein. It is unlikely that this method would be used for the analysis of acrolein.

This chapter evaluates various derivatisation reagents for their suitability as an alternative to the DNPH method for the analysis of formaldehyde, acetaldehyde and acrolein in polluted environments where NO, NO_2 and CO are present.

The aim of the chapter is therefore to choose an alternative derivatisation which would perform well in a polluted environment, and form a stable derivative with acrolein. To achieve this, the objectives are listed below:

1. Choose the derivatisation reagents for evaluation based on the information from literature and criteria set.
2. Evaluate the various derivatisation reagents by identifying any chromatographic interferences from the reaction products formed when reacting with NO, NO_2 and CO, and possible identification of these reaction products.
3. Quantification of the destruction of the derivatisation reagent by NO, NO_2 and CO.
4. Choose a candidate method for the analysis of aldehydes in polluted environments, and determine the analytical performance of the method, and compare it to the DNPH method analytical parameters.

The results presented in this chapter for the oxidation of the aldehydes are preliminary results. This method was not successful in the quantitative analysis of the aldehydes, however, it may be possible to make improvements to the method to make it successful.

The reaction of the derivatisation reagents with ozone was left out of the study, as ozone is known to be extremely reactive with most compounds and would therefore react with and destroy the derivatisation reagents. The use of a KI cartridge for the removal of ozone during sampling is well established, as discussed in Chapter 2, and therefore any method that is chosen for the sampling of the aldehydes will include the use of such a cartridge.

5.2 Screening of alternative derivatisation reagents

The purpose of derivatisation of the aldehydes is to improve the selectivity of the analysis methods for the aldehydes and thereby also improving the sensitivity of the method by several orders of magnitude[89]. As the detector commonly used for HPLC is UV, the derivatisation reagent should contain a chromophore. The DNPH molecule contains two chromophore groups, an aromatic ring and a hydrazine functional group. Many of the proposed derivatisation reagents in literature also contain these functional groups. A derivatisation reagent for GC analysis usually is used to improve the thermal stability of the compound. In the case of GC analysis of aldehydes, the preferred derivatisation reagents were chosen not only to improve the thermal stability of the aldehydes, but to also add a selective label for detection using mass spectrometry (MS).

Many chemicals have been considered for the derivatisation of aldehydes for sampling and quantification purposes, as discussed in Chapter 2. Similarly to the literature on the DNPH method, these derivatisation reagents have not been extensively investigated in terms of the reactivity with NO, NO_2 and CO. The alternative derivatisation reagents were chosen because it specifically reacted with NO_2 and ozone to form the same reaction product, therefore making it easier to deal with the chromatographic interference[40, 41, 145]. A key factor in the DNPH sampling system in Chapter 4 was shown to be the effect that NO, NO_2 and CO have on the destruction of the derivatisation reagent. However, the reaction of NO, NO_2 and CO with the alternative derivatisation reagents have not been quantified.

Along with the reactivity of the DNPH with the polluting gases, the reaction of DNPH with acrolein to form the acrolein-DNPH derivative as well as some adducts, causes problems for the quantification of acrolein. Therefore, it is essential to find a derivatisation reagent that will form one stable derivatisation product with acrolein.

A critical evaluation of any derivatisation reagent used for the measurement of aldehydes in polluted environments is essential. The initial choices will be based on information gained from literature, which is summarised in Table **5.2**. The following criteria will be used to choose candidate derivatisation reagents for further evaluation:

- Ease of use of the derivatisation reagent or possible problems associated with the use of the derivatisation reagent.
- Commercial availability and the affordable cost of the reagent

- Formation of a single stable derivative with acrolein (includes E- and Z-isomers)
- Formation of reaction products of the derivatisation reagent with NO, NO_2 and CO which may interfere with the aldehydes' quantification
- Relatively short reaction time for the derivatisation of the aldehydes

5.2.1 Difficulties encountered with the handling of derivatisation reagents

The DNPH method has difficulties quantifying aldehydes in environments containing ozone, CO, NO, and NO_2, and it has been shown that sampling for longer than 6 hrs causes a low recovery for acetaldehyde[111]. Furthermore, the reaction of acrolein with DNPH forms not only the derivative, but also several adducts[96]. DNPH is a desensitised explosive[182], and therefore requires that cartridges be stored in refrigerators, with regulations governing the storage of the chemical in the laboratory.

Although the DNSH method is a good candidate based on the applicability to acrolein analysis, DNSH and its derivatives are prone to hydrolysis and the derivatives decompose after 15 minutes[40, 114, 129]. The samples would therefore degrade during the 8 hour sampling time and therefore the stability of samples are questionable, and excludes the DNSH method from the study.

Using 2-HMP is the alternative method for measurement of acrolein[30], however several reports of high background levels of formaldehyde and acetaldehyde have been made[30, 116, 120]. The high background levels increase the limits of detection and quantification for formaldehyde and acetaldehyde, and therefore makes the method unsuitable for low level quantification of these compounds. This eliminates 2-HMP as a candidate derivatisation reagent.

MNBDH derivatives are reported to be unstable in air[127] and therefore wouldn't be suitable for sampling times of 8 hours, and will therefore not be considered further. Not only is UDMH toxic and harmful to the environment, but it also reacts with oxygen and carbon dioxide to form dimethyl nitrosamine, which is also toxic[183]. The reactivity of UDMH with oxygen and CO_2 would further increase the destruction of the UDMH, thereby lowering the capacity of the method for aldehydes derivatisation. UDMH is therefore also excluded from the list of candidate derivatisation reagents.

Table 5.2: Summary of the derivatisation reagents considered for the measurement of aldehydes

Shorthand name	Reactivity with acrolein	Reaction products with NO, NO_2, CO and ozone	Reactivity with the aldehydes	Availability and cost (£/g)	Problems identified in literature
MDNPH	Unknown	Same reaction product formed with ozone and NO_2	20 minutes	Synthesis required	Low recovery for acetaldehyde
MNBDH	Possible with a pH adjustment	Same reaction product formed with ozone and NO_2	150 seconds	3220	Low recovery for acetaldehyde Derivatives are unstable in air
DNSH	Reacts with acrolein	Unknown	10 minutes	264	Prone to hydrolysis Derivatives decompose after 15 min
PFPH	Reacts with acrolein	Ozone destroys PFPH	3 days (24 hours at 60ºC)	6.89	-
PFBHA	Stable derivative formed	Unknown	15 minutes	57.40	-
2-HMP	Recommended method	Unknown	16 hours	8.98	High background levels for formaldehyde and acetaldehyde
MDMNTH	Unknown	Same reaction product formed with ozone and NO_2	30 minutes	Synthesis required	-
UDMH	Unknown	Unknown	20 minutes	0.41	Reacts with O_2 and CO_2
HBA	Unknown	Unknown	15 min – 4 hours	3.19	-
MBTH	Unknown	Possible interference observed	50 minutes	6.62	-
DAIH	Possible with a pH adjustment	Ozone destroys DAIH and aldehyde-derivatives	60 minutes	131.50	-
NBEA	No reaction	Unknown	Fast	1.53	-
Cysteamine	No reaction	Unknown	Fast	7.12	-

5.2.2 Availability commercially and cost

In a commercial laboratory the cost of analysis is always an important factor. For this criterion only the cost of purchasing the derivatisation reagent was taken into consideration. The cost of running and maintaining equipment for an analysis technique also adds to the cost, which could be considered at a later stage of the study. HPLC analysis methods are generally more expensive to run than GC analysis methods, due to the volumes of solvent used, as well as waste that needs to be disposed of.

Synthesis of the derivatisation reagents can be very time consuming and would increase the cost of a derivatisation reagent. MDNPH and MDMNTH are not commercially available, and need to be synthesised, and therefore are excluded from further study as candidate derivatisation reagents. Although MNBDH has already been eliminated from the candidate derivatisation reagents, the cost (£3220/g), which is more than a thousand times the cost of DNPH, eliminates this derivatisation reagent from the study.

5.2.3 Formation of aldehyde-derivatives and stability

The development of a single method for the analysis of formaldehyde, acetaldehyde and acrolein requires the reaction of the derivatisation reagent with each of the aldehydes, especially acrolein and forming stable derivatives. NBEA[115] and cysteamine[113] do not react with acrolein, therefore these derivatisation reagents will not be further considered in this study.

Due to low acetaldehyde recoveries when sampling for more than 6 hours, using MDNPH[151] and MNBDH[125] as derivatisation reagents would be less likely to be successful for an 8 hour personal sampling period. These derivatisation reagents have already been eliminated as candidates.

Certain derivatisation reagents have been confirmed to react with acrolein i.e. MNBDH[41], DNSH[128, 130], PFBHA[10], PFPH[133] and 2-HMP[30], as reported in literature, however MNBDH, DNSH, and 2-HMP have been removed the candidate derivatisation reagents. The other listed derivatisation reagents have no evidence whether these reagent do react with acrolein or not and these reagent will therefore need to be investigated if any are chosen as candidate derivatisation reagents.

5.2.4 Reaction with NO, NO_2, CO and ozone

In literature, the main interfering gases were identified to be NO_2 and ozone for the DNPH method, as discussed in Chapter 2, and subsequently this has been the focus of many studies on alternative derivatisation reagents in an environment containing these gases. Yet, no information was found on the reaction of any of the derivatisation reagents with CO, and therefore the reaction of CO with the derivatisation reagent will need to be studied for all the candidate derivatisation reagents.

MDNPH[151], MNBDH[41] and MDMNTH[145] were developed as alternative derivatisation reagents to DNPH, because each of these derivatisation reagents formed the same reaction product with NO_2 and ozone, respectively. The formation of only one reaction product makes the chromatographic separation of the reaction products from the aldehyde-derivatives easier. However, all three of these derivatisation reagents have already been excluded as candidates.

Ozone interferes with the quantification of aldehydes when using PFPH[136], PFBHA[10], and DAIH[141] as derivatisation reagents for the sampling of aldehydes. It is also anticipated that ozone would probably interfere with any derivatisation reagent and the derivatives due to ozone's high reactivity. This criterion does not eliminate any of the derivatisation reagents since the reaction of the derivatisation reagents with NO, NO_2 and CO has not been thoroughly studied and quantified.

5.2.5 Reaction time with aldehydes

The reaction time of the derivatisation reagent with the aldehydes is influenced by the sampling technique and device used to derivatise the aldehydes, the matrix of the aldehydes, temperature, pH, whether a solvent is used, and the concentration of the derivatisation reagent[89]. MNBDH[41] (excluded), DNSH[155] (excluded), PFBHA[163], DAIH[129] and UDMH[165] (excluded) all react with the aldehydes to form the respective derivatives in under an hour.

Longer reaction times may not problematic, because the transportation and storage time before analysis will allow for the derivatisation reaction time to pass by. This will only be possible if the sorbent used for sampling fully retains the aldehyde during sampling and storage. Derivatisation reagents with reaction times longer than 12 hours are 2-HMP[30], PFPH[131], HBA[143]. This criterion at this point did not eliminate any of the

derivatisation reagent candidates, but may be taken into account later in the study if necessary.

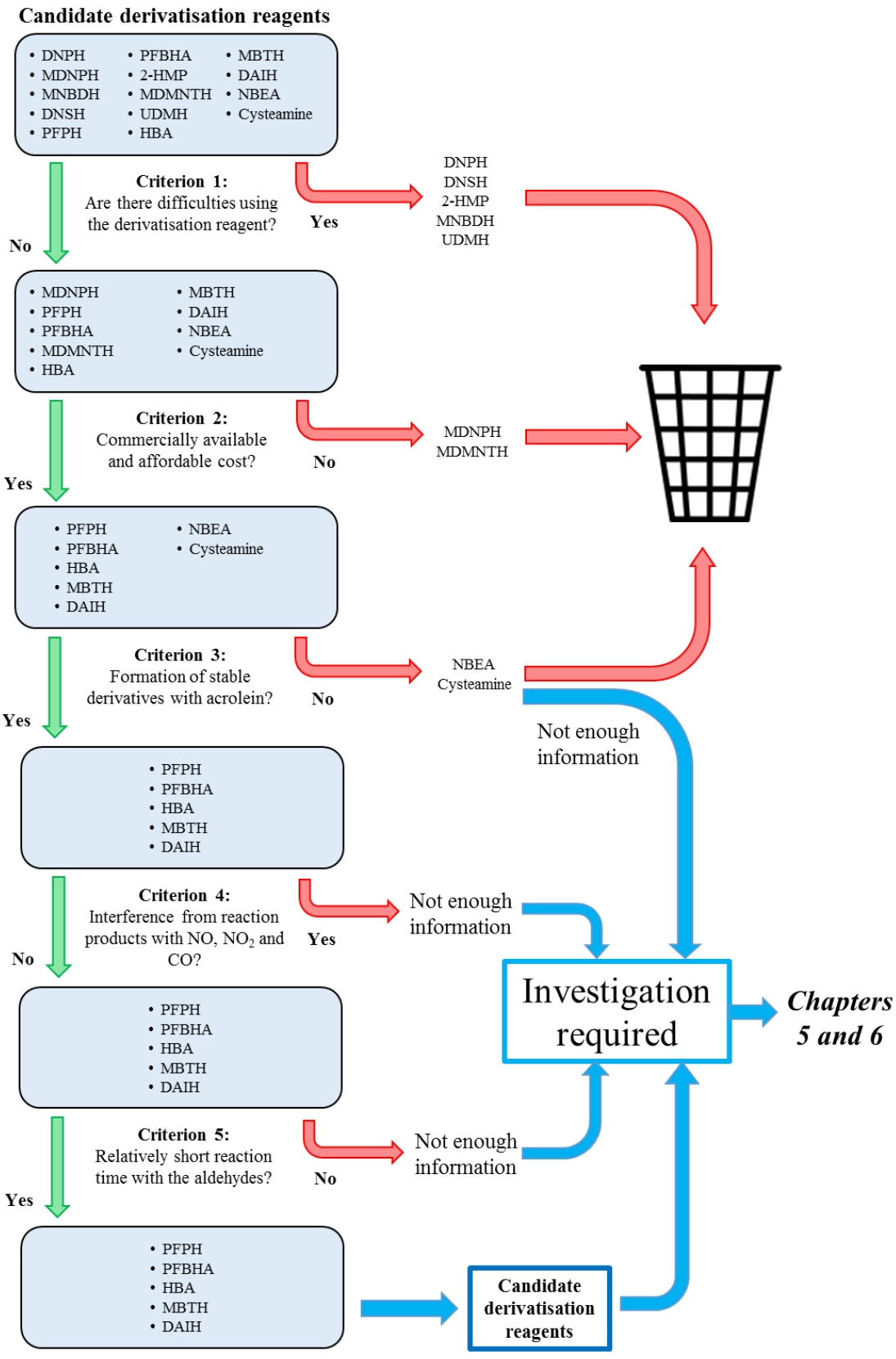

Figure 5.1: Screening of the alternative derivatisation reagents

5.2.6 Candidate derivatisation reagents

Following from the previous sections, the following derivatisation reagents were chosen for further exploration:

- MBTH
- DAIH
- HBA
- PFBHA
- PFPH

DAIH and PFBHA are relatively expensive derivatisation reagents as indicated in Table **5.2**. Also, it should be mentioned that MBTH and DAIH are toxic compounds.

5.3 Evaluation of the derivatisation reagents

The derivatisation reagent chosen are all compounds that contain a hydrazine functional group, or in the case of PFBHA an amide, which is similar to the hydrazine. The hydrazine functionality, or the amide in the case of PFBHA, is the reaction site for the aldehydes. The derivatisation reagents react with the aldehydes by nucleophilic addition of the amine in the hydrazine to the carbonyl group of the aldehyde, followed by the elimination of a water molecule, as illustrated in Figure **5.2**. Each derivatisation reagent has a different reactivity towards the aldehydes due to the difference in structures of the R-group attached to the hydrazine.

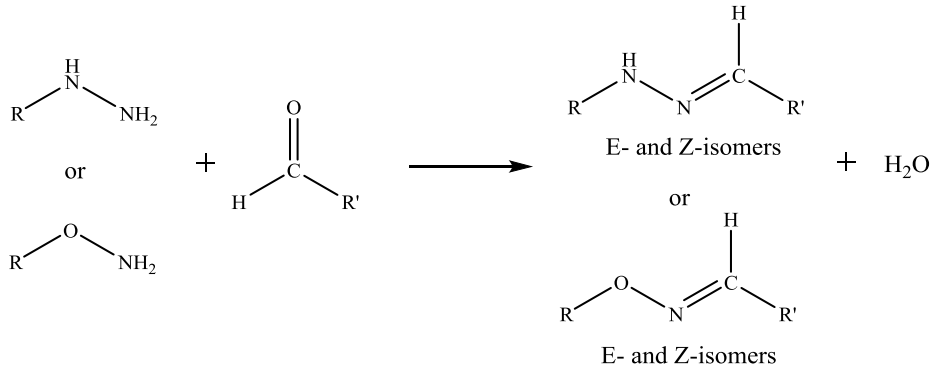

Figure 5.2: General reaction of a hydrazine with an aldehyde

The HPLC and GC methods used for the analysis of the respective derivatisation reagent solutions are described in Chapter 3. The methods are based on already published methods, which have been modified to suite the equipment and columns available.

5.3.1 Reaction of the derivatisation reagent with acrolein

Acrolein forms adducts with DNPH as it is a highly reactive compound, due to the conjugated double bond to the carbonyl functionality[1]. It is important that not only the derivatisation reagent react with acrolein, but that the acrolein derivative is stable, and does not form adducts with the derivatisation reagent. As indicated in Figure **5.2** it is expected that each aldehyde, except formaldehyde, will have an E- and Z-isomer, resulting in the possibility of two peaks being observed for each aldehyde on the chromatograms. The total of the peak areas of the E- and Z-isomers for each aldehyde-derivative should be used for the quantification of the aldehyde.

Each derivatisation reagent was prepared in solution, as described in Chapter 3, and mixed with a freshly prepared solution of acrolein. The solutions were left to react for 5 days, to ensure that even the slowest reacting derivatisation reagent (3 days for PFPH) has completed reaction with the aldehydes. The solutions were analysed using the respective analysis techniques for each derivatisation reagent, as described in Chapter 3. The results of the analysis are shown in Figure **5.3** to Figure **5.7**.

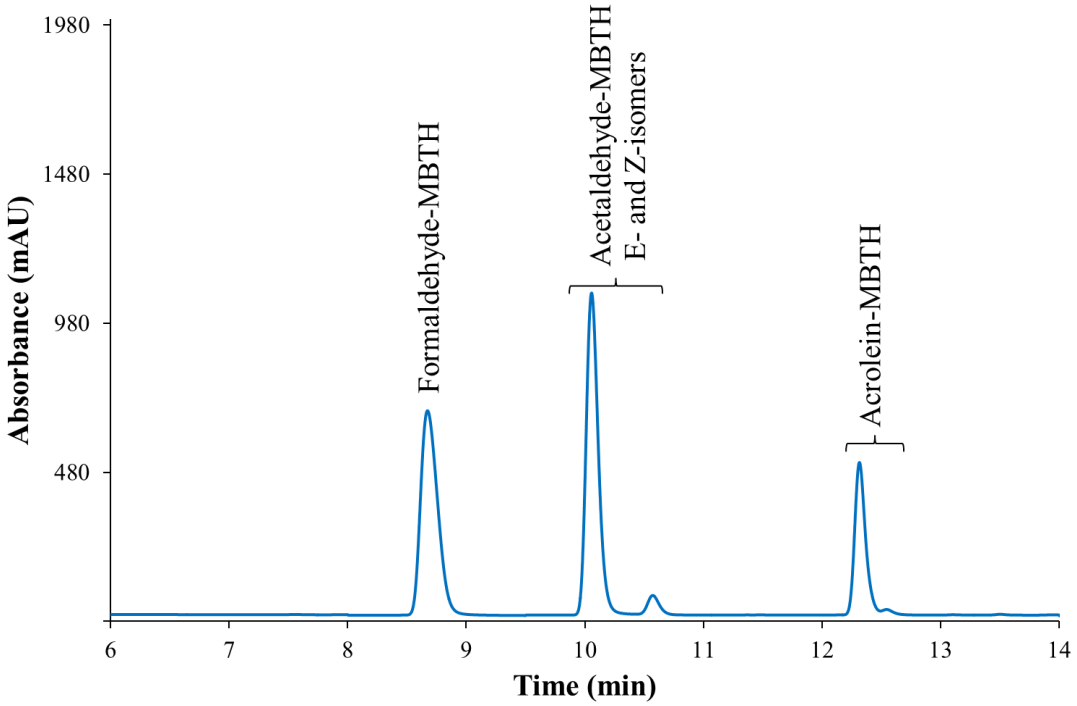

Figure 5.3: HPLC-UV chromatogram of the aldehyde-MBTH derivatives (310 nm)

The HPLC chromatogram of the aldehyde-MBTH derivatives (Figure **5.3**) revealed two peaks for each E- and Z-isomers of the acetaldehyde- and acrolein-MBTH derivatives. Therefore the acrolein-MBTH derivative is stable for 5 days in solution.

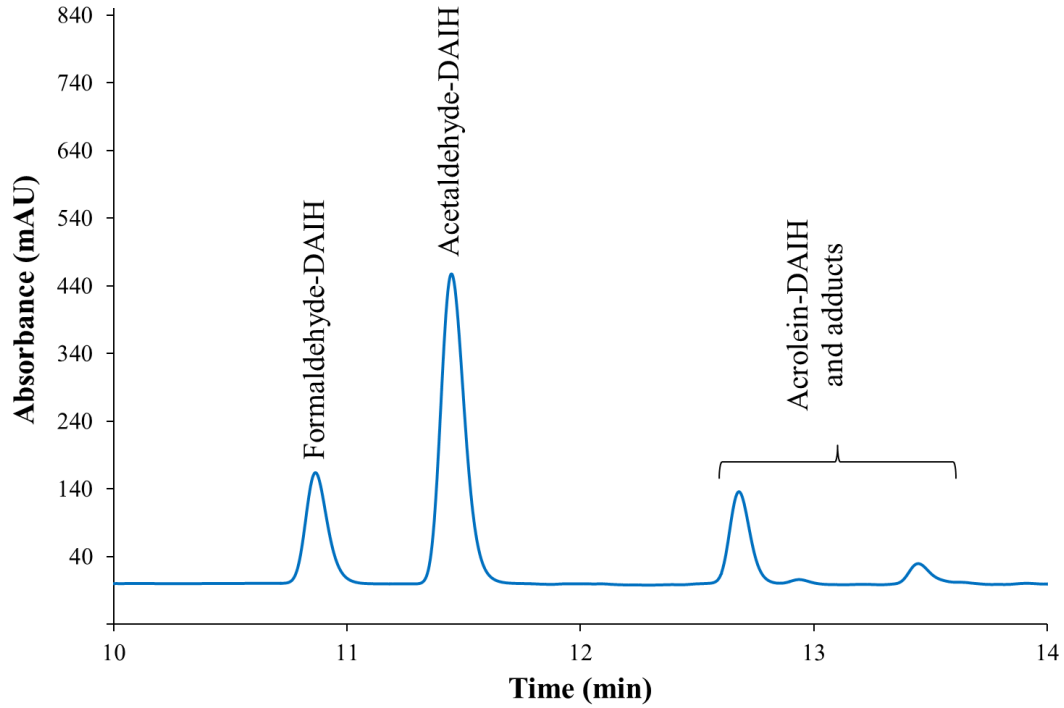

Figure 5.4: HPLC-UV chromatogram of the aldehyde-DAIH derivatives (240 nm)

Only one peak was observed for acetaldehyde-DAIH on the chromatogram of the aldehyde-DAIH derivatives (Figure **5.4**). The formation of E- and Z-isomers for acetaldehyde may be sterically hindered. Three peaks were observed for acrolein-DAIH., therefore at least two adducts could have been formed by acrolein and DAIH.

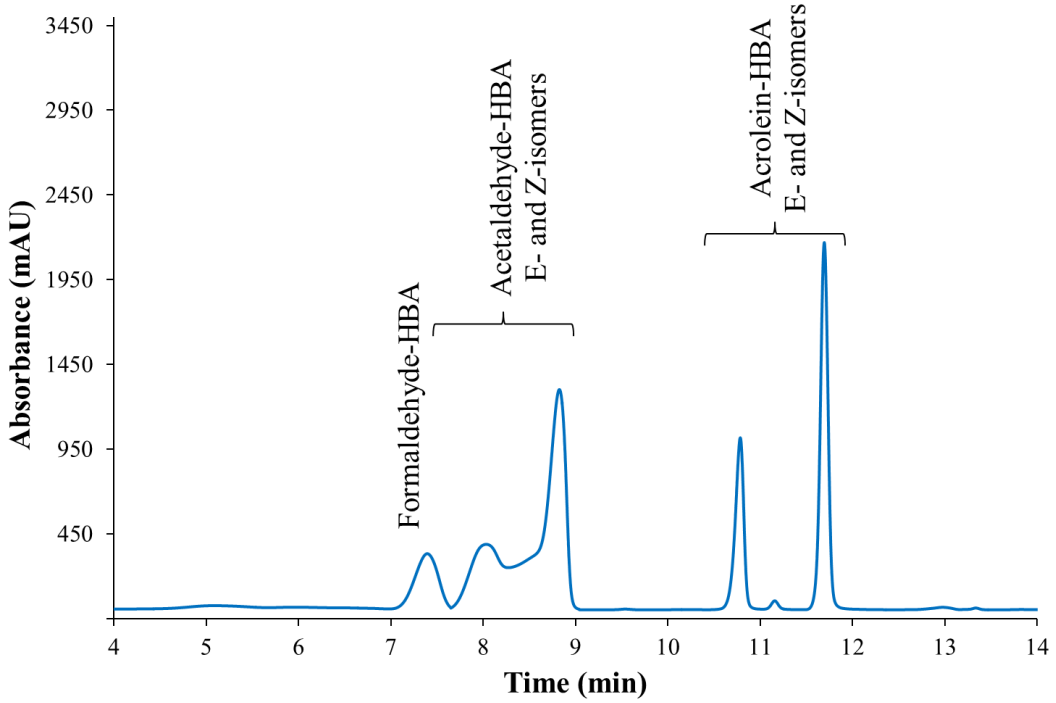

Figure 5.5: HPLC-UV chromatogram of the aldehyde-HBA derivatives (310 nm)

Similarly to DAIH, three peaks were detected for acrolein-HBA on the HPLC chromatogram for the aldehyde-HBA derivatives (Figure **5.5**). This suggests that HBA formed at least one adduct, as two of the peaks could be due to the E- and Z-isomers of the acrolein-HBA molecule. The E- and Z-isomers for acetaldehyde-HBA were also separated on the chromatogram.

The resulting gas chromatogram for the aldehyde-PFPH derivatives (Figure **5.6**), revealed two peaks for acetaldehyde-PFPH which represent the E- and Z-isomers. Only one peak was observed for the acrolein-PFPH, suggesting that the acrolein-PFPH derivative was stable in solution for 5 days.

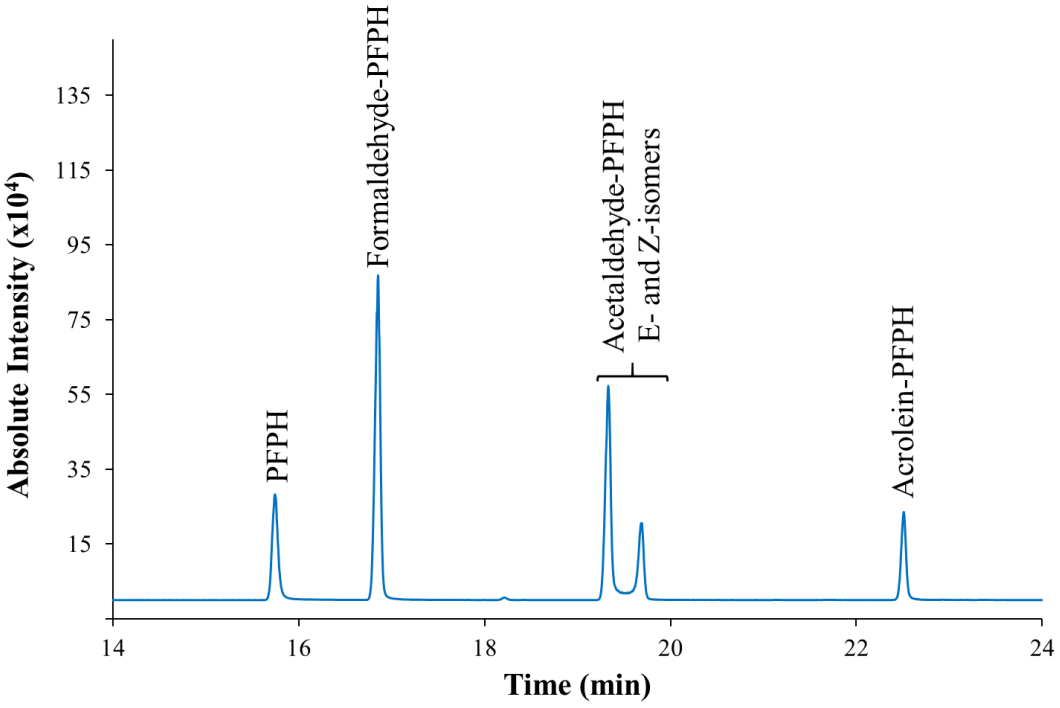

Figure 5.6: SIM GC-MS chromatogram of the aldehyde-PFPH derivatives (m/z 155)

Two peaks for each of the acetaldehyde- and acrolein-PFBHA derivatives were seen on the GC chromatogram for the aldehyde-PFBHA derivatives (Figure **5.7**). Therefore the GC method separates the E- and Z-isomers of the acetaldehyde- and acrolein-PFBHA derivatives. Also, this indicates that the acrolein-PFBHA derivative was stable in solution for 5 days.

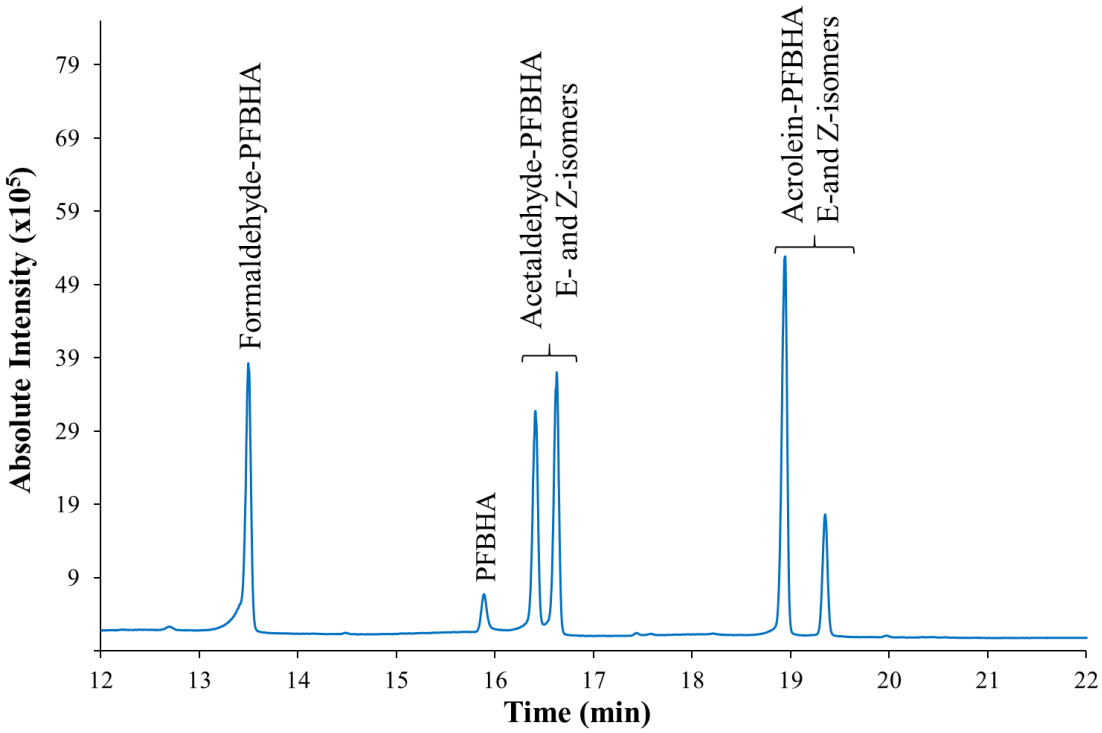

Figure 5.7: GC-MS chromatogram of the aldehyde-PFBHA derivatives (TIC)

5.3.2 Reaction of the derivatisation reagent with NO, NO_2, and CO

Chapter 4 made it evident that it is important to consider the effect NO, NO_2 and CO have on the sampling and accurate determination of aldehydes. Each of the derivatisation reagents react with the aldehydes in a similar way to the DNPH, and therefore it can be anticipated that these compounds will react with the NO, NO_2 and CO in a similar way. As discussed earlier, the derivatisation reagents being evaluated have different reactivity's due to their molecular structure, and therefore may have different rates of reaction with the NO, NO_2 and CO gases. Thus it is necessary to investigate whether the chosen derivatisation reagents react with NO, NO_2 and CO, and whether the resulting products interfere during the GC or HPLC analysis. If there is a reaction of the gases with the derivatisation reagents, it is essential to determine and quantify the destruction of the derivatisation reagents by the NO, NO_2 and CO during the sampling of aldehydes in polluted environments.

5.3.2.1 Chromatographic interference – Reaction of NO and NO_2 with the derivatisation reagents

The reaction of NO and NO_2 with the derivatisation reagents needs to be studied to determine whether the resulting compounds interfere with the GC or HPLC analysis of

the aldehyde-derivatives. If there are interferences from the NO, NO_2 and CO reaction products, the analysis methods can be further optimised to ensure the separation of the reaction products from the aldehyde-derivatives. However, if the compounds co-elute completely (resolution of <0.5) then the optimisation of the method to separate the peaks will be challenging.

Cartridges containing the respective derivatisation reagents were prepared as described in Chapter 3, and exposed to 0.188 mg of NO_2 and 0.123 mg of NO separately (Section 3.7.1.1), after which the cartridges were eluted with the appropriate solvent and analysed using HPLC and GC-MS. The resulting chromatograms were compared with the chromatogram of the respective aldehyde-derivatives, as shown in Figure **5.8** - Figure **5.12** to determine the interference. The eluents were all injected onto the GC-MS method as described in Chapter 3, to attempt the identification of the reaction products from the mass spectra.

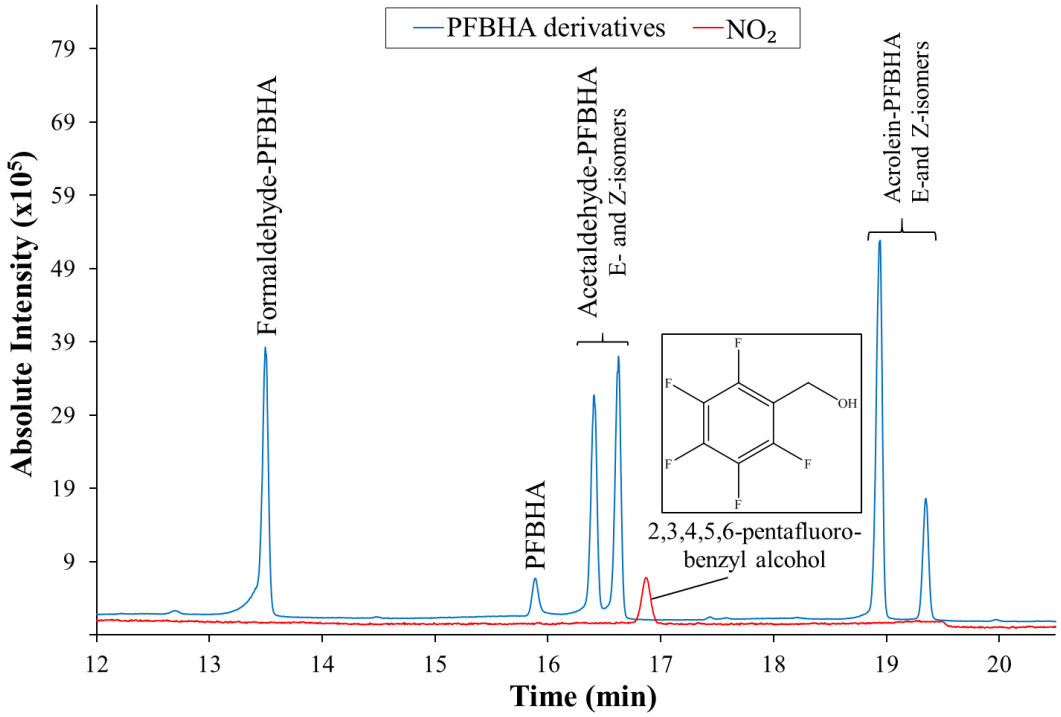

Figure 5.8: GC-MS chromatogram of PFBHA and NO/NO_2 reaction products (TIC)

Every single one of the derivatisation reagents reacted with the NO_2, each resulting in two reaction products, except for PFBHA which had only one reaction product. The reaction of the derivatisation reagents with NO formed the same reaction products as the

reaction with NO_2. The chromatographic interferences of NO and NO_2 are therefore discussed simultaneously.

The reaction product of PFBHA with NO and NO_2 was identified as 2,3,4,5,6-pentafluorobenzyl alcohol and eluted after the acetaldehyde-PFBHA isomers. The NO_x-PFBHA reaction product has a resolution of 1.0 from the acetaldehyde-PFBHA isomer, therefore is not resolved sufficiently to ensure accurate quantification of acetaldehyde. Consequently, the presence of NO or NO_2 in the sample matrix could cause an overestimation of the acetaldehyde concentration when using PFBHA as the derivatisation reagent during sampling.

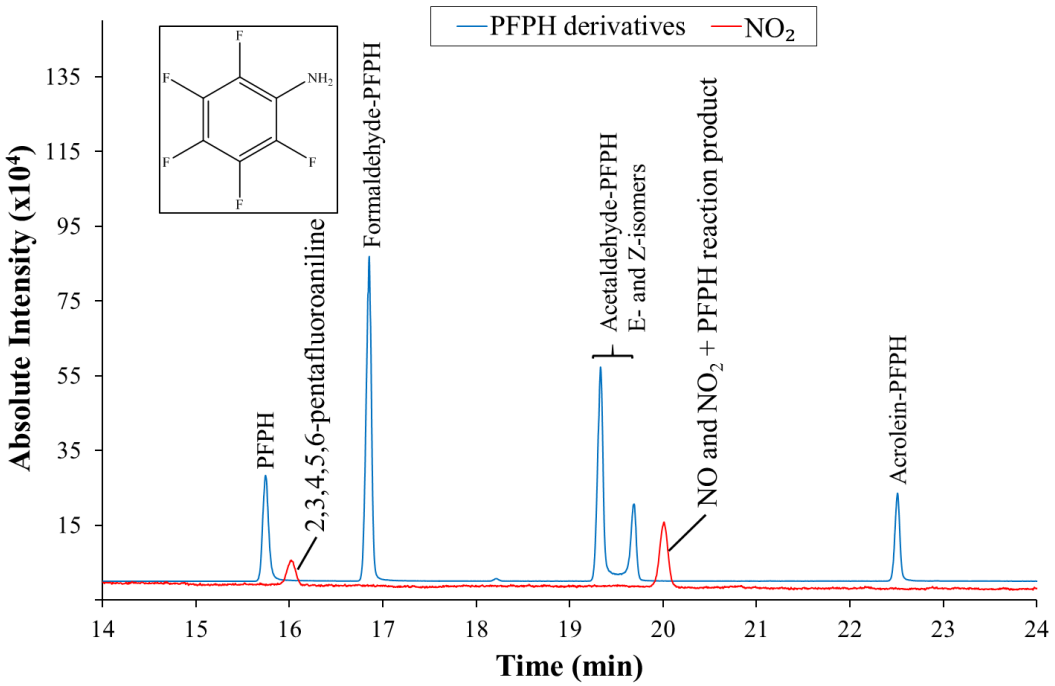

Figure 5.9: SIM GC-MS chromatogram of PFPH and NO/NO_2 reaction products (m/z 155)

The two reaction products formed during the exposure of the PFPH cartridge to NO and NO_2, are shown in Figure **5.9**. The first compound eluted after the PFPH peak and was identified to be 2,3,4,5,6-pentafluoroaniline, and the second compound eluted after the acetaldehyde-PFPH peak, which could not be identified. The PFPH and 2,3,4,5,6-pentafluoroaniline peaks have a calculated resolution of 1.2. The 2,3,4,5,6-pentafluoroaniline does not interfere with the aldehyde-PFPH derivatives, and therefore will not affect the accuracy of the quantification of the aldehydes. The acetaldehyde-

PFPH and the second NO_x-PFPH reaction product peaks have a resolution of 1.5, which means it is fully resolved from the acetaldehyde-PFPH peak, and will not interfere with the quantification of acetaldehyde. The reaction products of NO and NO_2 with PFPH will not interfere with the quantification of the aldehydes in air if PFPH is used as the derivatisation reagent during sampling.

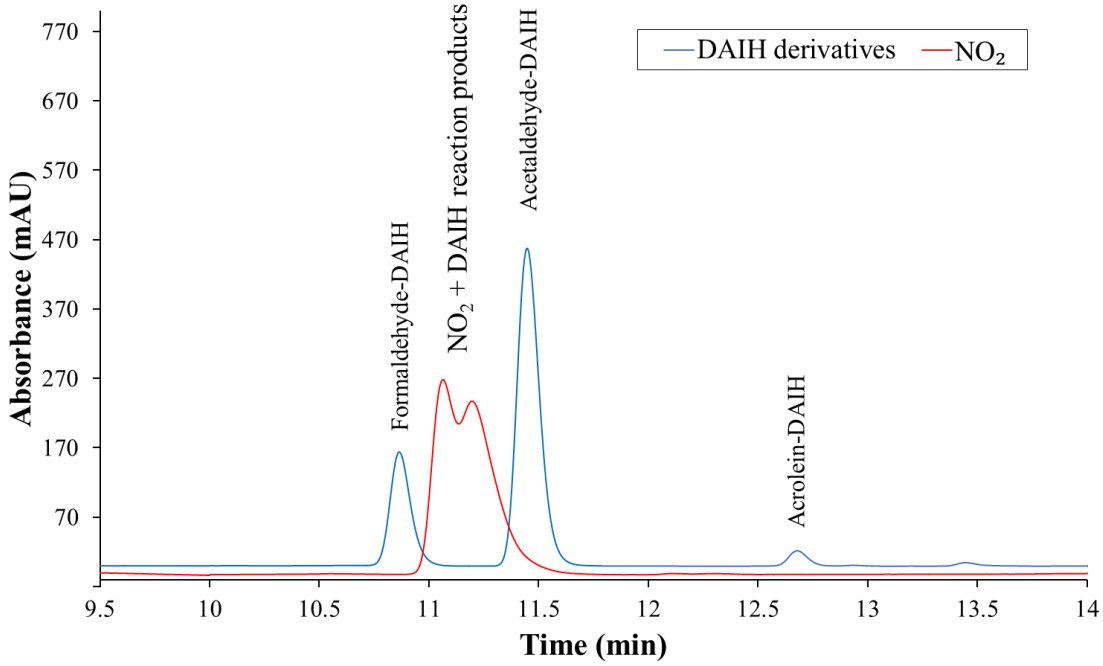

Figure 5.10: HPLC-UV chromatogram of DAIH and NO/NO_2 reaction products

DAIH reacted with NO and NO_2 to form two reaction products which eluted between the formaldehyde- and acetaldehyde-DAIH derivatives and co-eluted with each other (Figure **5.10**). The NO_x-DAIH peaks are not fully resolved from the formaldehyde-DAIH (resolution of 0.8) and acetaldehyde-DAIH (resolution of 0.7). The low resolution therefore indicates that there may be co-elution of the NO_x-DAIH reaction products with the aldehyde-DAIH derivatives, and thus the quantification of the aldehydes will be less accurate if there is NO or NO_2 present in the sampling environment. The reaction products could not be detected using GC-MS because the compounds may not be volatile enough for GC analysis, and therefore the compounds could not be identified.

The reaction of HBA with NO or NO_2 resulted in two reaction products, as seen in Figure **5.11**. One of the NO_x-HBA reaction products co-eluted with the acrolein-HBA peak, therefore any NO or NO_2 in the sample matrix will cause an overestimation of the acrolein concentration, when using HBA as the derivatisation reagent during sampling. The HBA reaction products could not be detected by GC-MS analysis, because the compounds are probably not thermally stable for GC analysis, and therefore the identity of the compounds could not be established.

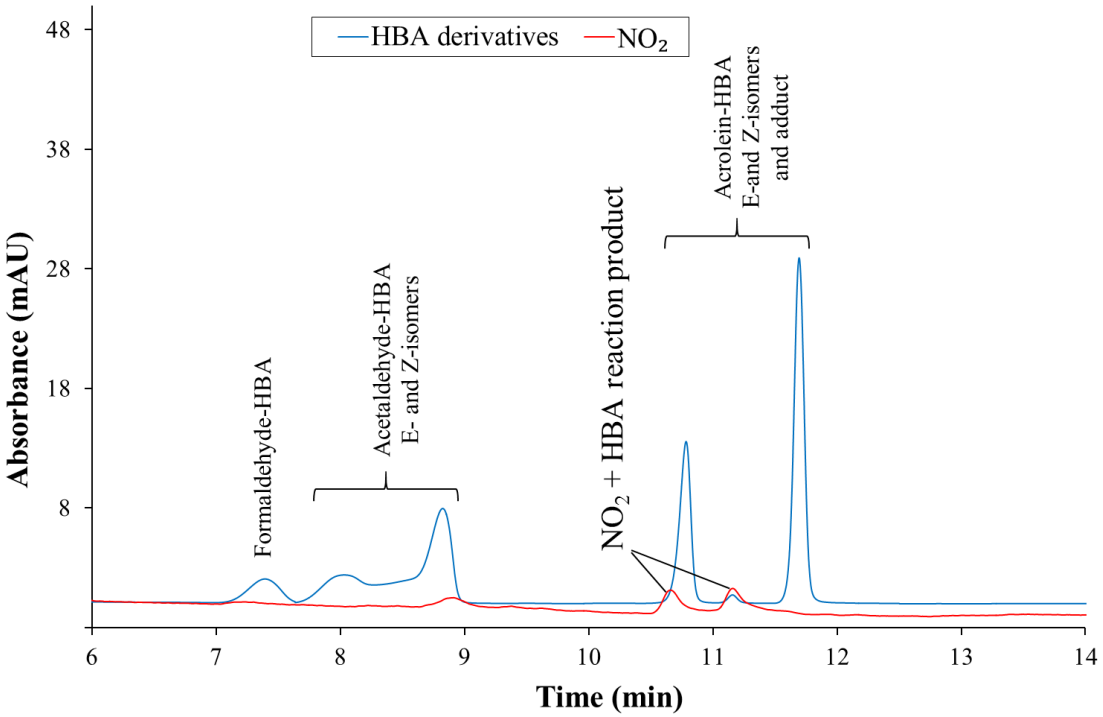

Figure 5.11: HPLC-UV chromatogram of HBA and NO_2 reaction products

The reaction of NO or NO_2 with MBTH also resulted in two reaction products forming. These reaction products elute several minutes after all the aldehyde-MBTH derivatives on the chromatogram, as shown in Figure **5.12**. The solution containing the reaction products of NO or NO_2 with MBTH was injected onto a GC-MS to identify the compounds. The two compounds were identified as 3-methyl-2(3H)-benzothiazolone and 3-methyl-1,3-benzothiazol-2(3H)-amine with the structures of these compounds included in Figure **5.12**.

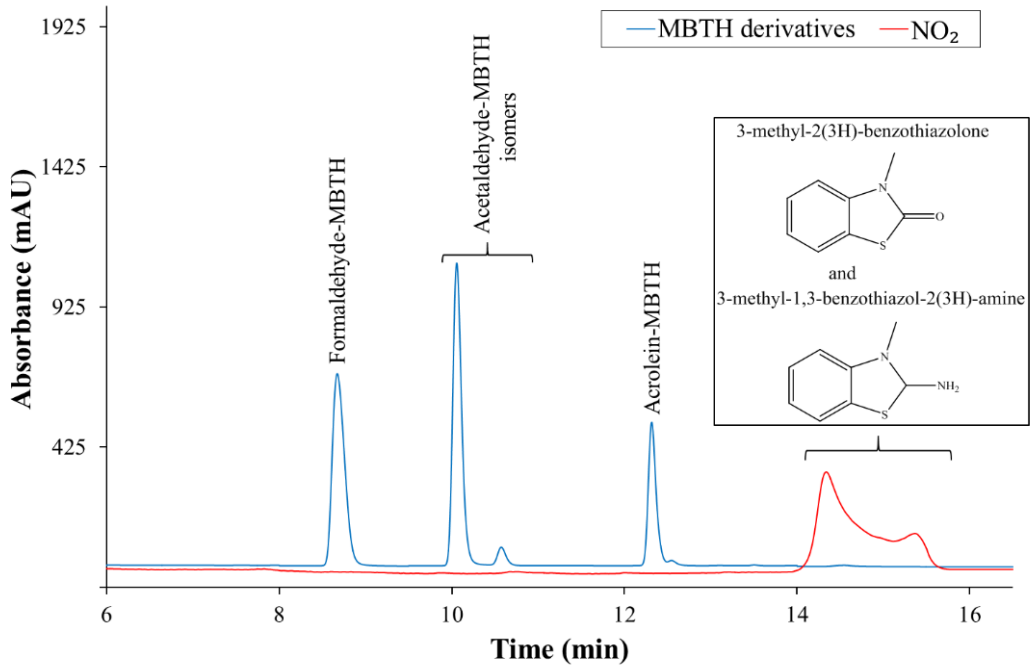

Figure 5.12: HPLC-UV chromatogram of MBTH and NO/NO_2 reaction products

The reaction of NO and NO_2 in the sample matrix with H_2O_2 on the cartridge was considered. Each of these gases would be oxidised by the hydrogen peroxide according to the following reaction equations:

$$2NO_2 + H_2O_2 \rightleftharpoons 2HNO_3 \quad [20]$$

$$2NO + 3H_2O_2 \rightleftharpoons 2HNO_3 + 2H_2O \quad [21]$$

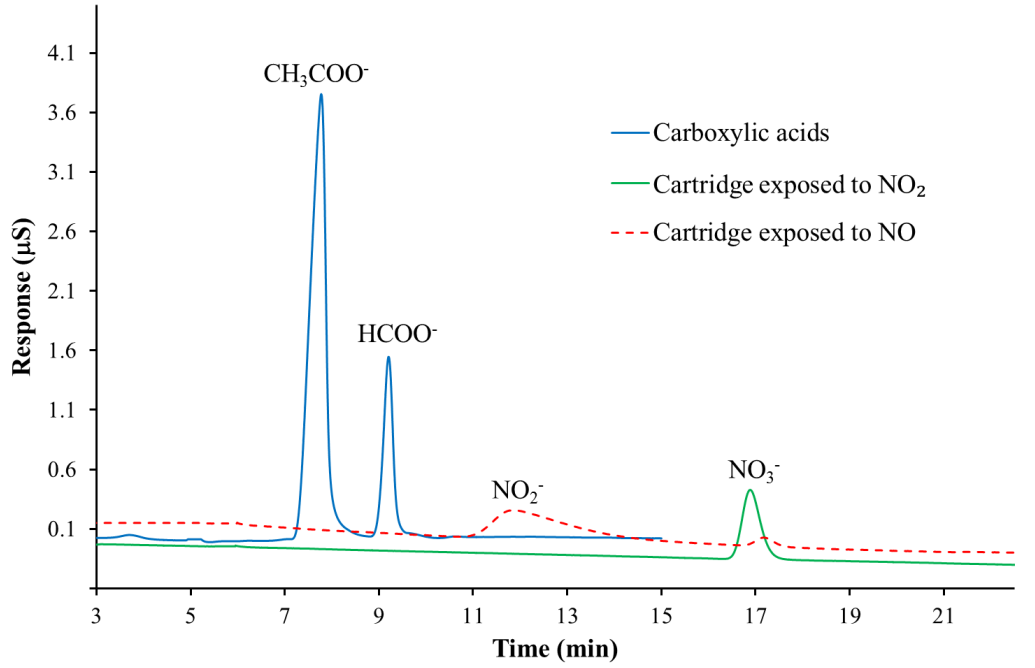

Figure 5.13: IC chromatogram of the anions formed from NO and NO_2 after oxidation

Cartridges containing hydrogen peroxide were exposed to NO and NO_2 respectively, as described in Section 3.7.1). The cartridges were eluted, and analysed using IC, and the resulting chromatograms are shown in Figure 5.13. The ions were identified according to their retention times when compared with standards. The oxidation of NO did not only result in the formation of nitric acid, but also nitrous acid (HNO_2), as is evident in the chromatogram.

The IC analytical method separates the resulting ions from the formate and acetate peaks, as expected, and therefore the ions will not interfere chromatographically with the quantification of the aldehydes in air. However, the H_2O_2 will be consumed by the gases and therefore the concentration of the H_2O_2 on the cartridge will need to be sufficient for the sampling and analysis of the aldehydes. As there is a response for each of the formed ions from the gases, this method could possibly simultaneously measure NO_x ($NO + NO_2$) and the aldehydes in air samples. This will be possible if the oxidation of the NO_x are quantitative, and no breakthrough of the gases occur.

5.3.2.2 Chromatographic interference from the reaction of CO with the derivatisation reagents

To identify interferences from CO with the derivatisation reagents, the prepared cartridges were exposed to CO. The cartridges were eluted and the eluent was analysed using GC or HPLC. The chromatograms of the reaction products of CO and the derivatisation reagents were compared with the aldehyde-derivative chromatograms (Figure **5.14** - Figure 5.19), as done previously.

Similarly to the reaction of the derivatisation reagents with NO and NO_2, all the derivatisation reagents react with CO to form two reaction products, except for PFBHA, which only forms one reaction product with CO, as shown in Figure **5.14**. The compound elutes almost two minutes after the acrolein-PFBHA derivatives, and therefore would not interfere with quantification of the aldehydes. The compound was identified from the mass spectrum to be a compound similar to acetone-PFBHA. This is similar to what was previously observed for the reaction product of CO with DNPH (Chapter 4), where acetone-DNPH was identified.

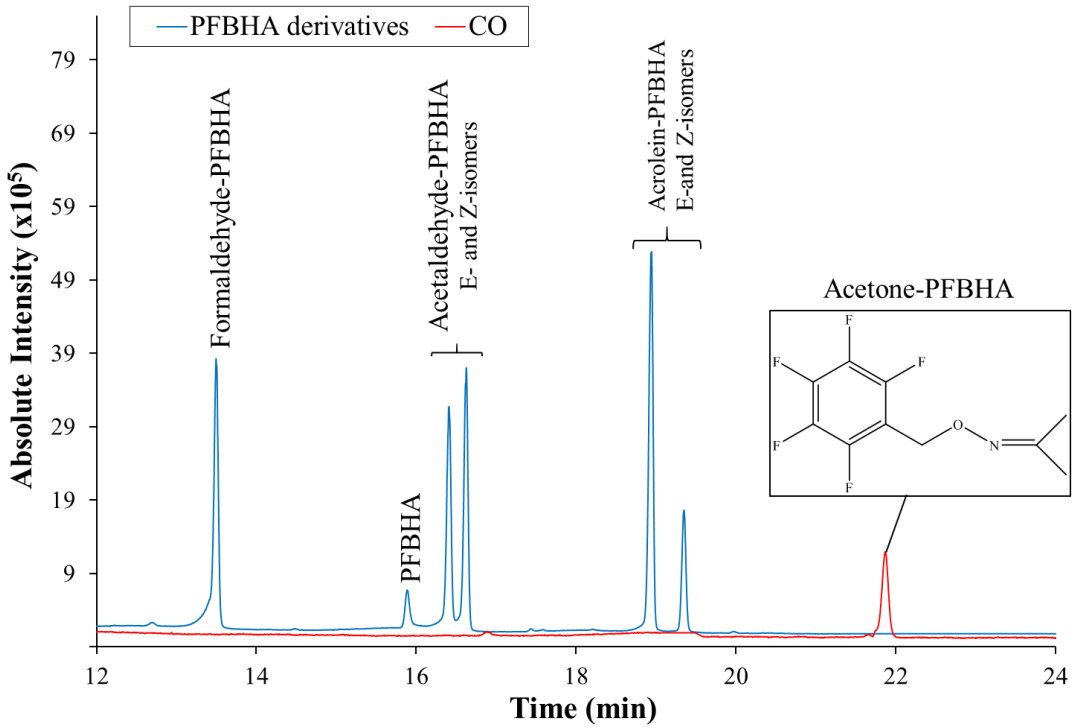

Figure 5.14: GC-MS chromatogram of PFBHA and CO reaction product (TIC)

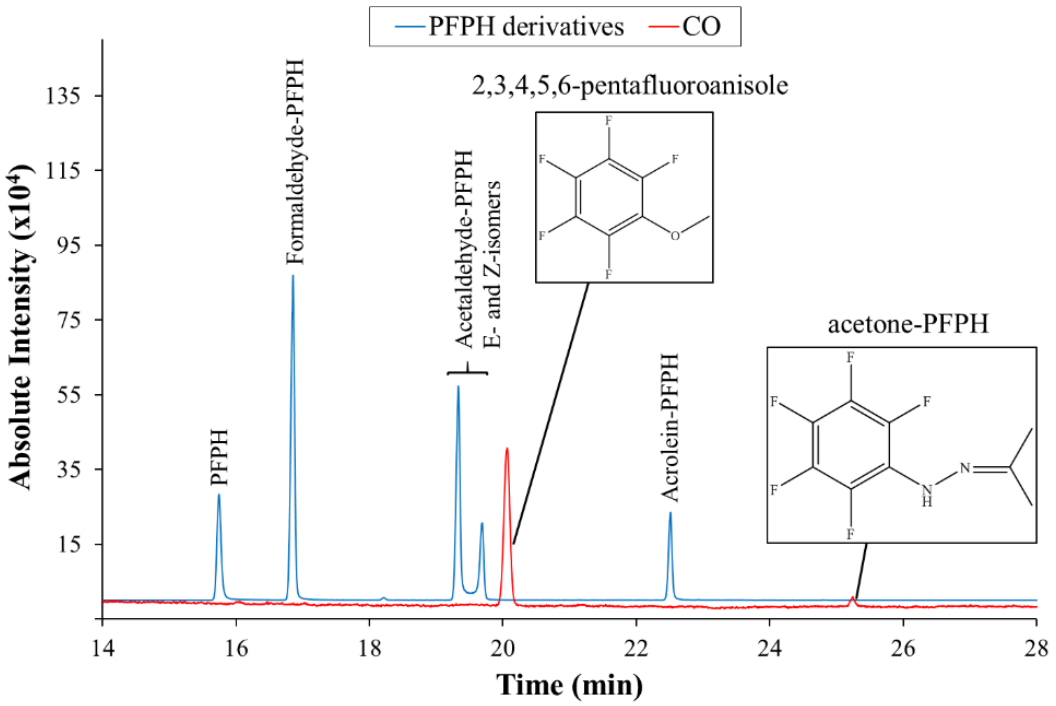

Figure 5.15: GC-MS chromatogram of PFPH and CO reaction products (m/z 155)

CO reacted with PFPH to form two reaction products, which were identified as 2,3,4,5,6-pentafluoroanisole and acetone-PFPH (similarly to the reaction of CO with DNPH and PFBHA). The 2,3,4,5,6-pentafluoroanisole eluted close to the second acetaldehyde-PFPH

isomer, with the resolution calculated as 1.3. As a result, the 2,3,4,5,6-pentafluoroanisole could interfere with the quantification of the concentration of acetaldehyde. The CO reacts with PFPH to form acetone-PFPH, which is problematic if it is necessary to quantify acetone in the air sample.

The reaction of DAIH with CO resulted in two reaction products, as seen in Figure **5.16**. The second peak of the reaction products and the acrolein-DAIH peaks are almost fully resolved (resolution = 1.4). Thus, the CO reaction product may interfere with the quantification of the acrolein concentration if the concentration of the CO is very high in the sample matrix. The reaction products could not be identified using GC-MS, probably due to the low volatility of the compounds.

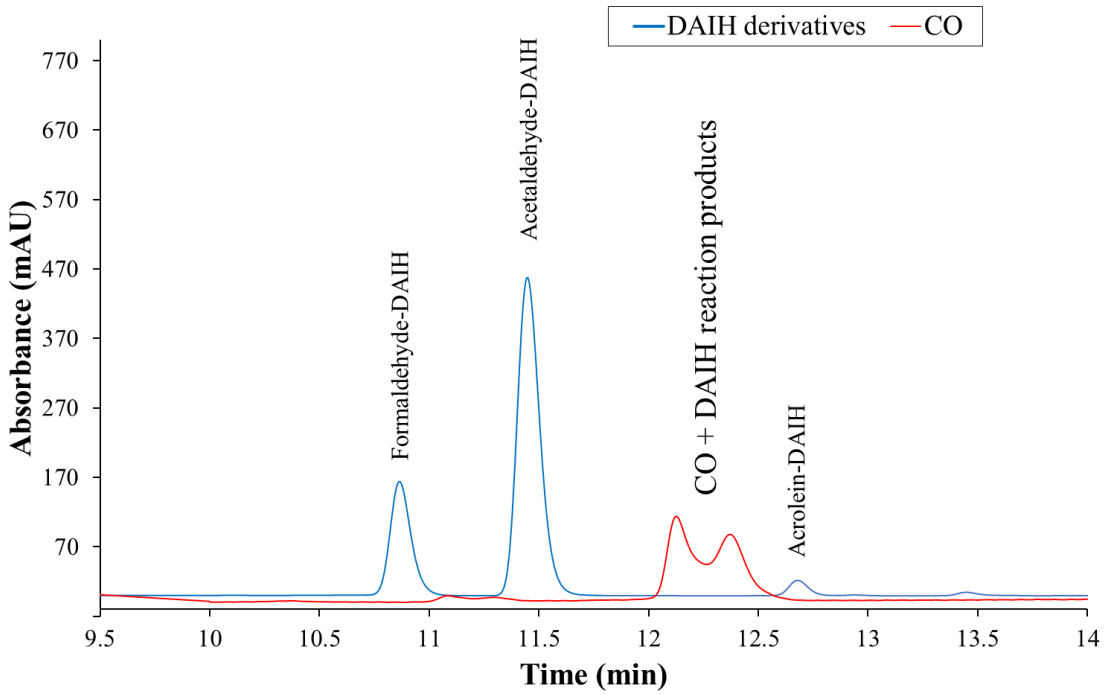

Figure 5.16: HPLC-UV chromatogram of DAIH and CO reaction products

The CO reacted with HBA to form two reaction products, which eluted between the acetaldehyde-HBA and acrolein-HBA isomers (see Figure **5.17**). The peaks were fully resolved from the aldehyde-HBA isomer peaks, and therefore will probably not interfere with the quantification of the aldehyde concentrations in the presence of CO. The CO and HBA reaction products could not be identified using GC-MS, as the compounds are probably not thermally stable.

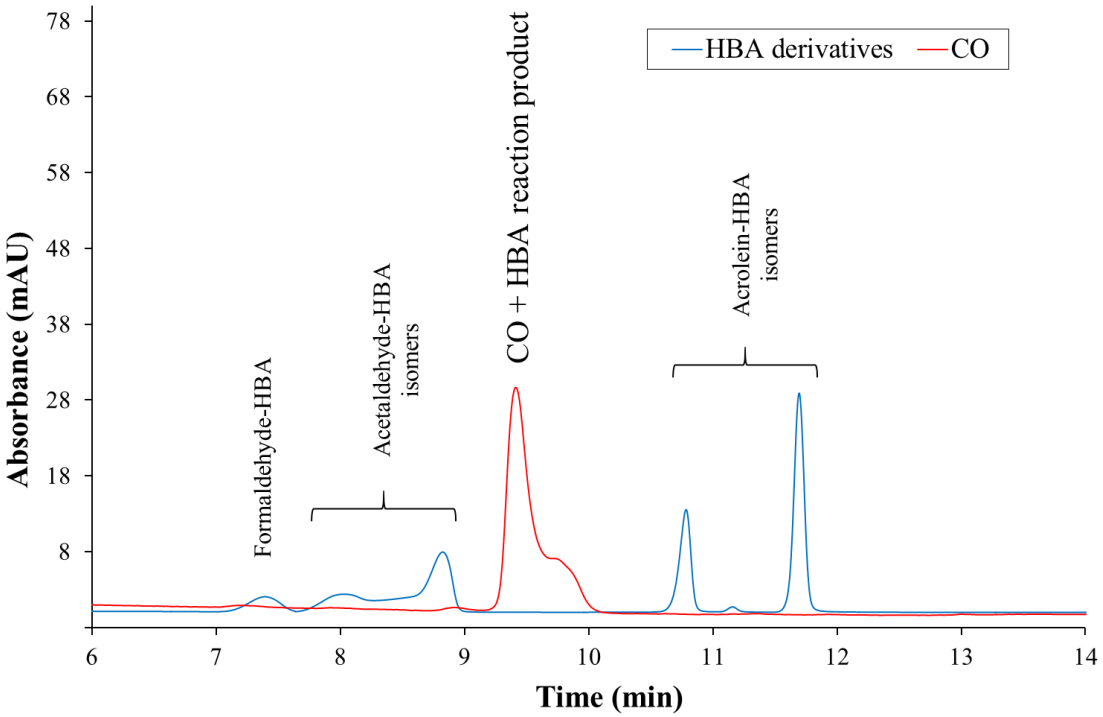

Figure 5.17: HPLC-UV chromatogram of HBA and CO reaction products

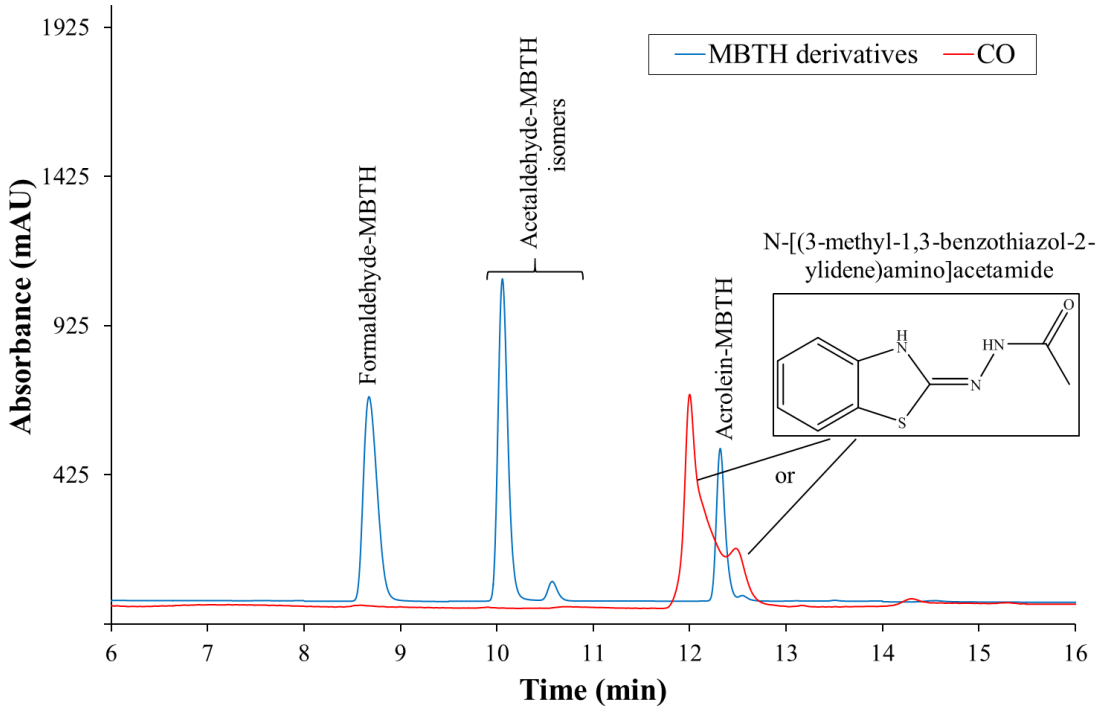

Figure 5.18: HPLC-UV chromatogram of MBTH and CO reaction products

The MBTH reacted with CO to form two reaction products, one of which was identified with GC-MS to be N-[(3-methyl-1,3-benzothiazol-2-ylidene)amino]acetamide. Both the

reaction products interfered with the acrolein-MBTH peak on the chromatogram (Figure **5.18**) and consequently there will be interference from the CO in the sample matrix on the quantification of the acrolein concentration, causing an overestimation of the amount.

The reaction of carbon monoxide with the hydrogen peroxide on the cartridge, results in carbon dioxide, as shown in the reaction equation below.

$$CO + H_2O_2 \rightleftharpoons CO_2 + H_2O \qquad [22]$$

The carbon dioxide formed will dissolve in the water and form carbonic acid (H_2CO_3). The IC method separates the resulting bicarbonate ion from the formate and the acetate peaks as shown in Figure 5.19.

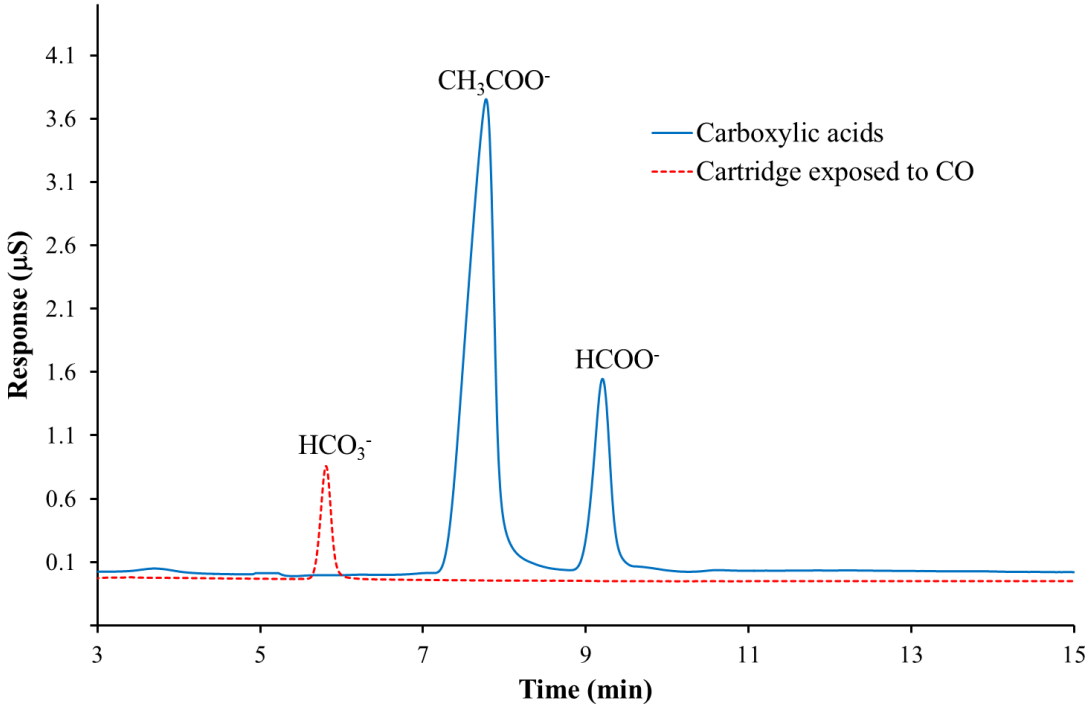

Figure 5.19: IC chromatogram of the anion formed from CO after oxidation

As there is a response for the carbonic acid formed, this method could measure CO with the aldehydes in air samples, if the oxidation of CO is quantitative and the carbonic acid is quantitatively captured on the cartridge.

From the results thus far, HBA and MBTH are not suitable candidates based on the interference of the NO_x and CO reaction products on the quantification of acrolein.

5.3.2.3 Destruction of the derivatisation reagents by NO, NO_2 and CO

It has been established in Section 5.3.2.1 that all the derivatisation reagents react with NO, NO_2 and CO. This reaction results in the destruction of the derivatisation reagent, and this loss needs to be quantified to determine the capacity requirements of the cartridges for the sampling of formaldehyde, acetaldehyde and acrolein in polluted environments.

To determine the destruction of the derivatisation reagents, known masses of each of the gases (Section 3.7.1.1) was pumped through the individually prepared cartridge containing the derivatisation reagent, as described previously in Section 5.3.2.1. The cartridges were eluted with the appropriate solvent, and analysed using either GC or HPLC. The eluent of unexposed cartridges were also analysed, to establish the response of the derivatisation reagent, before reaction. The destruction of the derivatisation reagent was calculated from the difference of the response of the derivatisation reagent peak before and after exposure to each gas. The moles derivatisation reagent destroyed per mole gas for each of the derivatisation reagents is shown in Figure **5.20**.

The amount of destruction of the HBA and the MBTH by NO, NO_2 and CO is extremely high, therefore these derivatisation reagents would rapidly be destroyed during sampling. Each of these derivatisation reagents has a chromatographic interference that also directly interferes with the quantification of acrolein.

DAIH shows the lowest destruction by NO, NO_2 and CO, resulting in the high availability of the derivatisation reagent for reaction with the aldehydes. PFPH has a high reactivity with NO_2, but very low with NO and CO. The PFPH method would therefore possibly have lower capacity for the aldehydes, due to destruction of the derivatisation reagent, in an environment with high NO_2 concentrations. PFBHA has a relatively low reactivity with NO_2 and CO, with a higher reactivity with NO.

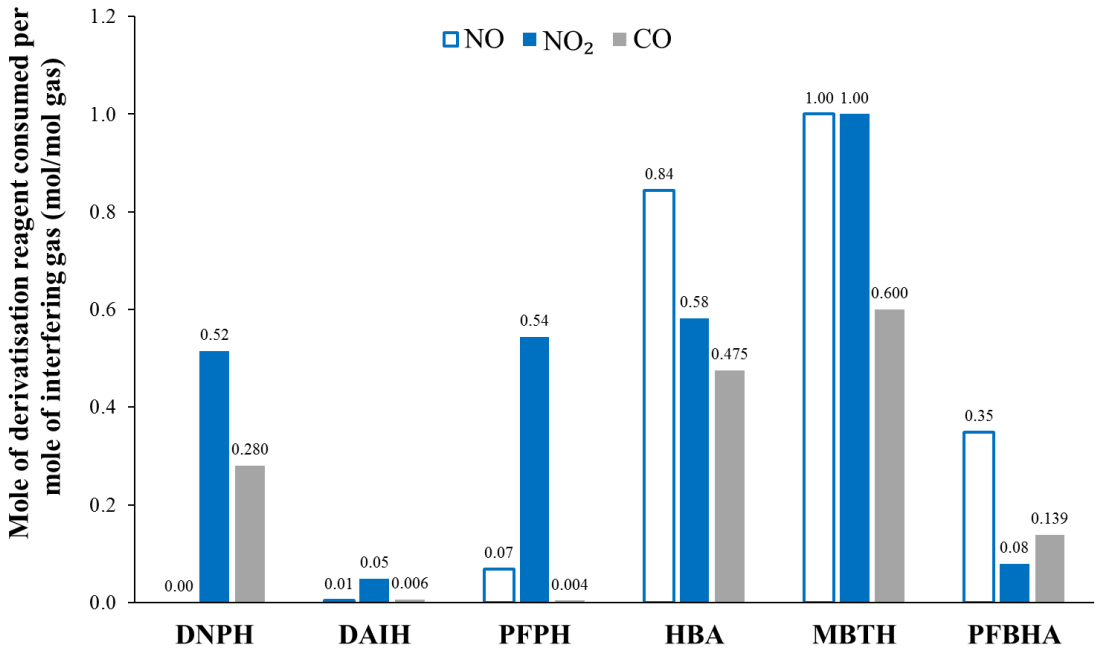

Figure 5.20: Derivatisation reagent destroyed per mole of interfering gas

Similarly to the DNPH capacity equation derived in Chapter 4, similar equations could be derived for each of the derivatisation reagents, using the data in Figure **5.20**, and using the general equation as shown below.

$$m_{DR} = 2 \times Mr_{DR} V_{sample} \left[\left(\frac{C_{CO}}{Mr_{CO}} \times a \right) + \left(\frac{C_{NO}}{Mr_{NO}} \times b \right) + \left(\frac{C_{NO_2}}{Mr_{NO_2}} \times c \right) + \left(\frac{C_{Form}}{Mr_{Form}} \right) + \left(\frac{C_{Acet}}{Mr_{Acet}} \right) + \left(\frac{C_{Acr}}{Mr_{Acr}} \right) \right]$$

[23]

Where:

m_{DR} = mass derivatisation reagent required (mg)

V_{sample} = Total volume of the sample (m^3) (Flow rate (m^3/min) x time (min))

C_x = Expected concentration of the relevant (x) gas (mg/m^3)

Mr_x = Molar mass of the relevant gas (g/mol)

Mr_{DR} = Molar mass of the derivatisation reagent (g/mol)

a, b, c = Moles of derivatisation reagent consumed per mole of the relevant gas

5.3.2.4 Sample stability when using hydrogen peroxide during sampling

The oxidation of the aldehydes to the carboxylic acids on a cartridge containing hydrogen peroxide was achieved, however, the oxidation does continue, and some of the carboxylic acids are also oxidised to form carbon dioxide. The carbon dioxide dissolves in water to form carbonic acid, which is visible on the chromatograms of both the HPLC and IC methods, although at lower concentrations in the acidic solution for the HPLC method.

The stability of the carboxylic acids after sampling is essential for a sampling method to be viable. The acids will be stored and transported on the cartridge to the laboratory before any elution for analysis will take place. The acids must not undergo further oxidation during this time.

The stability of the carboxylic acids on the cartridge was tested by spiking the aldehydes onto a prepared cartridge containing H_2O_2 (Section 3.4.7), which was left for a time and then eluted and analysed immediately. The concentrations in the sample eluted immediately after the spike was used as the base analysis, against which all subsequent concentrations were compared to. The results are shown in Figure **5.21**. These experiments were analysed using the HPLC method and therefore used 1 % phosphoric acid as its eluent.

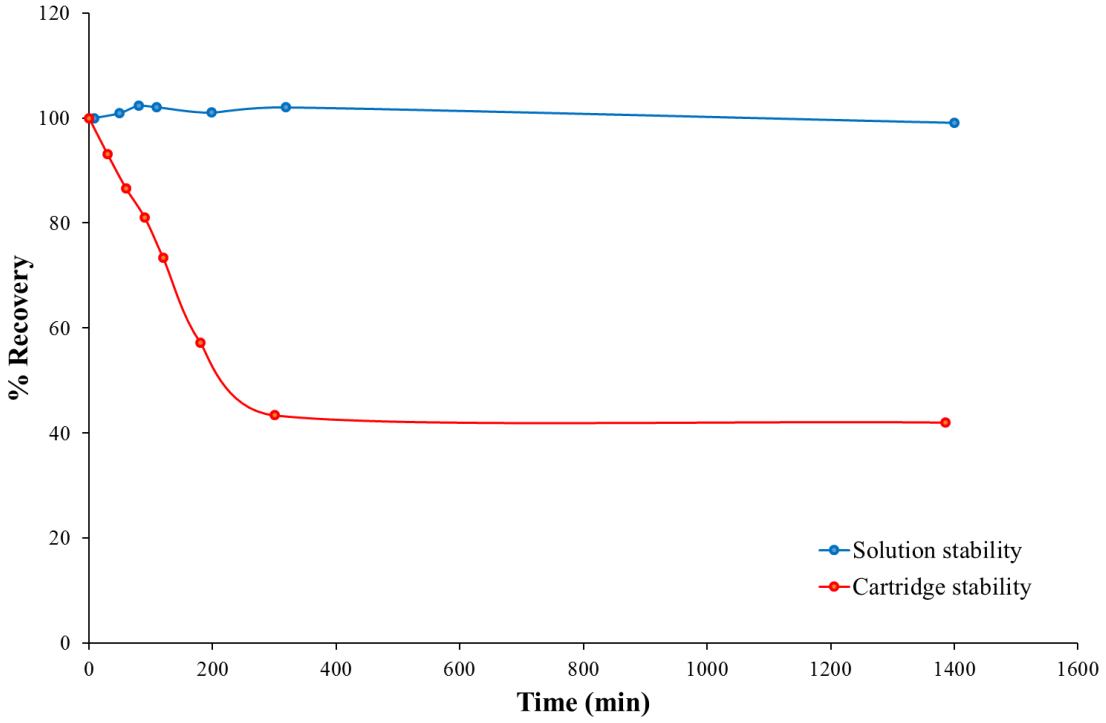

Figure 5.21: Stability of formic acid on the cartridge and in solution during storage

The stability of the carboxylic acids in solution, after elution from the cartridge was also monitored. The solution was stored in a refrigerator and the concentrations of the acids were monitored over time. These experiments were also analysed using the HPLC method. The results are also shown in Figure **5.21**.

Only formic acid was visible on the chromatogram, with the acetic acid completely oxidised. The formic was not stable on the cartridge in the presence of the H_2O_2. The oxidation of the acid continued over time and seemed to stop after 5 hours. This may be due to limited amount of H_2O_2 on the cartridge. The formic acid in solution was stable and did not oxidise further, even after 24 hours. Therefore it will be necessary to elute the carboxylic acids as soon as possible from the cartridge. This method will only be viable if it is possible to control the oxidation reactions on the cartridge. This could be achieved by using a weaker oxidising agent, such as permanganate or copper chloride.

The solution used for the elution of the cartridges was a 1 % H_3PO_4 solution, for HPLC analysis. When the same experiments to monitor the stability of the carboxylic acids was attempted using a basic solution for IC analysis, the results could not be replicated. The oxidation reactions are therefore slower in the acidic environment, although the reaction is probably quenched when using a basic solution for elution. This is contradictory to each other, and will need to be investigated further.

5.3.3 Derivatisation reagents method recoveries of the aldehydes

The derivatisation reagent methods were used to capture the aldehydes from the gas sampling bulb, which was used to determine the method recoveries for each of the derivatisation reagents, as described in Section 3.9. The method recovery is a measure of the accuracy of the method, how close the result is to the true value. The method recoveries for each of the derivatisation reagents are given in Table **5.3**, below.

Table 5.3: Method recoveries for the sampling of aldehydes with the derivatisation reagents

Derivatisation reagent	Method recovery (%)		
	Formaldehyde	Acetaldehyde	Acrolein
PFPH	19.9	41.4	24.2
PFBHA	95.0	100	55.9
HBA	14.8	51.0	0
MBTH	22.2	36.2	19.6
DAIH	94.7	69.6	66.8

The only reasonable method recoveries for the derivatisation reagents are for PFBHA and DAIH, as they both have recoveries of over 50 % for acrolein. Although the recovery of acrolein by PFBHA is not as high as DAIH, the recoveries of formaldehyde and acetaldehyde by PFBHA are very high, and therefore the PFBHA is favoured above all the derivatisation reagents, with regards to aldehyde method recoveries.

5.4 Conclusion

A summary of the interference results is given in Table **5.4**. The summary shows the amount of peaks seen for each of the acetaldehyde- and acrolein-derivatives, along with the number of reaction products with NO, NO_2 and CO. Formaldehyde only formed one derivative with each derivatisation reagent, and therefore was not included in the table. The DNPH data was included for comparative purposes.

Acetaldehyde forms the E- and Z-isomers with each of the derivatisation reagents, except with DAIH, probably due to steric hindrance of the derivatisation reagent, allowing for only one isomer to form.

Acrolein is very reactive and therefore readily reacts with the derivatisation reagents, however, with some reagents, the acrolein derivative is still reactive and will therefore react with other molecules available in the sample. This was seen for HBA and DAIH.

Table 5.4: Summary of the chromatographic results

Derivatisation reagent	Analysis technique	Number of peaks observed		Reaction products with gases		
		Acetaldehyde	Acrolein	NO	NO_2	CO
DNPH	HPLC	2	4	0	6	1
DAIH	HPLC	1	3	2	2	2
HBA	HPLC	2	3	2	2	2
MBTH	HPLC	2	2	2	2	2
PFPH	GC	2	1	2	2	2
PFBHA	GC	2	2	1	1	1

NO, NO_2 and CO react with all of the derivatisation reagents. The reaction products formed may interfere with the aldehyde quantification. These gases also destroy the derivatisation reagents, to varying degrees, as was shown in Section 5.3.2.3. The NO_2 and NO reaction products interfere with the aldehyde-derivative peaks for DAIH and HBA.

Only the MBTH aldehyde-derivatives were affected by the CO reaction product with MBTH.

This chapter has investigated how the derivatisation reagents are affected by the polluting gases, NO NO_2 and CO, which gives information for the fourth criterion in Figure **5.1**.

The HBA derivatisation reagent should not be considered further in this study, due to the multiple peak formation with acrolein, as well as the direct interference of the NO_2 reaction products on the quantification of the acrolein concentration using this method. DAIH forms at least one adduct with acrolein, and is an expensive derivatisation reagent and therefore, DAIH will not be considered further in this study. MBTH has a high reactivity with NO, NO_2 and CO, and has an interference of the CO reaction product on the quantification of acrolein. The MBTH derivatisation reagent will also no longer be considered for this study.

Due to time constraints, developing a method by oxidising the aldehydes for the sampling and analysis of aldehydes in air with hydrogen peroxide, was not possible. At this stage the method has several flaws, as the oxidation of the aldehydes to the carboxylic acids is not controlled, resulting in a loss of the aldehydes from the cartridge. However, if the method is successful, it may be possible to determine the aldehydes, NO_x and CO simultaneously. The method could be improved by using less hydrogen peroxide, or using a weaker oxidising agent, such as $KMnO_4$ or $CuCl_2$. The pH of the elution solvent seems to also play a major role in the control of the oxidation of the aldehydes, as well as the resulting carboxylic acids, and this needs to be investigated further. The method may also benefit from choosing a sorbent material for the capture of the aldehydes.

The method would also be relatively cheap compared to the derivatisation methods, and is greener because no organic solvents are used for sample preparation or analysis.

The derivatisation reagents that still can be considered are PFPH and PFBHA. Based on method recoveries, as determined in Section 5.3.3, PFBHA is the method of choice, as it has the highest method recoveries. The next chapter will describe the optimisation of the method, as well as give a description of the analytical performance of the method final method.

Chapter 6
Developing a new robust method for the sampling and analysis of aldehydes in a polluted environment

6.1 Introduction

The derivatisation reagent PFBHA was chosen to replace DNPH, due to its lower reactivity with NO, NO_2 and CO with minimal interference from the reaction products, and a stable derivative with acrolein. The next step would be to determine which sorbent would be optimal for the capture and retention of formaldehyde, acetaldehyde and acrolein. Silica gel serves as an effective sorbent for the capture of the aldehydes of interest, in the DNPH method for the analysis of formaldehyde and acetaldehyde. However, the silica gel may not be effective in capturing the acrolein.

In this chapter several sorbents for the capture of formaldehyde, acetaldehyde and acrolein from air samples will be evaluated. The performance of the sorbent will be measured by how well a given amount of the aldehydes are retained, which is measured by the collection efficiency.

The study includes the use of a hydroquinone coated silica gel cartridges. The reactivity of hydroquinone towards NO, NO_2 and CO will be studied and any artefacts formed will be identified, and if these compounds interfere chromatographically with the aldehyde quantification. Thereafter the post-sampling derivatisation with the derivatisation reagents will be tested to ensure that the aldehydes are able to react with the derivatisation reagent and the aldehyde derivatives are completely recovered from the cartridge for analysis.

The final method, where the best performing sorbent and derivatisation reagent are combined onto one cartridge, will be evaluated. The analytical performance of the method will be determined and compared with the performance of the DNPH method, to determine if the method is fit for the purpose of sampling and analysing the aldehydes in air in polluted environments.

The stability of the sample stored on the cartridge, as well as in the eluent after desorption will be determined as a final insight of the method performance. Finally, the cost of the analysis method will be determined, and compared to the DNPH method.

6.2 Collection efficiency of various sorbents

The sorbent material in the sampling cartridge plays the most important role in the sampling of analytes. The sorbent is used to capture the analyte from the sampled air and retain the compounds during transport and storage of the sample. The sorbent may also be coated with a derivatisation reagent, which would react with the analyte for analysis with HPLC or GC. The sorbent needs to retain the resulting derivatives until desorption for analysis can take place, and should not form artefacts with any of the analytes, derivatisation reagent, or compounds in the sample matrix[159].

Other sorbents commonly used are charcoal, alumina, molecular sieves, and porous polymers. Sorbents are useful for pre-concentration of the analyte, where a time-weighted average is required, or where the concentration in the sample is too low and a larger sample is necessary to reach the required analytical sensitivity[184].

Seven sorbents were chosen for the evaluation of the capture of formaldehyde, acetaldehyde and acrolein (Table 6.1). Tenax TA, is a porous polymer which is inert and hydrophobic. It is the most popular sorbent for thermal desorption techniques, although the sorbent only captures from n-hexane up to n-C_{26}+. Two graphitised carbon black sorbents were chosen, Carbograph 4TD and 5TD. These are non-specific carbon sorbents that have minimal artefact levels, and can therefore be used for trace analysis. However, the graphitised carbon black sorbents are less suitable for labile and highly reactive compounds, such as acrolein. A carbonised molecular sieve was chosen, Carboxen 1003, which is recommended for air monitoring. The molecular sieve is one of the strongest sorbents, ideal for trapping volatile compounds. A zeolite molecular sieve, 5Å, was chosen as it is a strong sorbent usually used for nitrous oxide monitoring. Silica gel was included with the group of sorbents for evaluation as it is the sorbent used for DNPH sampling.

Hydroquinone is used in acrolein standards to stabilise the compound to prevent polymerisation. Hydroquinone has also successfully been used on a cartridge for the removal of ozone, instead of the KI cartridge, during the sampling of aldehydes with DNPH[94]. Also, the hydroquinone coated cartridge has been shown to capture acrolein in air samples as well as formaldehyde and acetaldehyde[96].

If a hydroquinone coated cartridge is chosen as the optimal sorbent for the sampling method, the reaction of hydroquinone with NO, NO_2 and CO will also need to be evaluated.

Table 6.1: Sorbents and their characteristics

Sorbent	Sorbent strength	Material type	Analyte volatility range	Characteristic
Tenax TA	Weak	Porous polymer	n-C_6 – n-C_{30}	• Hydrophobic • Suitable for labile components • Higher artefact levels
Carbograph 4TD	Medium	Graphitised carbon black	n-$C_{4/5}$-n-C_{12}	• Non specific • Minimal artefact • Fairly hydrophobic • Not 100 % inert
Carbograph 5TD	Medium-Strong	Graphitised carbon black	n-$C_{3/4}$-n-$C_{6/7}$	• Non specific • Minimal artefact • Fairly hydrophobic • Not 100 % inert
Carboxen 1003	Strong	Carbonised molecular sieve	C_2 – n-$C_{5/6}$	• For most volatile compounds • Adsorption and molecular sieve principle • Not hydrophobic • Easily contaminated by higher boiling compounds
Molecular Sieve 5Å	Very strong	Zeolite molecular sieve	Permanent gases and N_2O	• Selective • Hydrophilic • High artefacts
Silica gel	Strong	Silica	Low boiling polar compounds	• Used for DNPH method
Hydroquinone coated silica gel	Strong	Hydroquinone and silica	C_1 – C_3	• Shown to adsorb C_1-C_3 aldehydes

The sorbent collection efficiency was tested by taking the packed cartridges (ca. 0.3 g of sorbent in a thermal desorption cartridge, as described in Section 3.4.6) and connecting a PFBHA cartridge after the sorbent cartridge. The purpose of the PFBHA cartridge was to capture any aldehydes that were not captured by the sorbent material in the packed cartridge. The set of cartridges was connected to the gas bulb, which contained a known

amount of the three aldehydes (described in Section 3.7.2). The capturing efficiency was calculated as follows:

$$Aldehyde\ capture\ efficiency = \left[1 - \frac{Mass\ \ on\ PFBHA\ cartridge}{Mass\ loaded\ in\ bulb}\right] \times 100\ \% \qquad [24]$$

The capturing efficiency results for each of the sorbents are summarised in Figure 6.1. Formaldehyde was acceptably captured (>75 %) by Carboxen 1003, the molecular sieve, Carbograph 4TD, and the silica gel coated with both DNPH and hydroquinone. Only the hydroquinone coated silica gel cartridge captured the formaldehyde to the preferred level (>90 %). Capture of acetaldehyde by the sorbents were poor, except by the DNPH and hydroquinone silica gel cartridges. Acrolein was captured by the Carboxen 1003 and silica gel coated with hydroquinone at acceptable levels.

The Carbograph 5TD had very low collection efficiencies for each aldehyde, as it is not specific for aldehydes. The capture of formaldehyde and acetaldehyde by Tenax TA had a high variation as it is not a strong adsorbent of the volatile compounds. The Tenax TA adsorbent captures organic compounds with 6 or more carbon atoms.

The capture efficiency results for the silica gel indicated that a low capture efficiency of acrolein by the sorbent also contributes to the low acrolein recoveries seen for the DNPH method (Chapter 4). The low result for acetaldehyde may be the reason for the low collection efficiencies for sampling longer than 6 hours[111], as discussed in Section 2.4.7. These low sorbent recoveries by the silica gel, combined with the reversible DNPH reaction could possibly explain the phenomenon that was seen for acetaldehyde with the DNPH method. The reaction of formaldehyde and acetaldehyde with DNPH therefore aids in the capture of the aldehydes on a silica gel sorbent.

Although the Carboxen 1003 is used for air monitoring it did not capture acetaldehyde and showed a large variance on the capture of acrolein. The sorbent of choice therefore would be the silica gel coated with hydroquinone. Since hydroquinone could be reactive with NO, NO_2 and CO, it is now necessary to investigate the reactions of hydroquinone with these gases. The investigation follows in Section 6.4.

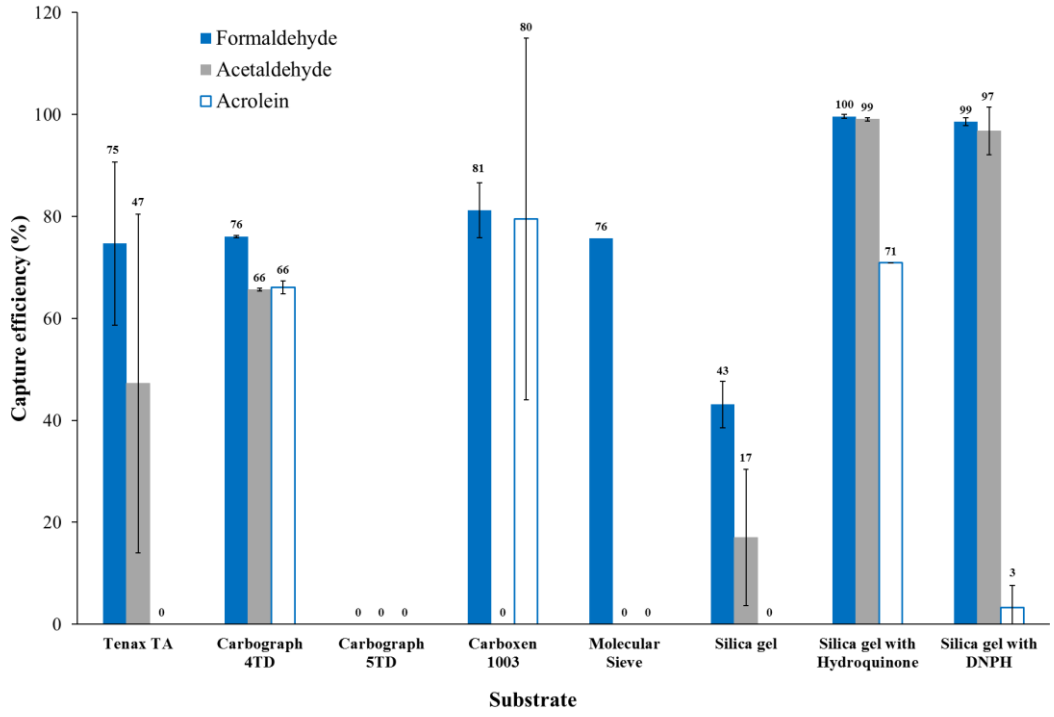

Figure 6.1: Sorbent capture efficiency of the aldehydes

6.3 Recovery of the aldehydes from the hydroquinone cartridge using various derivatisation reagents

A good collection efficiency needs to be complemented by a good recovery of the aldehyde derivatives from the cartridge. The aldehydes will be derivatised post sampling for detection and analysis on HPLC or GC. The sample preparation before analysis will therefore include a derivatisation step using a suitable derivatisation reagent. Although PFBHA is the derivatisation reagent of choice (Chapter 5), the interference from NO, NO_2 and CO have been removed by the hydroquinone on the cartridge, as well as the post sampling derivatisation step, making it possible to use any derivatisation reagent.

To determine the recovery of the aldehydes from the hydroquinone cartridge after derivatisation, silica gel cartridges coated with hydroquinone were spiked with a known amount of a mixture of aldehydes in solution. The aldehydes were derivatised on the cartridge by adding the derivatisation reagent to the cartridge and left to react, as described in Section 3.8. The reaction time was 3 hours, as it should have given enough time for all the derivatisation reagents to completely react with the aldehydes, except for PFPH, which has a reaction time of 3 days (Section 5.2.5). The aldehyde derivatives were

desorbed with an appropriate solvent (Section 3.6) and the solutions were analysed using HPLC or GC. The results are presented in Figure 6.2.

The recovery of the aldehyde-HBA derivatives were all below the acceptable level (75 %), and therefore is not suitable for this method. Both PFPH and DAIH had poor recoveries for two of the three aldehydes, and therefore are also not suitable for the method. The low recovery of PFPH is probably due to the incomplete derivatisation reaction. MBTH had good recoveries for all the aldehydes with the recoveries for formaldehyde and acetaldehyde higher than 98 %, with acrolein recovery at 81 %. However, PFBHA once again is the derivatisation reagent of choice, as the recoveries for formaldehyde, acetaldehyde and acrolein were all above 96 %.

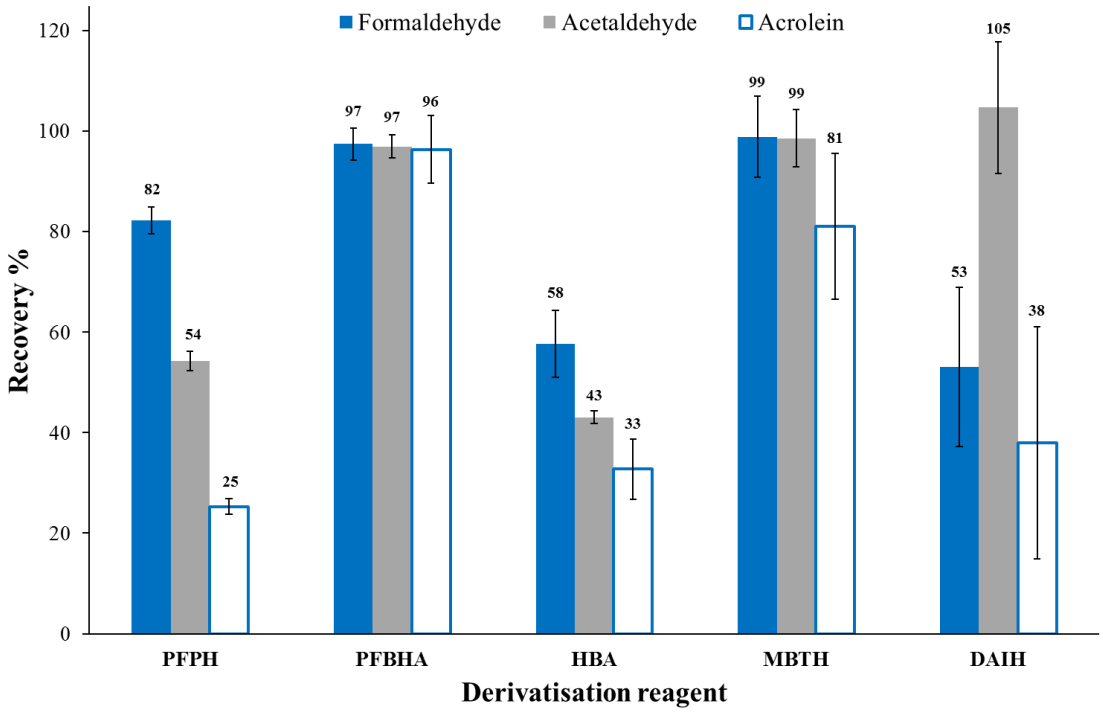

Figure 6.2: Influence of the presence of hydroquinone on the recovery of aldehyde derivatives after 3 hours

6.4 Reaction of hydroquinone with NO, NO_2 and CO

The possibility of hydroquinone reacting with NO, NO_2 and CO during sampling in a polluted environment exists. Consequently, it is necessary to establish whether the reaction with the gases would, in fact, occur, and subsequently quantify the consumption

of hydroquinone by the gases. Also, if these gases do react with the hydroquinone, it is necessary to determine if these compounds would co-elute with any of the aldehyde-PFBHA derivatives on the GC-MS chromatogram, and therefore cause an overestimation of any of the aldehyde quantities.

Cartridges coated with hydroquinone were attached to the outlet of the gas bulb and the experimental procedure described in Section 3.7.1 was followed. The hydroquinone cartridge was eluted afterwards, and the eluent was injected onto the GC-MS. The resulting chromatogram for the reaction of NO_2 with hydroquinone is shown in Figure 6.3. The hydroquinone reacted with NO_2 to form p-benzoquinone, and 2-nitrobenzene-1,4-diol as indicated in the chromatogram. No reaction products were observed for the reaction of NO and CO with hydroquinone. Hydroquinone only reacts with NO_2 and therefore makes it necessary to determine the consumption of the hydroquinone by nitrogen dioxide.

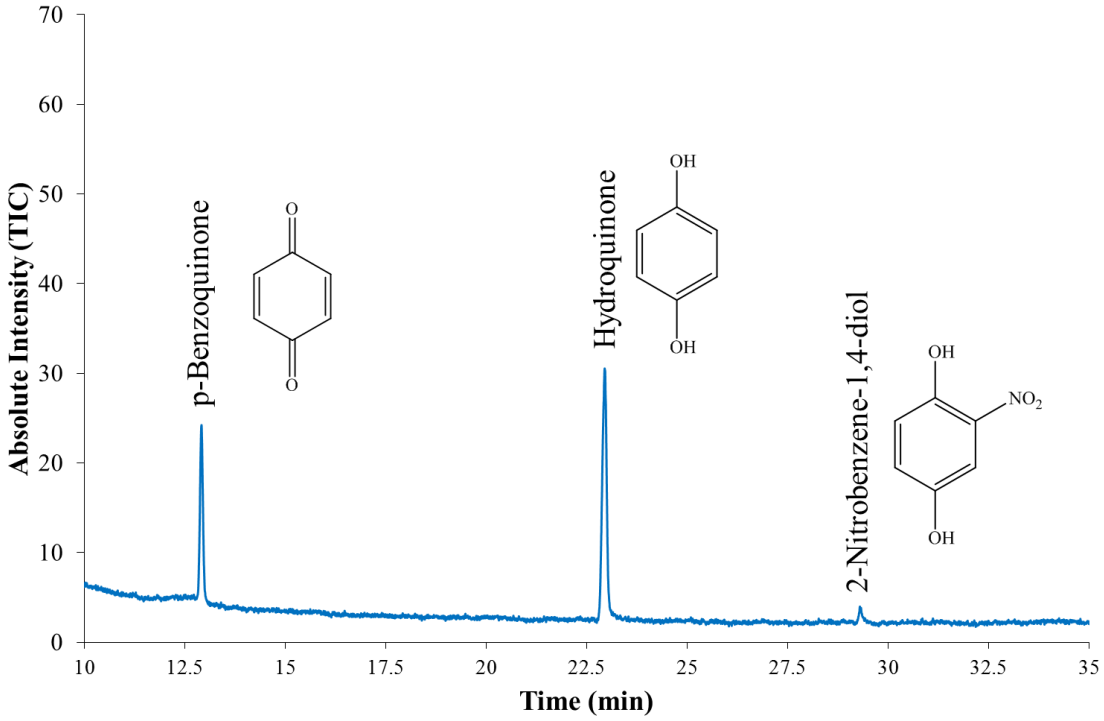

Figure 6.3: GC-MS chromatogram of hydroquinone and its reaction products with NO_2 (TIC)

The NO_2 gas acts as an oxidising agent to oxidise the hydroquinone to para-benzoquinone, NO and water, according to the reaction shown in Figure 6.4. The small amount of water formed could dissolve small amounts of the nitrogen dioxide to form a

dilute nitric acid solution. The nitric acid in turn also reacts with hydroquinone by substitution of the phenol in the ortho position[1, 185](Figure 6.4).

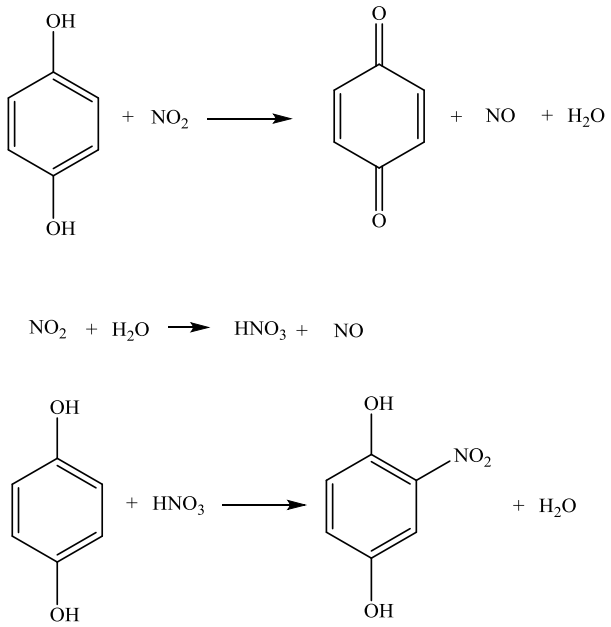

Figure 6.4: Reaction of NO_2 with hydroquinone

6.5 Advantages of using hydroquinone as part of the sorbent material

Hydroquinone has been shown to enhance the collection efficiency of the silica gel in the capture of acrolein. Hydroquinone is an antioxidant and is used to stabilise acrolein, so that no polymerisation takes place, resulting in fewer reaction products with the derivatisation reagents. Hydroquinone has been used as an alternative to the KI cartridge for the effective removal of ozone from air samples, prior to the DNPH cartridge[94]. Hydroquinone reacts with NO_2, therefore it may be possible to quantify NO_2 simultaneously with the aldehydes, by measuring the reaction product, p-benzoquinone, using GC-MS.

Hydroquinone does not react with the aldehydes, and only acts as an adsorbent for the aldehydes during the sampling step of the method. The consumption of hydroquinone by NO_2 may therefore not affect the capacity of the cartridge for the aldehydes. This will be investigated in the following chapter, during the simulated polluted environment tests.

The use of the hydroquinone coated cartridge for the sampling of the aldehydes means that any derivatisation reagent can be used in the derivatisation step. The derivatisation reagent will not be exposed to NO_2, and therefore this interference is removed from the analysis method. The chosen derivatisation reagent is PFBHA due to its lower reactivity

towards the gases, and minimal interferences from the reaction products. In Section 6.3, all the derivatisation reagents were evaluated to determine whether a full recovery of the aldehydes from the cartridge was possible after derivatisation. Using PFBHA and MBTH as derivatives after sampling with hydroquinone gave the best aldehyde recovery results, however PFBHA was the only derivative to give an almost full recovery of acrolein.

6.6 Combining HQ with PFBHA

Combining the hydroquinone coated silica gel sorbent with a coat of PFBHA for derivatisation during sampling presents several advantages. Firstly, it reduces the sample preparation time required, by eliminating the post-sampling derivatisation step. Secondly, less sample preparation steps also reduce the amount of errors introduced during the handling of the samples. Finally, the introduction of the PFBHA may improve the recovery of acrolein because the PFBHA reacts with acrolein to form a stable derivative. From the literature review (Section 2.5.7) it was noted that PFBHA eluted between the formaldehyde- and acetaldehyde-PFBHA derivatives[131]. Therefore the amount of PFBHA that can be loaded on a cartridge will be limited, thus limiting the capacity. By combining the hydroquinone and PFBHA on one cartridge, a higher capacity should not be necessary.

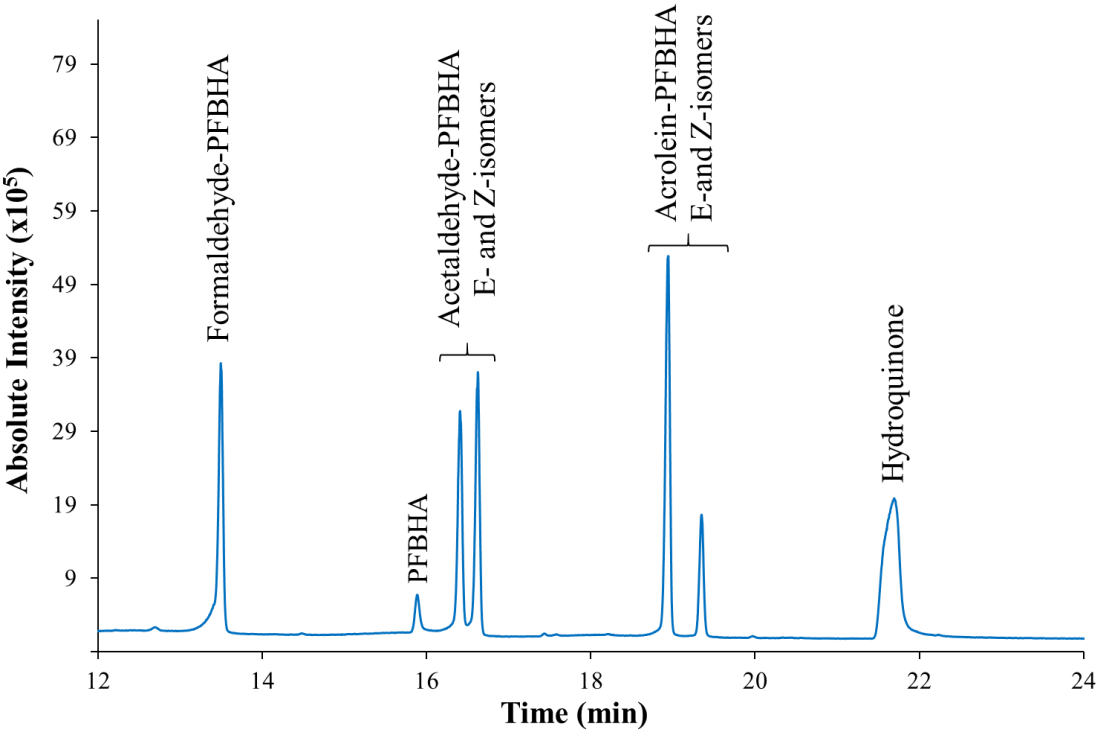

Figure 6.5: GC-MS chromatogram of the aldehyde-PFBHA derivatives with hydroquinone

To be able to combine the two methods in one step, it is necessary to ensure that the compounds are separated from each other. The GC-MS chromatogram showing the aldehyde-PFBHA derivatives along with hydroquinone is shown in Figure 6.5. The hydroquinone peak is fully separated from the aldehyde-derivatives and would therefore not cause interference on the quantification of the aldehydes.

The reaction product of NO_2 with hydroquinone, p-benzoquinone, contains two carbonyl functional groups, which could react with PFBHA or any other derivatisation reagent used. The hydroquinone cartridge that was exposed to NO_2, and therefore contained the benzoquinone was eluted and allowed to react with PFBHA. The resulting mixture was analysed with GC-MS to determine if p-benzoquinone reacted with PFBHA. No reaction product between p-benzoquinone and PFBHA was observed.

The chromatogram of the hydroquinone reaction products with NO_2 was compared with the chromatogram of the aldehyde-PFBHA mixture, as shown in Figure 6.6. Hydroquinone and its reaction products do not co-elute with any of the aldehyde-PFBHA derivatives, and therefore do not interfere with the quantification of the aldehydes.

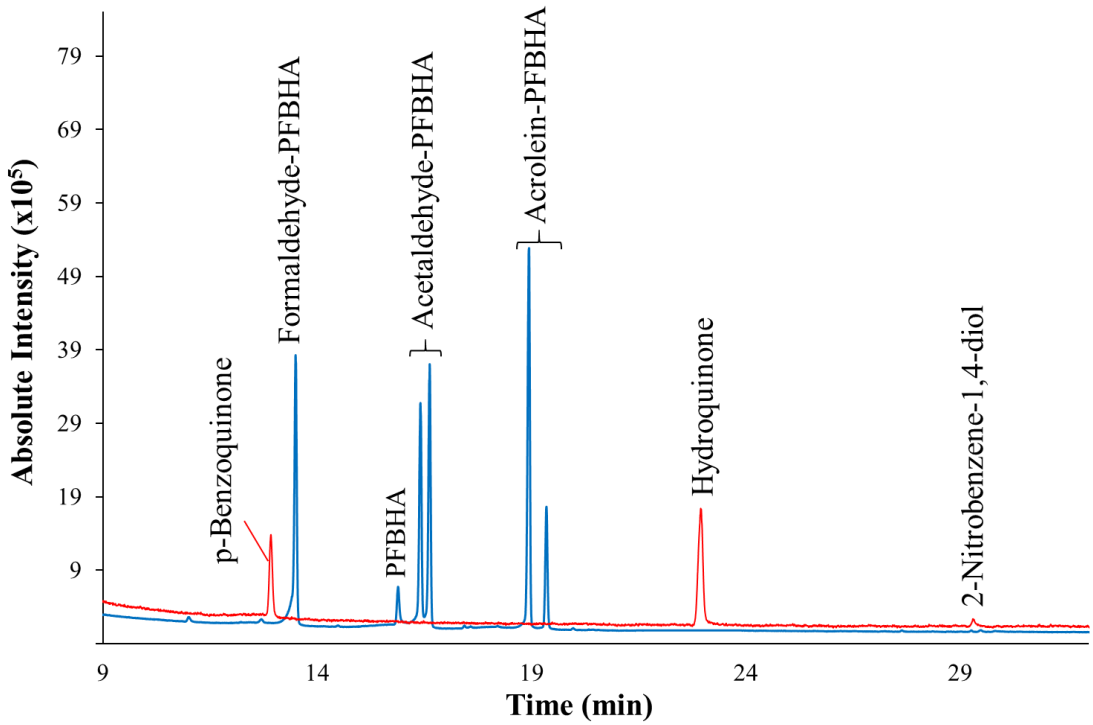

Figure 6.6: Comparison of the GC-MS chromatograms for the hydroquinone reaction products with the aldehyde-PFBHA derivatives

The consumption of hydroquinone by NO_2 was determined as was previously done to determine the consumption of the derivatisation reagents in Chapter 5, and as described in Section 3.7.1.1. NO_2 destroyed 0.51 mol of hydroquinone per mol of NO_2.

The hydroquinone cartridge may be very useful in the sampling of aldehydes in polluted environments, due to the reaction of hydroquinone with NO_2. The possibility of using a hydroquinone cartridge to remove NO_2 from the sample matrix was tested by connecting a hydroquinone cartridge to the outlet of the gas bulb, with a DNPH cartridge connected to act as a breakthrough cartridge. NO_2 gas was pumped through the cartridge at a flow rate of 0.5 L/min as described in Section 3.7.1.1. If any NO_2 was not captured by the hydroquinone cartridge and broke through, the NO_2 would react with the DNPH, and form DNPA, as described in Section 2.4.2. The HPLC analysis of the DNPH cartridge showed no evidence of any formation of DNPA and therefore the capture efficiency of NO_2 on a hydroquinone cartridge is 100 %. The hydroquinone cartridge will be effective in removing NO_2 from the sample matrix.

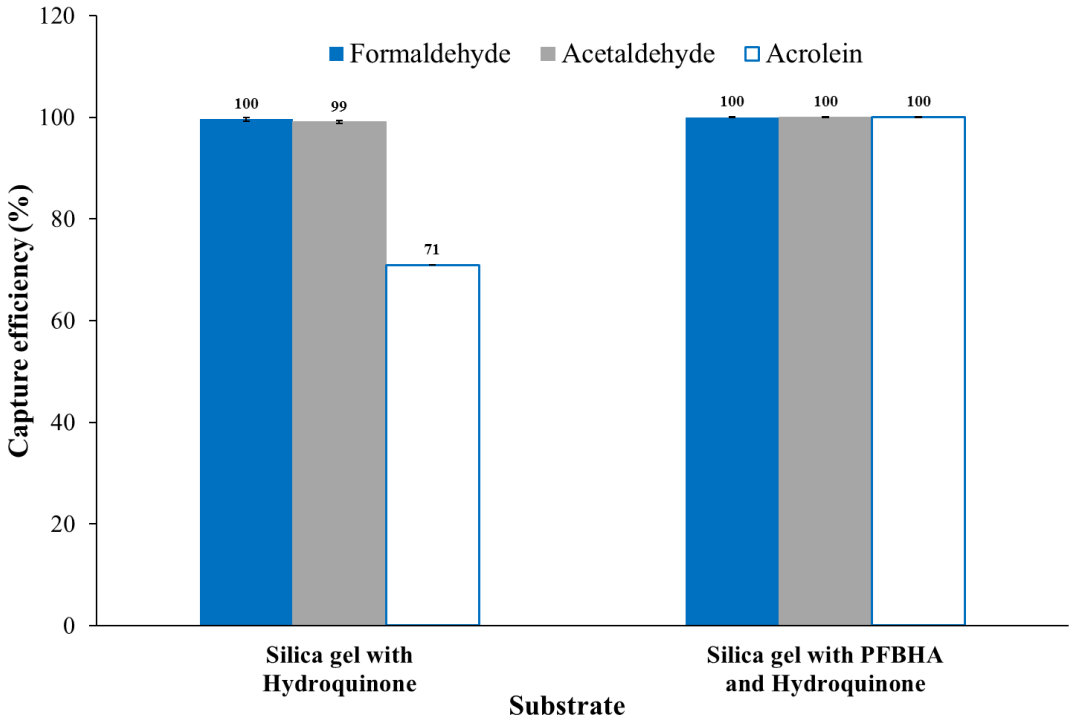

Figure 6.7: Comparison of collection efficiencies of prepare cartridges

Silica gel cartridges coated with a combination of hydroquinone and PFBHA were prepared as described in Section 3.4.5. To determine if the combination of hydroquinone and PFBHA would be more effective in the capture of acrolein, the collection efficiency

of the newly prepared cartridge was determined as described in Section 3.3.6. The results in Figure 6.7 show that the collection efficiency for formaldehyde and acetaldehyde was still effective. The lower method recovery for acrolein is due to the collection efficiency of the sorbent, as the recovery from the cartridge is 96.4 % and the acrolein-PFBHA derivative is stable, as shown in Chapter 5.

The combination of PFBHA with the hydroquinone coated onto the silica gel improved the acrolein collection efficiency to 100 %. This method is therefore the best method for the sampling of the formaldehyde, acetaldehyde and acrolein. The next step would be to validate the method and determine the performance of the method, which is discussed in the following section.

6.7 Determining the optimum derivatisation reaction time for post-sampling derivatisation

The method at this point involved the capture of the aldehydes using the hydroquinone cartridge, followed by the addition of PFBHA to derivatise the captured aldehydes, and subsequent elution of the aldehyde-PFBHA derivatives into a solution for analysis using GC-MS. Hydroquinone acts as an inhibitor of reactions and therefore may slow down the reaction of the aldehydes with the PFBHA. The reaction time of the aldehydes with PFBHA in the presence of hydroquinone needs to be established, so that sufficient time is given for complete reaction with PFBHA, otherwise an error in the results will occur.

A mixture of aldehydes was sampled onto the hydroquinone cartridges using the gas bulb, after which the cartridges were spiked with PFBHA, and allowed to react. After increasing amounts of time the cartridges were desorbed and analysed using GC-MS. The response of the GC-MS was followed for each of the aldehyde-PFBHA derivatives, as shown in Figure 6.8.

The reaction of formaldehyde and acetaldehyde with PFBHA was complete after 20 minutes. This reaction time is approximately the reaction time that has been reported in literature (15 minutes[139]). Acrolein takes slightly longer, with a constant response of the GC-MS after 90 minutes. The sampling could therefore be performed using the hydroquinone-coated silica gel cartridges, followed by PFBHA derivatisation reaction in the laboratory for 90 minutes, after which the sample could be desorbed and analysed with GC-MS.

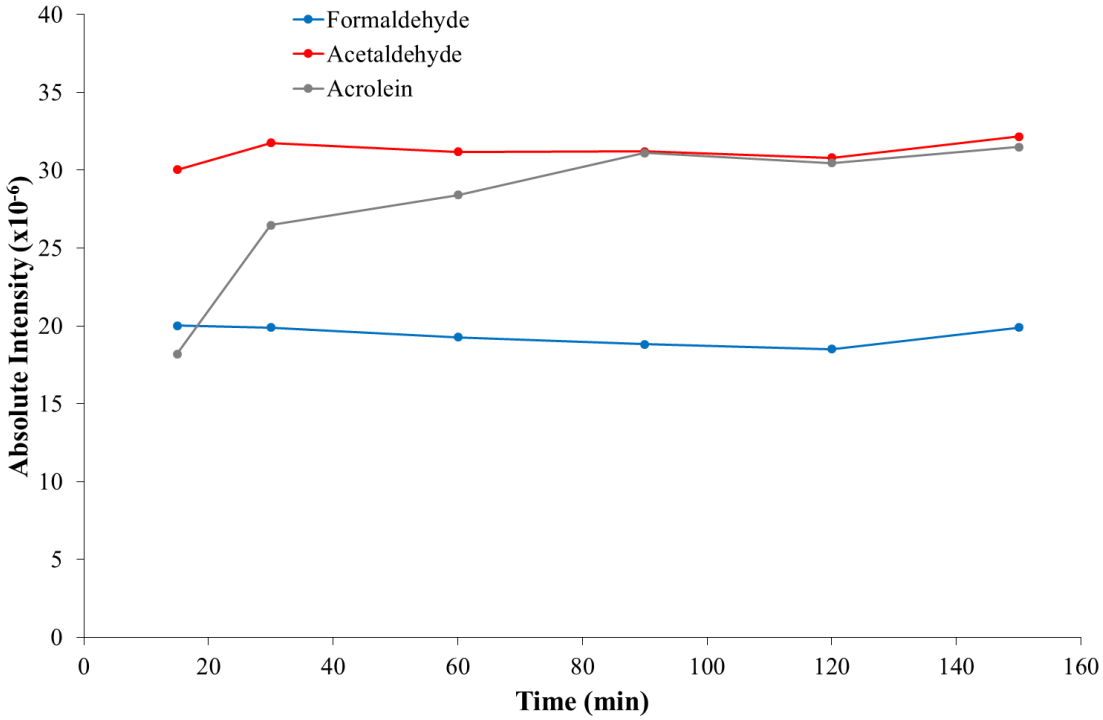

Figure 6.8: Reaction time of the aldehydes with PFBHA in the presence of hydroquinone

6.8 Description of the new method using a cartridge coated with PFBHA and hydroquinone

The final method for the sampling and analysis of the aldehydes in polluted environments involves the use of a silica gel cartridge which is coated with a mixture of PFBHA and hydroquinone as described in Section 3.4.5. The air is sampled by using a pump to draw the air through the two cartridges (analysis, and breakthrough) at a given flow rate (0.5 – 2.0 L/min), for 8 hours. The cartridges are disconnected from the pump and capped after sampling, and taken to the laboratory. The aldehydes react with the PFBHA on the cartridge, and are eluted using 5 mL of acetonitrile. The eluent is place in a GC vial, and the samples is injected onto a GC-MS for quantification. A sample volume of 1 µl with a 1.0 split is injected onto the GC column (Agilent DB5-MS (5% phenyl arylene polymer) 25 m x 0.25 mm I.D. x 0.25 µm). The oven temperature is initially held at 45°C for 2 minutes after injection, thereafter the oven temperature is increased to a final temperature of 250°C at a rate of 5°C/min. The mass spectrometer is operated in electron ionization (EI) mode at 70 eV and the GC/MS interface temperature was set at 280 °C. The ion source temperature was set at 260°C, and a total ion current mass range of m/z

35 – 500 was scanned. Selective ion monitoring (SIM) of the PFBHA derivatives at m/z at 181 is performed for quantification purposes. The peak areas on the resulting chromatogram are related to the concentrations of the aldehyde-PFBHA derivatives in the eluent solution. The E- and Z-isomer peaks are added together for each aldehyde, where necessary. From the aldehyde concentrations in the solution, the mass of each aldehyde captured on the cartridge can be determined, and using the flow rate during sampling, the concentration of the aldehydes in the air sample can be calculated.

6.9 Analytical method performance

The performance of the proposed derivatisation method was determined. A set of standard concentrations of the aldehydes were injected into the sampling bulb and captured on the hydroquinone and PFBHA coated cartridges, as described in Section 3.9. The aldehyde-PFBHA derivatives were desorbed, and analysed using GC-MS, and these results were used to obtain calibration curves for the three aldehydes. The first step was to determine the analytical performance of the GC-MS method, with the results shown in Table 6.2. The validation parameters were compared to those of DNPH method and are included in Table 6.2.

Table 6.2: Performance data for the hydroquinone and PFBHA method as compared to the DNPH method

Parameter	Formaldehyde		Acetaldehyde		Acrolein	
	PFBHA	**DNPH**	**PFBHA**	**DNPH**	**PFBHA**	**DNPH**
Linearity (R^2)	0.999	0.999	0.998	0.999	0.997	-
Repeatability (RSD)	1.25	3.52	2.01	2.97	4.88	-
Sensitivity (counts/(µg/mL))	1049201	1.74	883589	1.52	717492	-
Retention time Precision (RSD)	0.11	0.25	0.16	0.17	0.13	-
LOD (µg/m³)	2.40	1.38	6.49	1.48	2.70	-
LOQ (µg/m³)	14.7[a]	4.19[a]	39.3[b]	4.49[b]	16.4[c]	-
Method recovery (%)	100	99	100	99	100	-
Precision (RSD)	1.23	4.9	2.78	6.5	2.19	-

[a] Formaldehyde WEL = 2.5 mg/m³
[b] Acetaldehyde WEL = 37 mg/m³
[c] Acrolein WEL = 0.05 mg/m³

The new method results are more precise than the DNPH method. Although the limit of detection and quantification for the new method is higher than the DNPH method, these limits are well below the workplace exposure limits (formaldehyde 0.1 %, acetaldehyde 0.02 %, acrolein 5.4 % of the WELs for each aldehyde), and therefore the new method will be able to measure aldehyde exposure levels in the workplace. The new method is able to measure acrolein in air, where the DNPH method does not.

The proposed method, using a hydroquinone and PFBHA coated silica gel cartridge for the sampling and derivatisation of the aldehydes in air, has been shown to be an improvement of the DNPH method.

6.10 Sample stability tests

Storage stability of the samples need to be determined, as analysis is not always possible directly after sampling, due to the need to transport the samples to the analytical facilities as these will not be available on site. The sample stability after elution also needs to be determined. The cartridges were spiked with a solution of aldehydes, capped and stored in a fridge at 5°C. One cartridge was eluted and analysed each day to determine the method recovery (Section 3.9) of each of the aldehydes. The stability of the cartridge in storage was monitored over 9 days, and the results are shown in Figure 6.9. The aldehyde recovery stayed within the acceptable recovery range[168], and the sample analysis repeatability (RSD) for the 9 days for formaldehyde, acetaldehyde and acrolein were 5.5, 3.9 and 6.0 %, respectively.

The samples were stable for 9 days in the fridge at 5°C. The hydroquinone on the cartridge stabilises the sample and the PFBHA forms a stable acrolein derivative, as reported in literature[10].

The stability of the derivatives in the eluted samples that were stored in the fridge was tested over 8 days. The aldehyde-PFBHA derivatives were desorbed from the cartridge using acetonitrile. The eluent was analysed every day for 8 days, and the results are given in Figure 6.10.

The aldehyde-PFBHA derivatives are stable in solution for 8 days, with an analysis repeatability (RSD) for formaldehyde, acetaldehyde and acrolein of 2.9, 1.3, and 3.8 %, respectively.

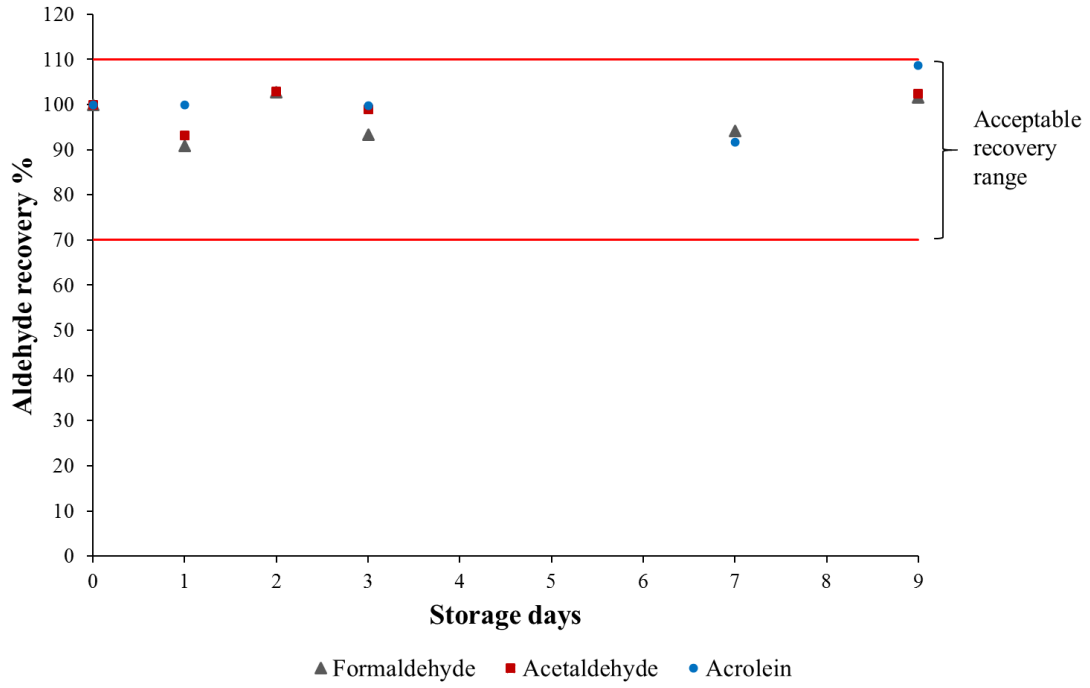

Figure 6.9: Storage stability of the aldehydes on the cartridge

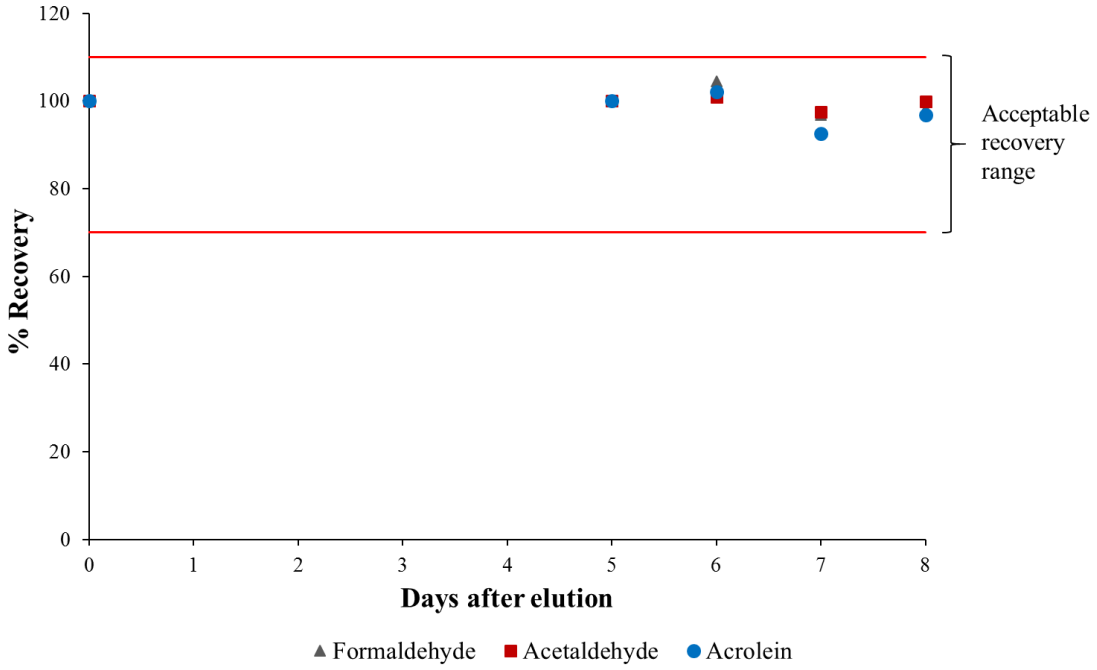

Figure 6.10: Storage stability of the aldehyde-PFBHA derivatives in solution

6.11 Shelf-life of the hydroquinone and PFBHA cartridge

The shelf-life needs to be determined before sampling, to establish if there is any degradation of the derivatisation agent. This will influence the frequency of the preparation of sampling cartridges for sampling.

Taking into consideration the repeatability of producing the cartridges the shelf life of the cartridges were constant (RSD 6.2 %) for 11 days. On the 12th day, the recovery of the PFBHA on the cartridge reduced to 80 % of the initial amount loaded. The hydroquinone on the cartridge was stable over the 13 days test period (RSD of 2.4 %).

6.12 NO_2 quantification using the PFBHA method

A possible additional advantage of including hydroquinone is making use of the reaction with NO_2 in the sample. The reaction of the NO_2 with hydroquinone results in the formation of p-benzoquinone and 2-nitrobenzene-1,4-diol. The p-benzoquinone is the major product formed with NO_2, and therefore should be used to quantify NO_2.

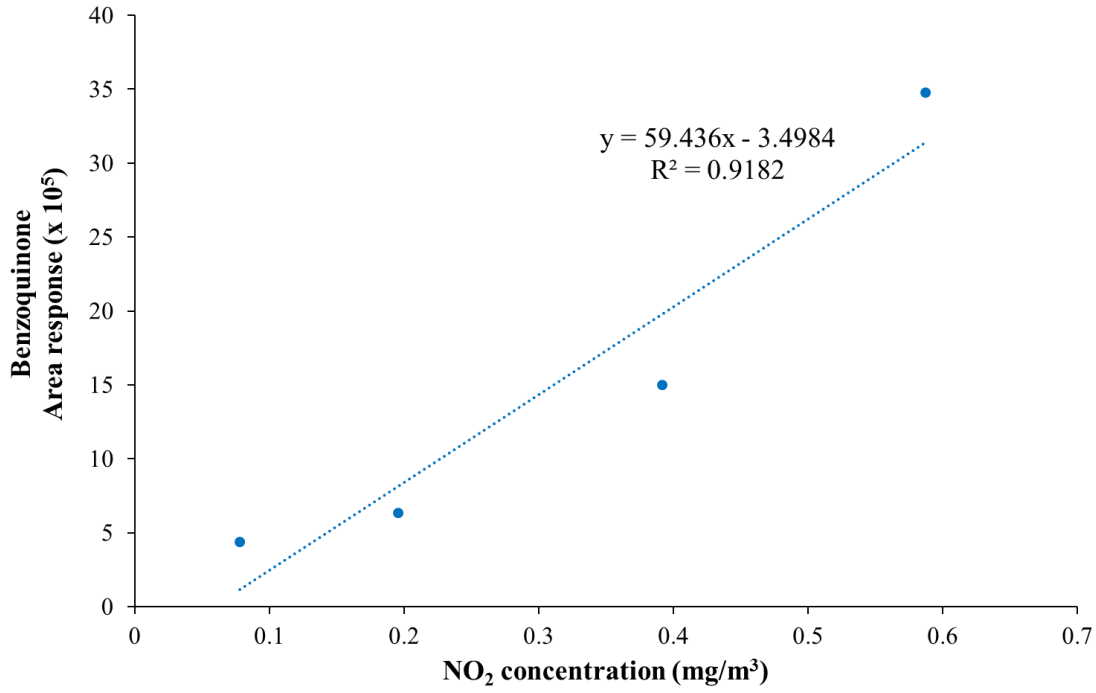

Figure 6.11: Calibration curve for NO_2 using benzoquinone

The response for p-benzoquinone was used and plotted against the NO_2 concentration to determine if there is relationship between the amount of the reaction product formed and the amount of NO_2 that the cartridge was exposed to, as shown in Figure 6.11. The relationship is relatively linear. This method shows some potential for the analysis of NO_2 along with the aldehydes in a polluted environment. Further work to fully validate the method is required.

6.13 Cost analysis of the new method

The cost of preparing a cartridge coated with hydroquinone and PFBHA should preferably not be more expensive than purchasing the DNPH cartridges with the equivalent capacity. The cost of the preparation of a single cartridge was calculated from the prices of the individual components on Sigma-Aldrich Company Ltd and are listed in Table 6.3 below. The costs were rounded up to the closest penny. The amounts of PFBHA and hydroquinone are based on the capacity requirements for the aldehydes and NO_2, respectively and the equation given in Chapter 5.

Based on current chemical prices, the cartridge would cost £1.47 to prepare. An extra cartridge is needed for breakthrough purposes during sampling, and so the cartridge cost for sampling is £2.94. The cheapest DNPH option costs £34.62, taking capacity requirements into account, which is almost twelve times the cost of the new method cartridge. Also, the DNPH method would require 25 mL of acetonitrile compared to 10 mL of acetonitrile for the new method. Moreover, the cartridge could possibly measure the NO_2 concentration of the sampled air as well. GC-MS running costs are cheaper than those for HPLC.

Table 6.3: Cost of the cartridge components (Sigma-Aldrich Company Ltd)

Component	Specification	Cost (£)
Cartridge	Empty 3 mL polypropylene cartridge with PE frits	1.20
Silica gel sorbent – 350 mg	High-purity grade (Davisil Grade 633), pore size 60 Å, 200-425 mesh particle size	0.08
PFBHA – 3 mg	For GC derivatisation ≥99.0 % (AT)	0.18
Hydroquinone – 2.4 mg	ReagentPlus® ≥99.5 %	0.01
Labour	£14 per hour, 5 cartridge per hour	2.80
TOTAL		4.27

6.14 Conclusion

The aim was to determine the best sorbent for the sampling of aldehydes from air, and then to select the best derivatisation reagent that would suite the sorbent of choice. In both cases it was necessary to ensure a good capturing efficiency and recovery of the aldehyde derivatives from the cartridge for analysis. The best sorbent was identified to be a silica gel coated with hydroquinone. There are several advantages to using hydroquinone on silica gel as a sorbent for the sampling of aldehydes:

- Hydroquinone stabilises the acrolein, therefore no polymerisation takes place, resulting in less reaction products with the derivatisation reagent.
- It may be possible to quantify NO_2 simultaneously with the aldehydes, by measuring p-benzoquinone using GC.
- Hydroquinone is an antioxidant and therefore may remove the ozone from the sample before it destroys the aldehydes.
- If derivatisation was to take place post sampling, any derivatisation reagent could be used for the derivatisation of the aldehydes. The reaction of ozone, NO, NO_2 and CO with the derivatisation reagent would be removed, and no interference from the reaction products would be encountered. This would require taking into account the recovery of the aldehydes derivatives from the cartridge.
- The capacity of a hydroquinone coated cartridge for aldehydes will probably not be affected as much by the presence of NO, NO_2 and CO, because the capture of the aldehydes is not dependent on the reaction of the aldehydes with the hydroquinone on the cartridge.

Hydroquinone does not react with NO and CO, however, there was substantial reaction observed with NO_2. When combined with the PFBHA derivatisation reagent, the reaction products of hydroquinone with NO_2 do not interfere with the aldehyde-PFBHA derivatives on the GC-MS chromatogram.

Using a hydroquinone cartridge for the sampling of aldehydes, requires an effective sample preparation step where the aldehydes are recovered fully from the cartridge for analysis. The derivatisation of the aldehydes with PFBHA and the elution after gave the best results and therefore this method was chosen for the sampling of formaldehyde, acetaldehyde and acrolein in air, although the method recovery for acrolein was just below the acceptable recovery level. The method was further optimised by adding the

PFBHA along with the hydroquinone as a coating onto the silica gel cartridge. Sampling with the combined cartridge improved the acrolein method recovery to 100 %. The cost of the new PFBHA method was calculated to be more cost effective than the DNPH method, when comparing capacity requirements.

The method validation showed that the method is fit for the purpose of sampling and analysing formaldehyde, acetaldehyde and acrolein in air, simultaneously, to the required levels for workplace exposure determination. For the first time, a method for the simultaneous determination of formaldehyde, acetaldehyde and acrolein has been developed, taking into account the interferences from NO, NO_2 and CO. This method could be applied in various polluted environments, for the analysis of aldehydes.

Chapter 7
Testing the new method performance in simulated and real-world environments

7.1 Introduction

A method for sampling and analysis of formaldehyde, acetaldehyde and acrolein has been developed using a hydroquinone and PFBHA coated silica gel cartridge with analysis on GC-MS. The aim of this work is to develop a method that simultaneously analyses for the three aldehydes in polluted environment.

The method so far is able to analyse the three aldehydes with the same method, and evidence obtained in Chapter 5 and Chapter 6 so far shows that hydroquinone and PFBHA are only slightly affected by the presence of NO, NO_2 and CO. It is therefore necessary to determine whether these gases have any effect on the capture and retention of the aldehydes during sampling. This will be tested in two ways: by simulated environments and a real-world sampling campaign. The DNPH method was included during the evaluation for the purpose of comparison. It is anticipated that in these polluted environments that the DNPH would be consumed by NO, NO_2 and CO, and therefore would give underestimated results for the aldehydes, as discussed in Chapter 4.

According to the study by Ho and Yu (2002)[161] ozone only interferes with the sampling and quantification of acrolein when using PFBHA, with no effect observed on the quantification of formaldehyde and acetaldehyde. No other information was found in literature on the impact of ozone on the destruction of PFBHA. The effect of ozone on the cartridge has yet to be determined, as the presence of hydroquinone may protect the PFBHA and the aldehyde derivatives on the cartridge. Any destruction of the PFBHA on the cartridge will result in a reduced capacity of the cartridge for the aldehydes. If ozone destroys the aldehyde-PFBHA derivatives, this will result in the underestimation of the aldehyde concentrations in the samples.

7.2 Method performance in the presence of ozone

Hydroquinone coated silica gel cartridges have been used for the removal of ozone from the sample matrix. Although the hydroquinone is present on the cartridge, it is expected that ozone would interfere with the quantification of the aldehydes, as it is such a reactive compound. If the reaction of ozone with hydroquinone is faster than any of the other

possible reactions on the cartridge, the hydroquinone will remove the ozone from the sample matrix and protect the PFBHA as well as the aldehyde-PFBHA from destruction by the ozone.

To understand the effect that ozone will have on the new method, blank cartridges containing PFBHA and hydroquinone were exposed to 15.59 µg/m^3 (8 hr TWA) ozone, resulting in the destruction of 49.7 mol PFBHA per mol of ozone and 11.64 mol hydroquinone per mole ozone. The reaction of ozone with PFBHA is therefore preferred over the reaction with hydroquinone, and therefore the hydroquinone does not protect the PFBHA from destruction by ozone. This would result in a lower capacity for the aldehydes of the cartridge. The use of the KI cartridge is therefore essential during sampling to remove the ozone from the sample.

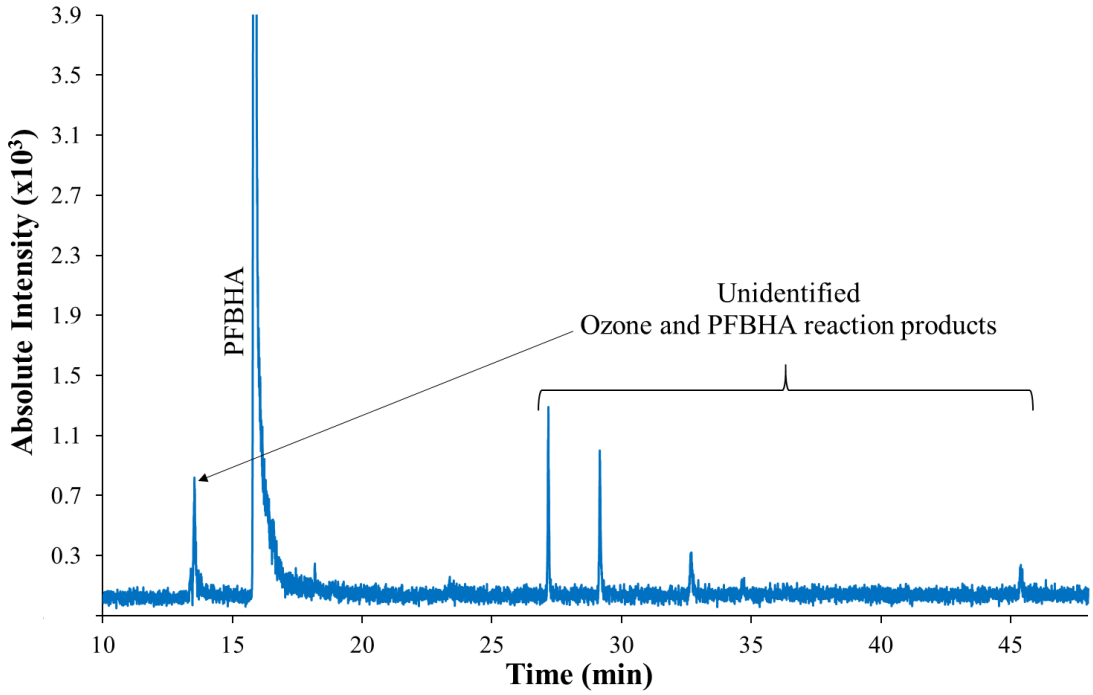

Figure 7.1: GC-MS chromatogram (m/z 181) of the breakdown products of PFBHA caused by ozone

Figure 7.1 shows the resulting chromatogram of the destruction of the PFBHA by ozone. Several breakdown products were observed on the chromatogram, but could not be identified. The compound eluting at 13.5 minutes could co-elute with formaldehyde-PFBHA, and therefore cause an overestimation of the formaldehyde concentration.

PFBHA and hydroquinone cartridges, spiked with the aldehyde PFBHA solution, were prepared, as described in Section 3.4.7. The cartridge containing the aldehyde-PFBHA derivatives, were exposed to 15.59 μg/m^3 (8 hr TWA) ozone to determine the effect of the gas on the derivatives in the presence of hydroquinone. The results in Figure 7.2 show that there is very little effect of the ozone on the formaldehyde- and acetaldehyde-PFBHA derivatives. These results confirmed the results observed by Ho and Yu (2002)[161] where the ozone had no effect on the formaldehyde and acetaldehyde results. Ozone had a considerable effect on the acrolein quantification, as only 63 % of the acrolein spiked onto the cartridge was recovered, which is lower than the 91 % recovery seen by Ho and Yu (2002).

The GC-MS chromatogram only contained peaks corresponding to formaldehyde-, acetaldehyde-, and acrolein-PFBHA derivatives. No other peaks were observed on the GC-MS chromatogram. Any products formed in the destruction of the acrolein-PFBHA derivative may be retained on the cartridge during elution of the derivatives, or are lost during sampling if they are volatile.

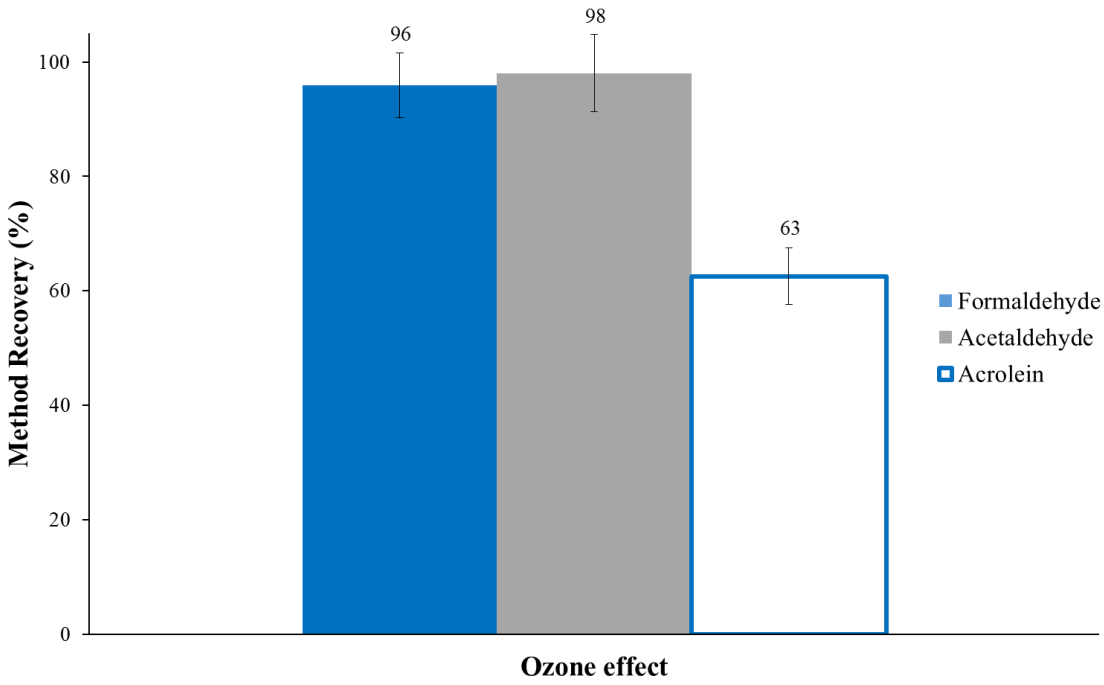

Figure 7.2: Effect of ozone on the PFBHA and hydroquinone cartridge

The use of an ozone removal cartridge is still necessary to remove the ozone during sampling, to prevent the destruction of the PFBHA and acrolein-PFBHA derivative. It is recommended that a KI-cartridge would be used before the new PFBHA and hydroquinone cartridge, instead of a hydroquinone cartridge because the aldehydes would be captured as was demonstrated in Chapter 6, making the aldehydes susceptible to destruction by ozone.

7.3 Performance in simulated environments

The interferences from the individual gases on PFBHA and hydroquinone, respectively, have been established (Section 5.3.2 and 6.4). Hydroquinone reacts with NO_2 to form p-benzoquinone, and PFBHA forms low amounts of reaction products with the NO, NO_2 and CO, but these products do not interfere with the quantification of the aldehydes. The performance of the method in a polluted environments needs to be established to determine if the method will be successful in the accurate analysis of the aldehydes in polluted environments. The combined effect of the gases may have a different effect than the individual gases during sampling, and this effect, if any, should be determined.

A mixture of the gases, NO, NO_2 and CO (0.62, 0.47, 2.16 mg/m^3 TWA for 8 hours, respectively), was made with a gas mixer (representing typical NO_2 concentrations in a polluted workplace[176]), as described in Section 3.7.1.5, to simulate a polluted environment. The gas mixture with constant concentrations of NO, NO_2 and CO was pumped through the gas bulb which had a mixture of varying amounts of the aldehydes injected into it, and a sampling cartridge along with a second breakthrough cartridge was attached to the outlet of the bulb. After sampling from the bulb, the cartridges were desorbed using the appropriate eluent, and analysed, and the collection efficiency was determined using equation [186] in Section 3.3.6. The results are shown in Figure 7.3.

Breakthrough of acrolein occurred when the total mass of the aldehydes was 36.13 μg as formaldehyde (point 2 in Figure 7.3), but stayed above the preferable collection efficiency (CE) of 90 %, until the total mass of aldehydes equalled 144.5 μg as formaldehyde (point 4). At this point, acetaldehyde also started breaking through. Formaldehyde started breaking through at point 5 where the total aldehyde mass was 216.8 μg as formaldehyde. The total cartridge capacity was 423 μg as formaldehyde, which is only exceeded at point 6 (Figure 7.3). Breakthrough was predicted to occur at point 6, taking into account the

destruction of the PFBHA by the interfering gases. The breakthrough of the aldehydes is therefore not due to the capacity (availability of the derivatisation reagent) of the sampling cartridge, but the presence of NO, NO_2 and CO, which could be competing with the aldehydes for adsorption sites.

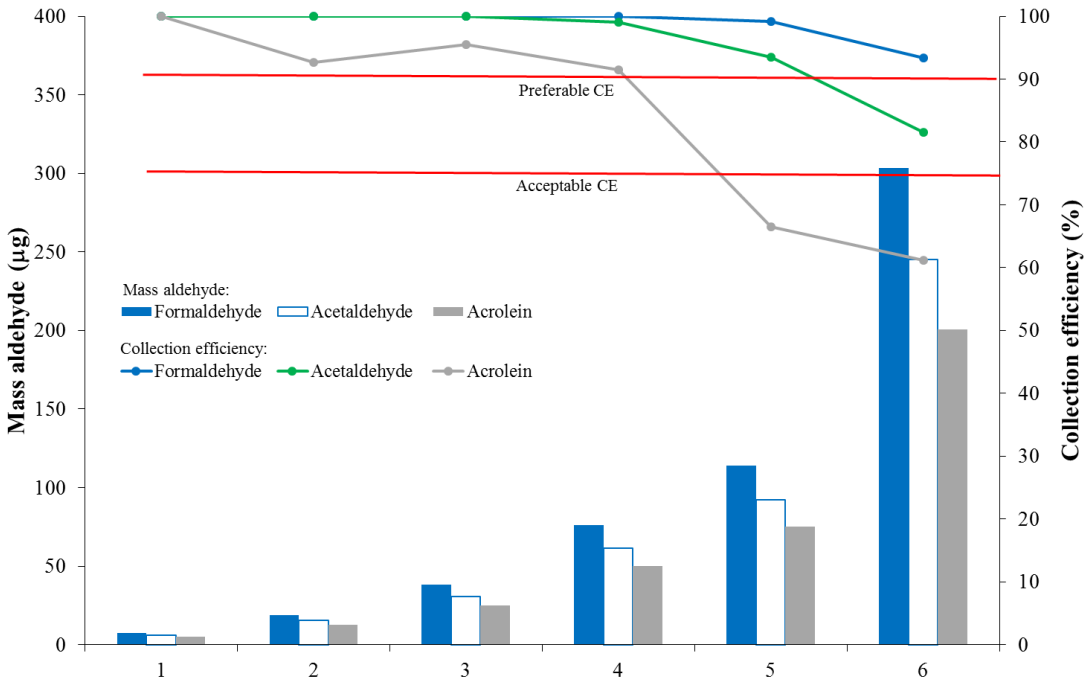

Figure 7.3: Collection efficiency of the PFBHA and hydroquinone cartridge in a polluted environment

Although breakthrough of the aldehydes occurred earlier than predicted by the availability of the derivatisation reagent, the collection efficiencies were above the preferable collection efficiency threshold until point 4 (Figure 7.3), and stayed above the acceptable collection efficiency threshold (75 %) for formaldehyde and acetaldehyde up to point 6.

The DNPH cartridge (LpDNPH S10) has a total capacity of 150 µg as formaldehyde, and the predicted breakthrough (availability of DNPH) should occur at point 5 in Figure 7.3 (216 µg as formaldehyde), when assuming there is no destruction of the DNPH by NO, NO_2 and CO. However, at the experimental concentrations of the NO_2 and CO (0.47, 2.16 mg/m^3), the DNPH will be entirely destroyed by the NO_2 and CO present. The aldehydes and the interfering gases will be competing for adsorption sites on the cartridge, and the gases will be displacing the aldehydes (as established in Chapter 4). The cartridge was

therefore tested at point 4 (144.52 μg as formaldehyde), which is below the capacity of the cartridge.

The experiment was performed in triplicate, and no peaks for the aldehyde-DNPH and DNPH were observed on the HPLC chromatogram. The aldehydes were therefore not captured or retained, and the DNPH was completely destroyed by the CO and NO_2, as predicted. This result is similar to what was observed by 4-Rail Services Ltd.

The new PFBHA method outperforms the DNPH method at the same conditions. The PFBHA method gives collection efficiencies for the aldehydes above 90 %, where no result could be obtained using the DNPH method.

The PFBHA method performed within the limits required of a method, as set out in the validation guidelines given by OSHA for air sampling methods utilising chromatographic analysis[167].

7.4 On-site sampling using the new PFBHA method[187]

A gas monitoring campaign was undertaken at the Arriva Rail North's train depot at Neville Hill which is located in the eastern part of Leeds. The depot consists of two sheds, a repair shed and a service shed, where routine maintenance of trains as well as repairs on the engines of the trains take place. The monitoring was primarily targeted within the repair shed section of the depot, over a one-week period. The gases that were monitored were NO, NO_2, NO_x, CO and the aldehydes (formaldehyde, acetaldehyde, and acrolein).

Figure 7.4: Horiba APNA-370 NO_x analyser

The NO_x, NO and NO_2 concentrations were monitored every 3 minutes throughout the 8 hour period, using a chemiluminescence detector (Horiba APNA-370 instrument, Figure 7.4). The CO measurements were read off the already installed CO monitoring equipment (Environmental Scientifics Group) every hour. The installation was a Diesel

Exhaust Detection System, which detects CO in the range of 0 to 50 ppm, but is cross sensitive to other gases e.g. nitric oxide and nitrogen dioxide[188].

A large percentage of Arriva Rail North's train fleet have diesel fuelled engines with no aftertreatment system for the exhaust gases. Several engine tests are performed, which include frequently starting and stopping the engines and running the engines for long periods, during which the exhaust emissions are being emitted and accumulating in the shed. The depot would not be classified as a confined space, however, due to the testing of diesel engines without aftertreatment systems for the exhaust gases, elevated levels of pollution gases would be present.

The aldehyde and NO_x concentration data will be used to assess the current air quality within the shed and compared with the WELs for each of the gases measured.

The aldehyde sampling cartridges and pumps were co-located with the Horiba APNA-370 in the repair shed of the Neville Hill depot. The aldehyde sampling unit, along with the NO_x analyser, was placed in a high NO_2 gas concentration area, which was identified by previous measurements with NO_2 diffusion tube measurements. The aldehydes were sampled over 8 hours for the time-weighted average concentration, with the NO_x concentrations being measured every 3 minutes over the 8 hour period.

7.4.1 Depot Specifications: Neville Hill

Neville Hill depot (194 Osmondthorpe Lane, LS9 9BJ) is located about 3 miles east of Leeds Train Station. The depot consists of two sheds, a repair shed for heavy maintenance and repair work and a service shed for lighter maintenance. The Repair shed has five roads (train platforms) with roads 1 and 2 designated for electric trains and roads 3 to 5 for diesel trains. The Repair shed is sealed at the eastern side of the shed, with trains entering and leaving the shed via a single series of rolling doors at the western entrance.

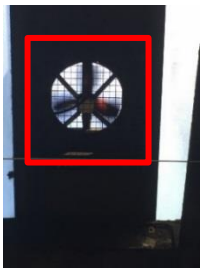

Figure 7.5 Roof fan in the repair shed of Neville Hill depot

There are 28 roof extraction fans (see Figure 7.5), which are evenly spaced along the roof of the repair shed. There is no variable speed control of the fans, which work on an on/off basis, as required. Some of the fans are not operational. The layout of the fans in the Repair shed is shown in Figure 7.6.

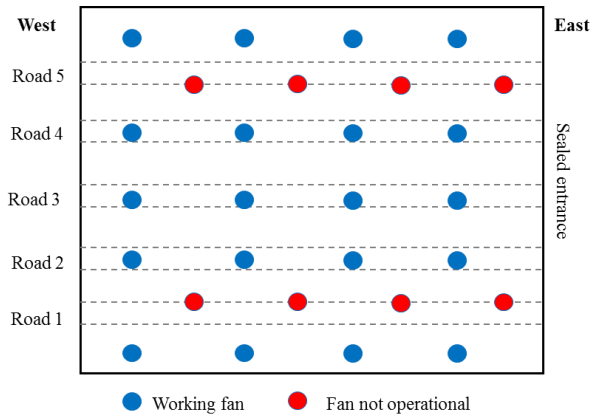

Figure 7.6: Fan layout in the Neville Hill depot Repair shed

The Repair shed has overhead Ambirad radiative heaters, as shown in Figure 7.7, which are used to maintain an ambient temperature of at least 13°C, with an automated system in place to switch these on when the temperature drops below this. These heaters did not switch on at any time during the sampling campaign.

Figure 7.7 Ambirad radiative heaters in the repair shed of the Leeds depot

In addition, the Repair shed has a glass roof, as is observed in Figure 7.7, allowing for natural light to enter the shed. Along with the presence of formaldehyde, which is an ozone precursor, the presence of ozone in the shed is therefore anticipated. The use of a KI-cartridge for the removal of ozone during sampling was implemented.

7.4.2 Trains present in the Repair shed

Two train companies supply diesel engine trains, called diesel multiple units (DMU) to Arriva Rail North, namely Angel Railways and Porterbrook. The engine types are mainly Cummins NT855 engines, with a Perkins 2006-TWH and MTU 6R183TD13 engines also present.

7.4.3 Monitoring and sampling locations in the Repair shed

The sampling and monitoring locations were chosen based on previous NO_2 diffusion tube results from the Repair shed. The highest concentrations of NO_2 were observed at the centre of Road 5 and Road 3. However, a convenient sampling location next to Road 3 was not possible, as the sampling and monitoring equipment would obstruct the passage next to road. The location in the middle of Road 5 was labelled Location A, as indicated in Figure 7.8. Location B was chosen as an area where the NO_2 concentrations measured using the diffusion tubes were at the lowest. The low concentrations of NO_2 is due to the location being next to the entrance doors, which are regularly opened and closed during the day, allowing for the dilution of the gas.

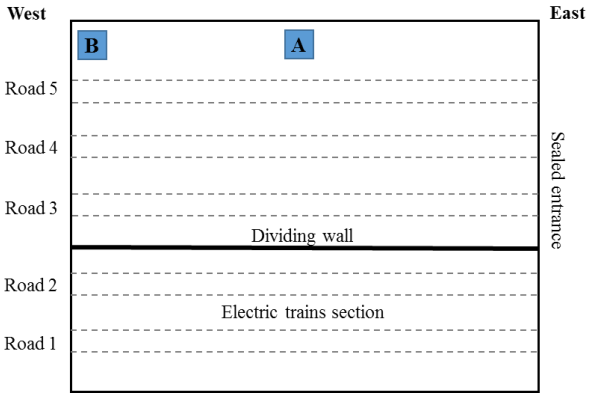

Figure 7.8: Sampling locations in the Repair shed

At both sampling points the DNPH and the new PFBHA cartridges were used in parallel, to compare the method results. The samples were taken for 5 consecutive days, for 8 hours a day. The total NO_x, NO and NO_2 gases were monitored every 3 minutes throughout the 8 hour period, using a Horiba APNA-370 instrument. CO measurements were read off the already installed CO monitoring equipment (Infinite Automation Systems) every hour.

7.4.4 Sampling procedure

The aldehydes were collected by drawing air through the PFBHA and DNPH sampling cartridges (with a breakthrough cartridge) simultaneously using the Gemini twin port connected to the personal sampling pump (ESCORT Elf® Air sampling pump, Zefon International and SKC, USA) at a flow rate of ~0.5 L/min for each cartridge. The flow rate of the pumps were checked before and after sampling using a Restek ProFLOW 6000 Electronic Flowmeter. The sampling time was for 8 hours (07:30 – 15:30, corresponding to the day shift). A potassium iodide (KI) ozone removal cartridge was placed upstream of both the sampling cartridge sets in order to prevent the interference of ozone.

After sampling, the cartridges were disconnected, capped and sealed with parafilm and transported back to the laboratory. The samples were immediately eluted and analysed on return to the laboratory. Each sampling set on a day included one field blank each for the DNPH and the PFBHA method.

7.5 Results

7.5.1 Matrix determination and observations

The routine repairing and maintenance work in the Repair shed was done on a shift basis, with the shift changes at 07:30 and 15:30 during the day. The sampling times matched the day shift starting at 07:30 in the morning. The majority of the train movements in and out of the Repair shed took place during the times of the shift changes, but there was some train movement during the day as well. Work on the engines would start around 08:00, after movement of the trains (arrival and departure) and some initial engine tests were performed. As the work progressed during the day, the individual engines from each DMU would be started up for testing for various lengths of time. Not all the roads had trains on them every day, but the Repair shed contained at least 10 DMUs every day. A pit cleaner, which also runs on diesel, was also intermittently used during the day, which emitted large amounts of dark grey clouds of smoke.

The doors to the roads were sometimes opened when the engines on the road were running, depending on the ambient temperature in the shed, and the comfort of the workers. The extraction fans were switched on during most of the engine tests. The NO_2 and CO concentrations during each 8 hour sampling period for each day is shown in Figure 7.9 and Figure 7.10.

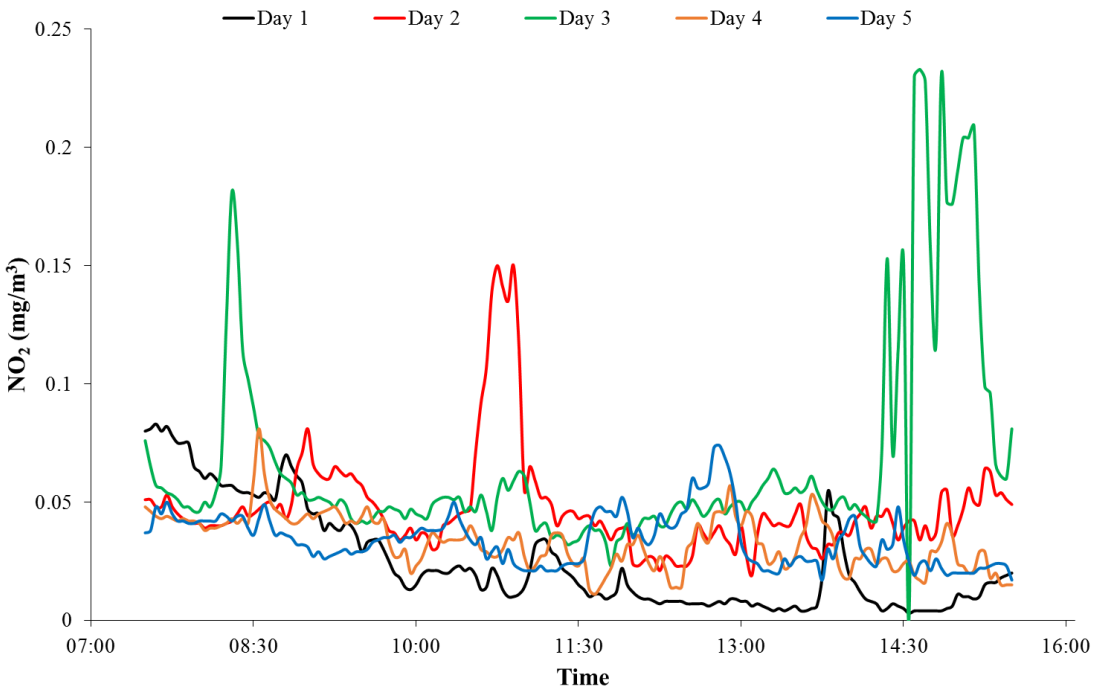

Figure 7.9: Nitrogen dioxide concentrations at Location A during each of the 5 days of monitoring

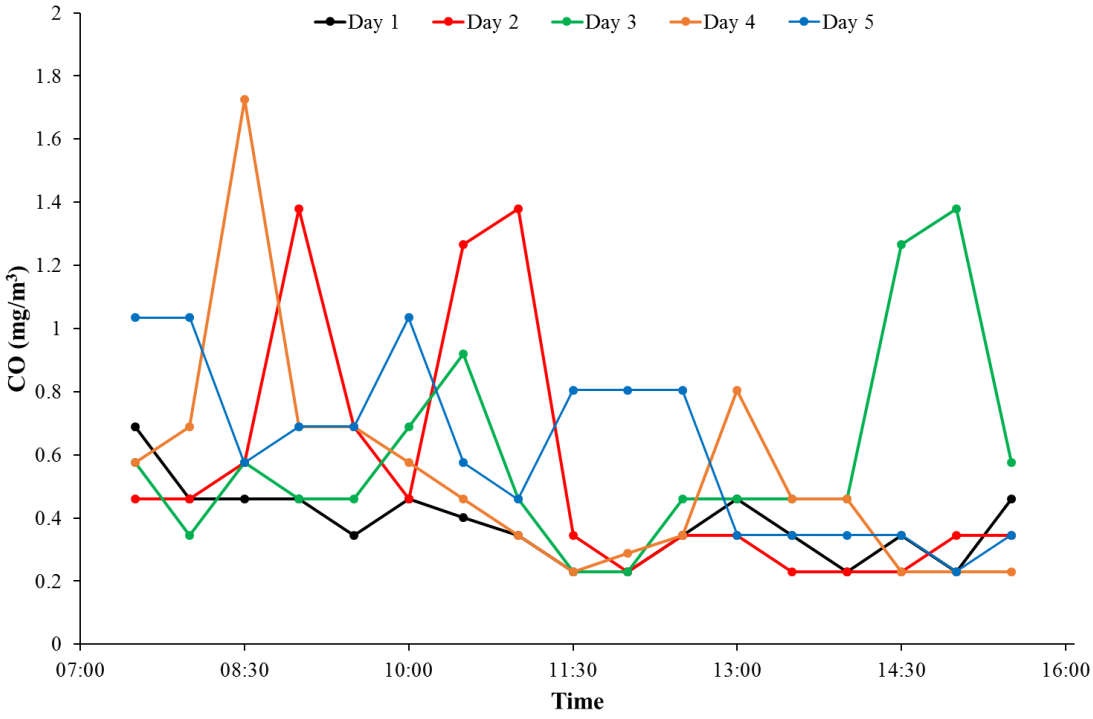

Figure 7.10: Carbon monoxide concentrations close to Location A during the 5 days of monitoring

The NO_2 concentration chart show periods on days 2 and 3 where the concentration of NO_2 was elevated. These periods correlate to times when many DMU engines were

running, and the period at the end of day 3, several DMU engines were running with the extraction fans switched off and the doors were kept closed. Similar periods can be seen on the CO concentration chart (Figure 7.10), however, these periods did not seem excessively high compared to the rest of the time periods.

The maximum concentrations of NO_2 and CO never exceeded the workplace exposure limits of 0.9 and 23 mg/m^3, respectively.

7.5.2 Comparison of the aldehyde measurements

The PFBHA sampling of the aldehydes was done in parallel with the DNPH method, to compare the results. The results obtained for formaldehyde with both methods at location A and B are shown in Figure 7.11 and Figure 7.12, respectively.

The concentration trends over the 5 days follow a similar trend. The concentration levels of formaldehyde were in the range of 3.84 – 9.09 µg/m^3, according to the new PFBHA method, with Day 3 showing a maximum concentration, which correlates with the observations and NO_2 and CO measurements. These levels are far below the UK WEL of 2.5 mg/m^3 for formaldehyde.

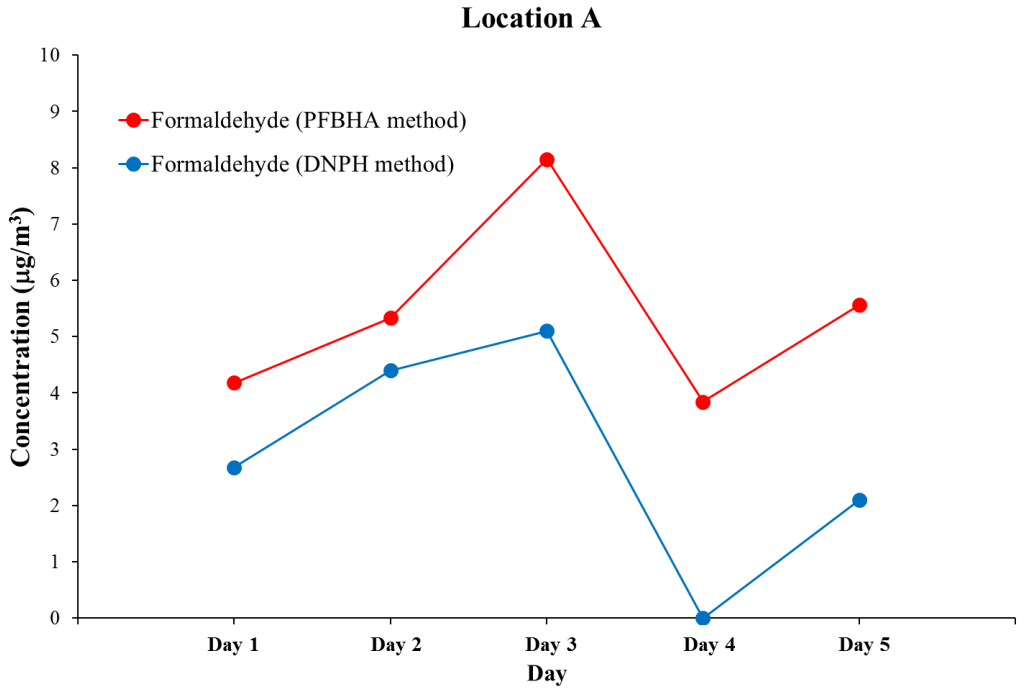

Figure 7.11 Comparison of the PFBHA and DNPH method's formaldehyde results at Location A (WEL 2.5 mg/m^3)

The DNPH method underreported the formaldehyde results by 18 – 93 %, as was expected in the presence of CO and NO_2.

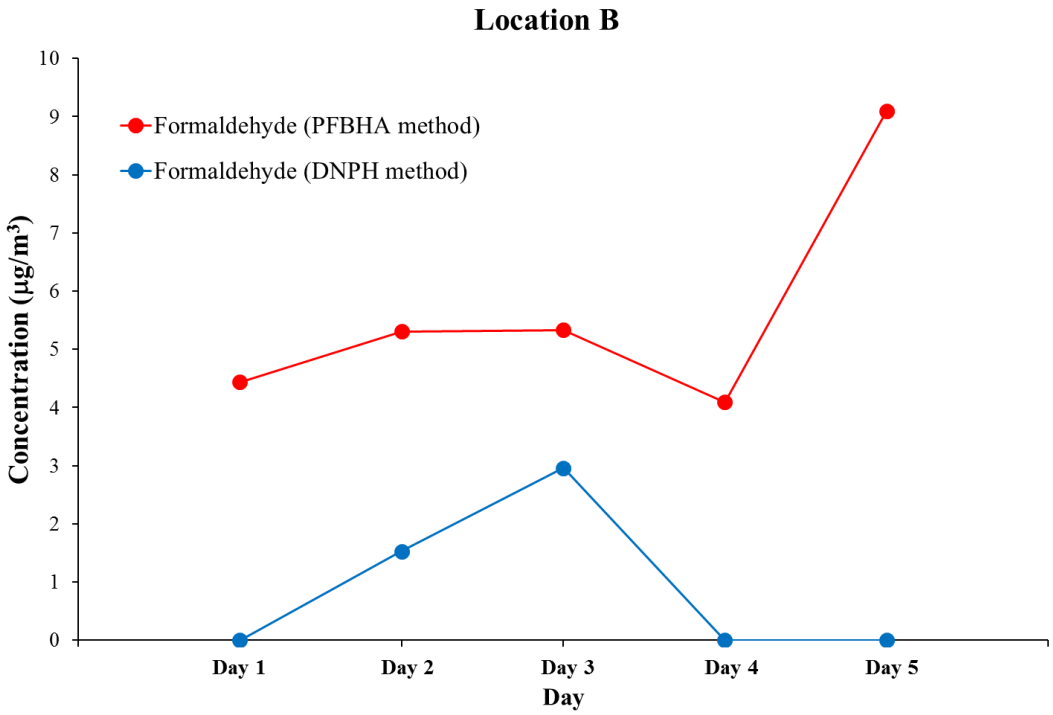

Figure 7.12: Comparison of the PFBHA and DNPH method's formaldehyde results at Location B (WEL 2.5 mg/m^3)

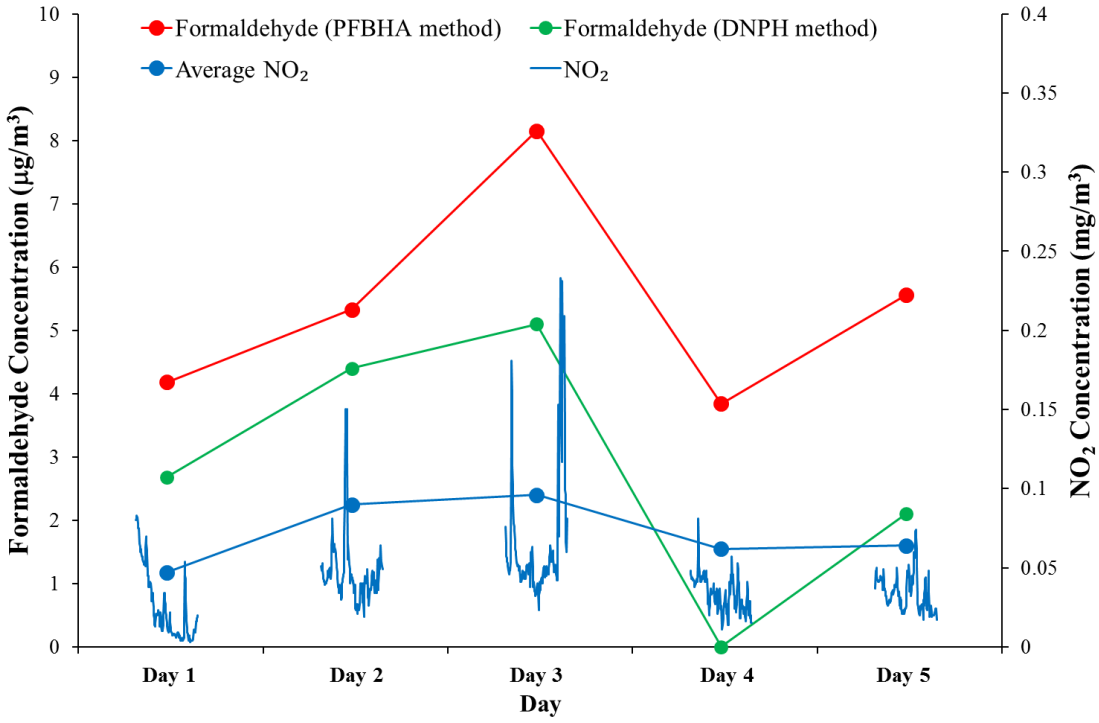

Figure 7.13: Formaldehyde (both PFBHA and DNPH methods) and NO_2 concentrations comparison

The formaldehyde concentrations measured for each day were compared with the NO_2 concentrations for each day, as shown in Figure 7.13. The formaldehyde concentration trend followed the NO_2 concentration trend, except for Day 5. Similarly, the CO concentrations were compared to the formaldehyde concentration, and are represented in Figure 7.14.

Days 1 to 3 followed a similar trend to that of NO_2, increasing each day. However, on Day 4 there was a spike in the CO concentration. On Day 4 the DNPH method did not detect formaldehyde, which is due to the CO consuming the DNPH and displacing the formaldehyde from the cartridge. Acetaldehyde and acrolein were also not detected by the DNPH method on Day 4. During Day 5 the formaldehyde, NO_2 and CO concentrations were similar to Day 1.

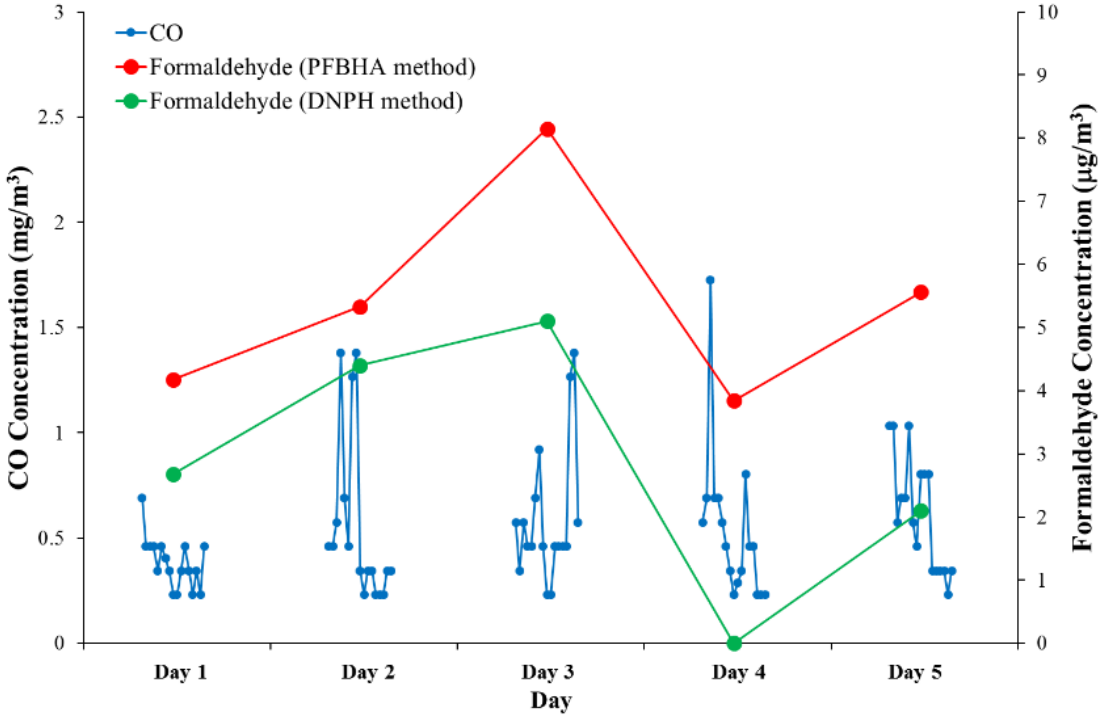

Figure 7.14: Formaldehyde (both PFBHA and DNPH methods) and CO concentrations comparison

The formaldehyde concentrations are relatively low as compared to measurements at bus stations (38.8 – 115 µg/m^3)[45, 83] and traffic tunnels (5 – 38.5 µg/m^3)[62, 77], as the ventilation from the open doors was good. The formaldehyde concentrations measured are comparable to rural and urban pollution levels (0.8 - 65.5 µg/m^3)[57, 60, 79].

Acetaldehyde was not detected by either method over the five days. Acetaldehyde concentrations are generally lower than formaldehyde concentrations, as is summarised in Table 2.1 and Table **2.2** from literature reports.

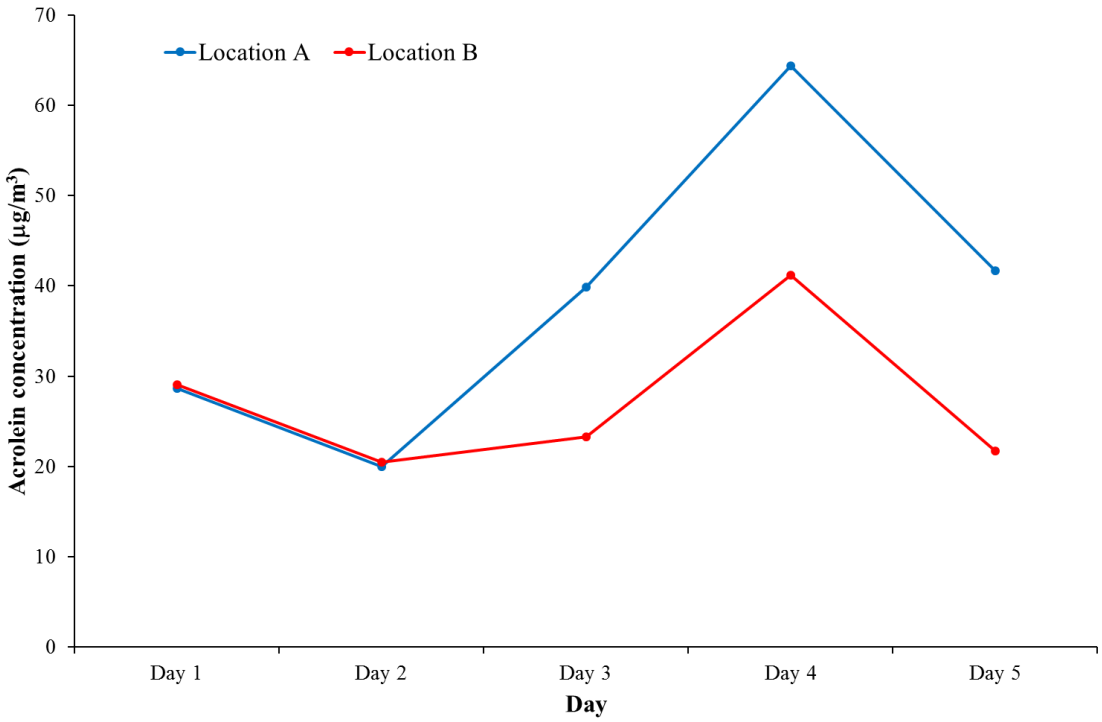

Figure 7.15: Acrolein concentrations for locations A and B over 5 days (WEL 0.05 mg/m^3)

The acrolein concentrations obtained by the PFBHA method for location A and B are shown in Figure **7.15**. The concentrations followed the same trend over the 5 days, but location B had lower concentrations for Days 3 to 5. Location B is closer to the open doors, and therefore is a better ventilated area, and therefore the concentrations are diluted. The acrolein concentrations were close to the WEL of 50 µg/m^3, and on Day 4 the acrolein concentration exceeded the WEL at location A. The acrolein concentrations for location A were compared to the NO_2 (Figure 7.16) and CO (Figure 7.17) concentrations. The higher concentrations of acrolein on Day 4 also correlate to a higher concentration of CO. The DNPH method cannot be used to measure acrolein, and therefore no data was obtained.

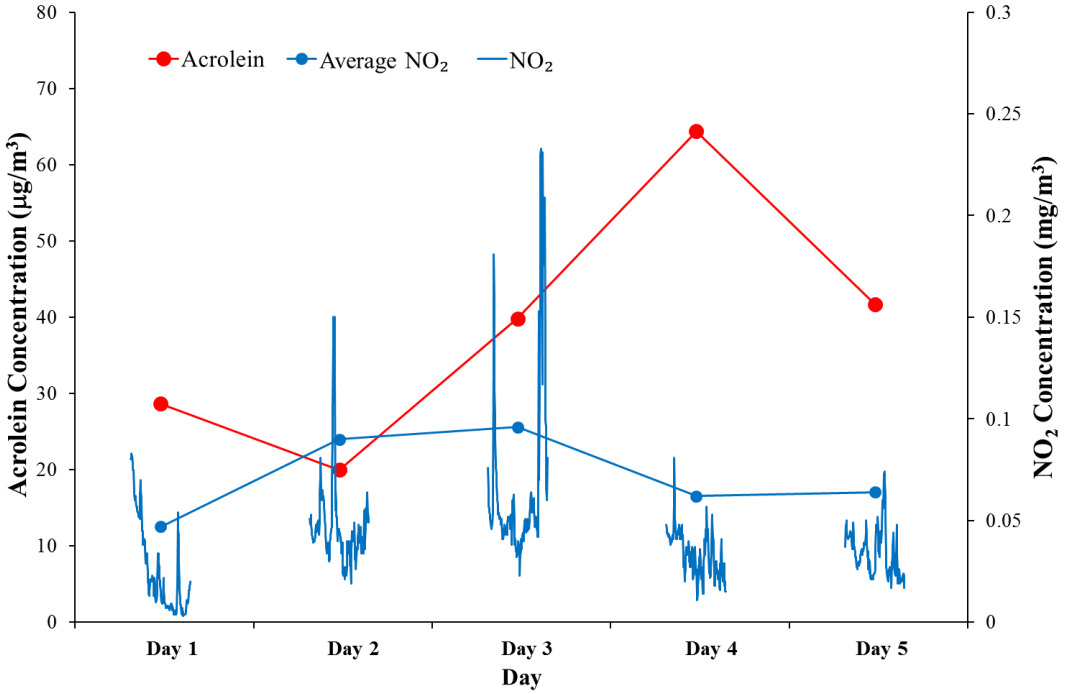

Figure 7.16: Comparison of the acrolein and NO_2 concentrations for location A

Similar acrolein concentrations were seen in areas around a refinery, coal mine and power plants [57].

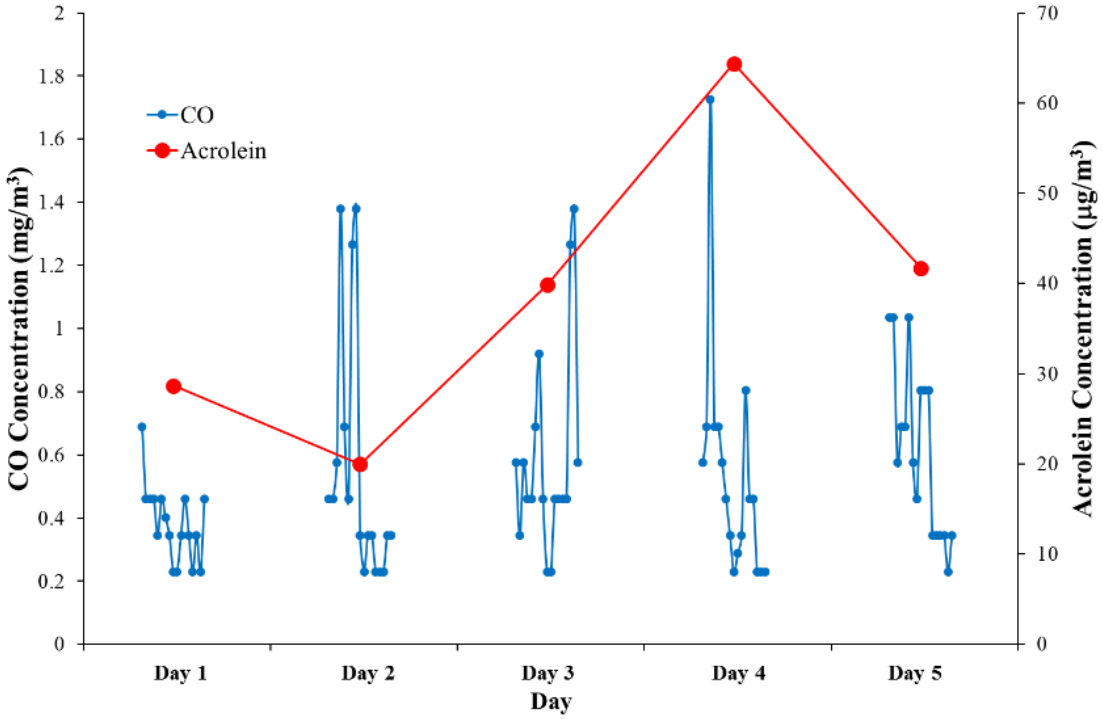

Figure 7.17: Acrolein and CO concentration comparison for Location A

7.5.3 Measurement of NO_2

Due to the reaction of the NO_2 with the hydroquinone to form p-benzoquinone, the NO_2 concentration could be measured by monitoring the p-benzoquinone peak on the GC-MS chromatogram. The results from the PFBHA method were obtained as a time-weighted average over 8 hours, and compared to the average of the results from the APNA NO_x analyser, as shown in Figure 7.18. The graph shows some correlation between the concentrations measured by each technique. The results are within the same order of magnitude, however, there is still a slight discrepancy between the results, with the PFBHA results being lower than measured by the APNA NO_x analyser.

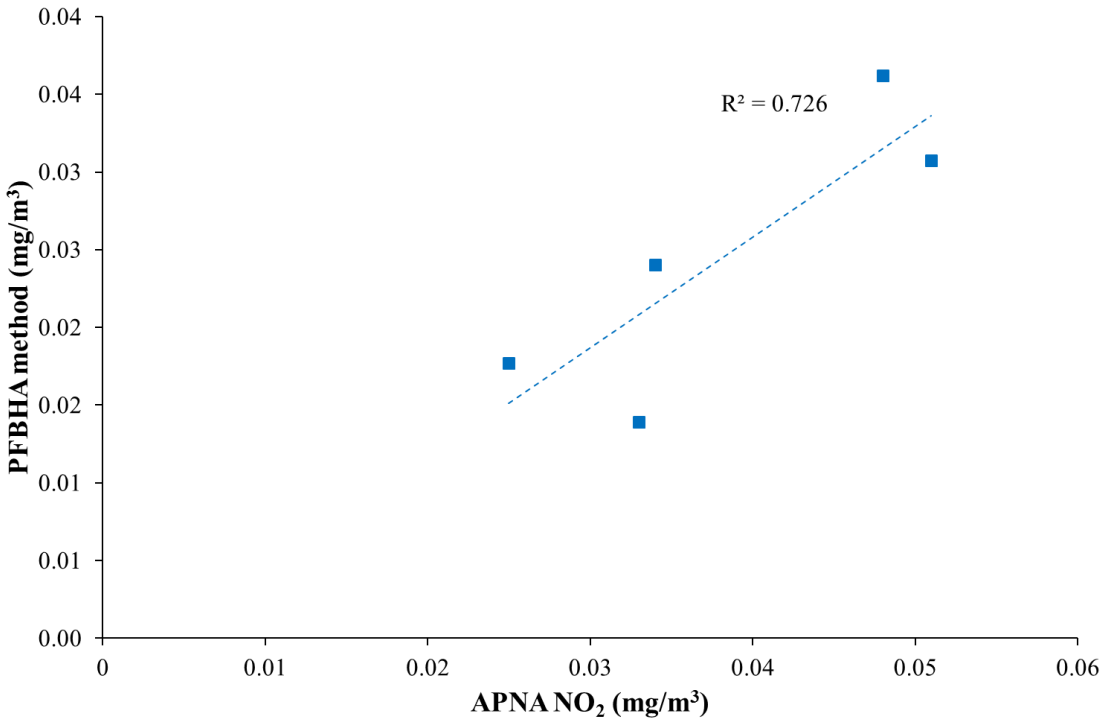

Figure 7.18: Correlation of the APNA NO_2 measurements with the PFBHA NO_2 results

7.6 Conclusion

The new PFBHA method was tested in various polluted environments (simulated and real-world). First, the effect of ozone on the PFBHA cartridge was tested, and it was found that ozone severely affected the accuracy of the acrolein result. It was therefore deemed necessary to use a KI cartridge to remove ozone from the sample.

Secondly, the method was tested in a simulated polluted environment, which included a mixture of NO, NO_2 and CO, along with formaldehyde, acetaldehyde and acrolein, to establish how the combination of the gases affect the sampling of the aldehyde, thereby establishing a collection efficiency of the cartridge. The collection efficiency of acrolein stays above the 90 % threshold up to a mass of 144.5 μg total aldehydes as formaldehyde. At these same conditions the DNPH method failed to measure any of the aldehydes, due to a complete destruction of the DNPH by CO and NO_2, and displacement of the aldehydes by these gases. The failure to measure the aldehydes using the DNPH method is the same as results described by 4-Rail Services Ltd for the London Underground maintenance sites. The PFBHA method is superior to the DNPH method in polluted environments.

Lastly, the aldehyde concentrations were measured in a train depot at Neville Hill in Leeds, where DMU repair and maintenance take place. The concentrations of CO and NO_2 were measured along with the aldehyde concentrations. The DNPH method was used in parallel with PFBHA method for comparison. The PFBHA method measure higher concentrations of formaldehyde than the DNPH method. This was due to the presence of CO and NO_2 in the air sampled, which affects the DNPH method accuracy. The discrepancy in the concentration of formaldehyde measured by the DNPH method means that in most cases it is probable that the actual concentration of formaldehyde is higher, and in some cases the WEL could be exceeded.

The acetaldehyde concentrations were not detected by either method. It was possible to measure the acrolein concentration with the PFBHA method, which is not possible with the DNPH method. The acrolein concentrations were close to, and one day exceeded the WEL for acrolein.

As an added possible benefit, the NO_2 concentrations were measured using the PFBHA cartridge. The concentrations were below those obtained by the chemiluminescence detector. The NO_2 measurement, using the PFBHA method, requires validation to fully understand its interferences and limitations.

Chapter 8
Conclusion and Future Work

8.1 Conclusion

The introduction of this thesis articulates the increasing need for the accurate measurement of aldehydes due to environmental, health and safety concerns. The capture and derivatisation of the aldehydes on the DNPH cartridge and subsequent analysis on HPLC is the recommended method by the HSE UK and the most popular method applied in environmental and air quality measurements (Chapter 1). However, this method is known to be prone to interference from ozone and nitrogen dioxide. Acrolein has also been excluded from the list of aldehydes that can be measured by the DNPH, requiring a second measurement method for the determination of acrolein.

The measurement of the aldehydes was attempted by 4-Rail Services Ltd in the London Underground maintenance sites, using the DNPH method, but no results were obtained. Subsequently, 4-Rail Services Ltd approached the University of Leeds to develop a method which would be able to measure the aldehydes in a diesel engine environment in a confined space.

The London Underground maintenance sites are characterised to be confined spaces, with workers being exposed to diesel engine exhaust emissions from the plant equipment used. There is no sunlight to cause any secondary reactions, and therefore there are minimal secondary pollutants. Although the NO_x and CO WELs are generally adhered to in these London Underground maintenance sites, these levels of CO and NO_x are higher than Air Quality standards and thus these maintenance sites can be classified as polluted environments.

The aim of this thesis was to develop a method that could measure formaldehyde, acetaldehyde and acrolein, simultaneously, in a polluted environment, in a confined space.

The literature review in Chapter 2 revealed that, besides the major chromatographic interferences from O_3 and NO_2, that carboxylic acids, humidity, the sorbent material of the cartridge, and the sampling time also to a lesser extent contributed to problems with the DNPH method. Acrolein cannot be measured using the DNPH method because of its

high reactivity, creating dimers and adducts with the DNPH. However, these findings did not account for the failure of the DNPH method in the London Underground maintenance sites and further investigation was required. An in-depth review of alternative derivatisation reagents to DNPH showed that several substitutes were available. Most of the derivatisation reagents were found to react with ozone, but only a few were assessed in the presence of NO_2. For some of the derivatisation reagents the reaction with acrolein had been evaluated as well.

The first objective was to investigate the DNPH method and its shortcomings and to identify any other possible interferences from the main DEEE constituent gases to explain the failure of the method. It was also necessary to assess the impact of these interferences on the quantification of the aldehydes. In Chapter 4, the DNPH method was established and validated for formaldehyde and acetaldehyde. The problems with acrolein and the chromatographic interferences from ozone and NO_2 on the DNPH method were confirmed. It was determined that NO and the carboxylic acids, formic and acetic acid, did not react with DNPH, and therefore would not cause an interference on the quantification of the aldehydes. For the first time, CO was shown to react with DNPH and interfere with the determination of acetone using the DNPH method. The reaction product of CO and DNPH co-eluted with acetone-DNPH and was identified to have the same structure as acetone-DNPH according to the mass spectrum from GC-MS.

The effect of NO, NO_2 and CO on the capture and retention of the aldehydes using the DNPH method was determined. All three gases were found to hinder the capture of formaldehyde, and to a lesser extent, acetaldehyde, by competing for adsorption sites on the silica gel sorbent during sampling. In addition, NO_2 and CO decrease the available amount of DNPH for derivatisation of the aldehydes by reacting with the DNPH. The retention of the aldehydes on the cartridge were also affected by these gases, by possibly increasing the pH of the cartridge and thereby allowing the derivatisation reaction to be reversed, releasing the aldehydes. The overall effect of the gases on the DNPH method would result in the underestimation of the aldehyde concentrations in a polluted environment.

Finally, the destruction of DNPH by ozone, NO, NO_2 and CO was quantified, and an equation to calculate the required DNPH cartridge capacity when sampling in a polluted environment was proposed. An analysis was performed on the cartridge cost to increase the DNPH available through several scenarios i.e. lower sample flow rate, increasing the

amount of cartridges, increasing the DNPH loading of the cartridge, and increasing the size of the cartridge. The most cost effective option was to reduce the sample flow rate to 0.1 L/min (flow rate range of 0.1 – 2.0 L/min) and to use 5 cartridges instead of only 2 cartridges. Another alternative to consider was the replacement of the DNPH with another derivatisation reagent that is less reactive with NO, NO_2 and CO.

The work in Chapter 4 brought to light that using the DNPH method in a polluted environment should be done with caution. Any results obtained from the DNPH method during measurement in polluted environments, were probably lower than the actual concentration levels, which is concerning. In Chapter 2 the studies summarised in Table **2.2** report concentration levels lower than the WELs, but this may not be accurate, as almost all of these analyses were performed using the DNPH method. Some of the inaccuracy of the method could be corrected by increasing the capacity of the DNPH cartridge. However, the displacement of the aldehydes by the reversal of the DNPH derivatisation reaction cannot be resolved and therefore the method would still deliver diminished results.

The evaluation of alternative derivatisation reagents to DNPH, and how these reagents are affected by the identified interferences of the DNPH method, was the second objective. The criteria set for the screening of the derivatisation reagents included considering the difficulties associated with using the derivatisation reagent, commercial availability and affordability, one acrolein-derivative formation, reaction products formed with NO, NO_2 and CO, and a relatively short reaction time with the aldehydes. First, five derivatisation reagents were chosen, i.e. DAIH, HBA, MBTH, PFBHA and PFPH, from those identified in the literature review (Chapter 2), based on the criteria set for the new method. Secondly, the reaction of acrolein with each of the chosen derivatisation reagents was ascertained. MBTH, PFPH and PFBHA formed stable acrolein-derivatives, with DAIH and HBA forming at least one adduct that was visible on the chromatograms. Next, any chromatographic interferences by the reaction products of NO, NO_2 and CO with each derivatisation reagent were assessed, as no information on these reactions were found in the literature. An attempt was made to identify some of the reaction products formed, based on the mass spectrum obtained from GC-MS (Appendix B). All the derivatisation reagents reacted with NO_2, and the reaction products were visible on the various chromatograms, with the reaction products of DAIH and HBA interfering with the acetaldehyde-derivative, respectively. Each of the derivatisation reagents were found

to react with CO, however, only the reaction products of MBTH with CO interfered with the acrolein-MBTH peak. These chromatographic interferences are of concern, as it would cause inaccurate quantification of the aldehydes in polluted environments using DAIH, HBA and MBTH.

Interestingly, the reaction products of PFBHA and PFPH with CO was found to have a structure the same as that of acetone-derivative for each derivatisation reagent. This result is similar to the reaction product of DNPH with CO, with the formation of acetone-DNPH, as seen in Chapter 4. Therefore, the presence of CO would cause an overestimation of acetone when measuring the aldehydes using PFPH and PFBHA as the derivatisation reagent. The reaction products of other derivatisation reagents with CO could also yield an acetone-derivative, meaning it is possible that many methods are reporting an elevated concentration for acetone.

The destruction of the derivatisation reagents by NO, NO_2 and CO was quantified. A high amount of destruction of MBTH and HBA occurred in the presence of these gases, and would result in a lower amount of the derivatisation reagent being available for the derivatisation of the aldehydes. These derivatisation reagents are therefore not suitable for use in a method for the sampling and analysis of aldehydes in a polluted environment. DAIH was found to be the least susceptible to destruction by NO, NO_2 and CO. However, due to chromatographic interferences of the DAIH with NO_2, PFBHA was chosen as the preferred derivatisation reagent.

The evaluation of the alternative derivatisation reagents made it evident that these derivatisation reagents are also affected by the same parameters as the DNPH derivatisation reagent. If the derivatisation reagent is simply replaced by another derivatisation reagent, only taking into account the chromatographic interference (as was seen in the literature review), this will lead to the same type of problems encountered as with the DNPH method. It is therefore not as simple as replacing the DNPH with another derivatisation reagent. Some are less affected by the gases, and these make for good alternatives, however, other factors that affect the usefulness of the method need to be taken into consideration. Chapter 5 has widened the knowledge base of the derivatisation reagents and their performance in a polluted environment, and this knowledge could be used to make a more informed decision when choosing an alternative derivatisation reagent. An equation for the calculation of the mass required of each derivatisation reagent was proposed in Chapter 5.

An alternative method to the use of a derivatisation reagent was investigated in Chapter 5. The oxidation of the aldehydes to carboxylic acids using hydrogen peroxide was considered. The carboxylic acids would be measured as the formate and acetate ions using ion chromatography. However, the oxidation of the aldehydes to carboxylic acids could not be controlled, even in the acidic environment, and most experiments resulted in the aldehydes being oxidised to CO_2. Due to time constraints the work was abandoned. This work tried to address the third objective set, however, some more thought, and a lot more time is required to develop the idea.

Chapter 6 continued with the derivatisation analysis method development. The collection efficiencies for formaldehyde, acetaldehyde and acrolein by various sorbents were determined. It was found that despite these sorbent being regularly used for thermal desorption, they were mostly ineffective in the capture of all three aldehydes of interest. The silica gel captured formaldehyde and acetaldehyde but did not capture acrolein at all. This may partially explain the low recoveries seen for acrolein when using the DNPH method. By coating the silica gel with hydroquinone, it was found that the collection efficiency for acrolein improved tremendously, possibly due to the stabilising effect hydroquinone has on the acrolein molecule.

The reaction of hydroquinone with NO, NO_2 and CO was determined, as it would possibly be included in the method. The reaction of the NO_2 with hydroquinone yielded p-benzoquinone by oxidation, and in addition yielded 2-nitrobenzene-1,4-diol. These reaction products could interfere on the chromatogram during analysis, and later it was shown that these compounds did not interfere chromatographically with the PFBHA-derivatives. The destruction of hydroquinone by NO_2 was also quantified.

Coating the cartridge with a both hydroquinone and PFBHA for the sampling of the aldehydes resulted in 100 % collection efficiencies for all three of the aldehydes. The new method, where the hydroquinone and PFBHA were combined as the coating of the silica gel, was validated, and the results were comparable with those of the DNPH method, as was determined in Chapter 4. The method was therefore fit for purpose for the sampling and analysis of formaldehyde, acetaldehyde and acrolein in air samples, achieving the fourth objective set. The stability of the sample on the cartridge and in the eluent stored at 5°C was determined to be at least 8 days, and the shelf-life of the prepared cartridge was 11 days at room temperature. An added benefit of this cartridge was the possibility

that NO_2 could be measured simultaneously with the aldehydes. This completed the fourth objective where a new method had been developed that has taken into consideration the polluted environment that the sample would be taken in.

The last objective was achieved by testing the newly developed method in simulated environments to discover how well the cartridges captured and retained the aldehydes in polluted environments, as described in Chapter 7. The presence of the hydroquinone protected the formaldehyde- and acetaldehyde-PFBHA from destruction by ozone, however the acrolein recovery was severely affected. Also, the PFBHA showed signs of destruction on exposure to ozone. It was therefore deemed necessary to make use of the KI-cartridge before the sampling cartridges for the removal of ozone from the sample matrix.

The collection efficiency of the cartridge for the aldehydes in a polluted environment indicated that the cartridges had a high capacity for the aldehydes, despite the presence of NO, NO_2 and CO. The collection efficiency of acrolein was the first to be affected by the presence of these gases, at acrolein concentrations 6 times higher than the WEL.

A reliable, portable and cost effective method for the sampling and analysis of formaldehyde, acetaldehyde and acrolein in polluted spaces had been developed.

The newly developed method was used to measure the aldehyde concentration for 5 days in train maintenance depot, at Neville Hill in Leeds. The measurements were performed in parallel with the DNPH method to compare results. The results for formaldehyde using the new method were higher than those obtained using the DNPH method, confirming the postulation (Chapter 4) that the presence of NO, NO_2 and CO would result in the suppression of the measured aldehyde concentration using the DNPH method. This once again shows that many measurements performed in polluted environments (summarised in Chapter 2) would be underreporting the actual concentrations of the aldehydes.

The overall aim was therefore achieved with the development of a method using a cartridge coated with hydroquinone and PFBHA, and analysis of the aldehyde-PFBHA derivatives using GC-MS. It is therefore possible to measure formaldehyde, acetaldehyde and acrolein in a confined space in a polluted environment.

8.2 Limitations

Diesel engine emissions could also include SO_x gases, and these were excluded from this study. The influence that these gases would have on the quantification of the aldehydes on both the DNPH and the new PFBHA method needs to be investigated.

The kinetics of the reactions were not studied, although it may be useful in fully understanding the reaction pathways of each of the derivatisation reagents with the aldehydes as well as NO, NO_2 and CO. The influence of humidity was not included in the study, although it has previously been shown that humidity of the sample has an effect on the collection efficiency of DNPH, by aiding the capture of the aldehydes. The reaction of the carboxylic acids with PFBHA was not determined.

8.3 Future work

The newly developed method could be further expanded to include the quantification of other aldehydes. The ketones could also be included, however the measurement of acetone will be overestimated when CO is present in the sample matrix (Chapter 5).

PFBHA and the aldehyde-PFBHA derivatives are volatile and it is possible to use thermal desorption of the aldehyde-PFBHA derivatives as the sample introduction technique into the GC-MS[159]. It would remove the need for sample preparation, and therefore decrease the sample analysis turnaround time, and improve the accuracy of the method by eliminating sample preparation errors.

Although the hydroquinone coated silica gel sorbent effectively captures the aldehydes, other sorbents are available that were not evaluated in this study. The collection efficiency of formaldehyde using a cartridge containing Florisil as the sorbent, coated with DNPH, was determined to be 97.3 %, and no interferences were observed from NO_2, SO_2, and humidity, although the levels tested were not specified[36].

The oxidation of the aldehydes using hydrogen peroxide was unsuccessful. The use of weaker oxidising agents, such as $KMnO_4$ and $CuCl_2$, should be investigated. Also, the oxidation of the aldehydes should be performed post-sampling, and therefore using silica gel coated with hydroquinone (Chapter 6) for sampling may be useful. Hydroquinone is an antioxidant, and therefore may help to control the oxidation of the aldehydes to the carboxylic acids.

Finally the application areas for the newly developed PFBHA method should be explored. The air quality could be monitored for aldehydes in confined spaces with elevated concentrations of NO_2 and CO e.g. train stations, garages, tunnels and indoors with live fires. Aldehydes are combustion products and therefore would be present in fires, domestic or wild fires. Domestic fires are used to keep houses warm, by burning wood, and coal. The usefulness of the method in fire toxicity monitoring and research for the identification of hazards in fire, for the safety of fire fighters should be explored. A modification of the method so that it could be used in impingers for the monitoring of formaldehyde in stack emissions[189] needs to be examined.

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Appendix A
Calibration and validation data

A.1 DNPH

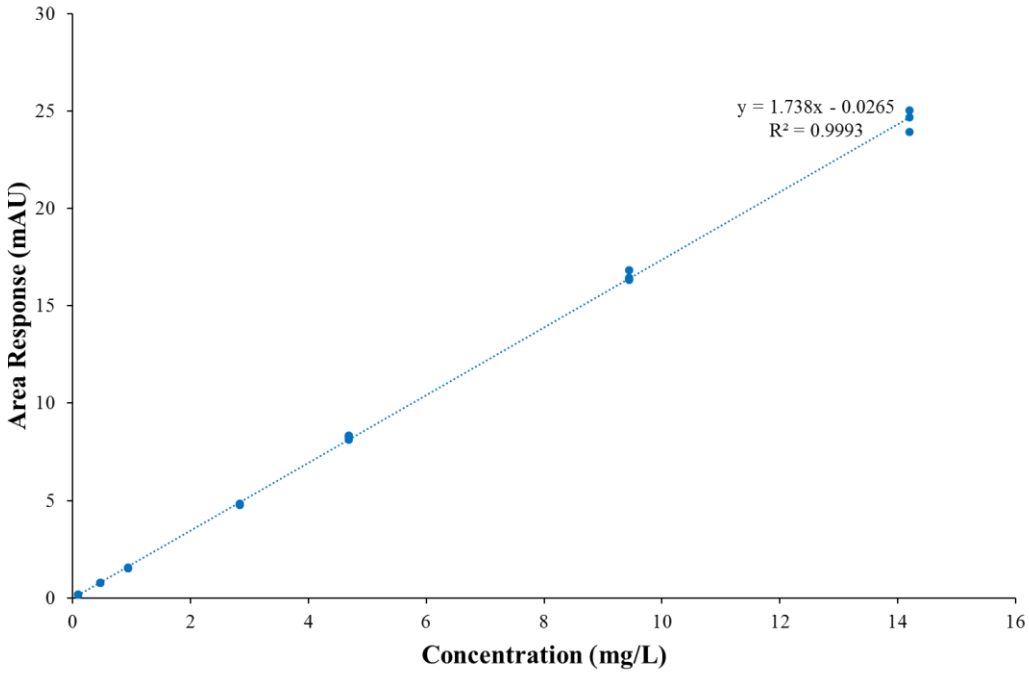

Figure A.1: Calibration curve for formaldehyde-DNPH

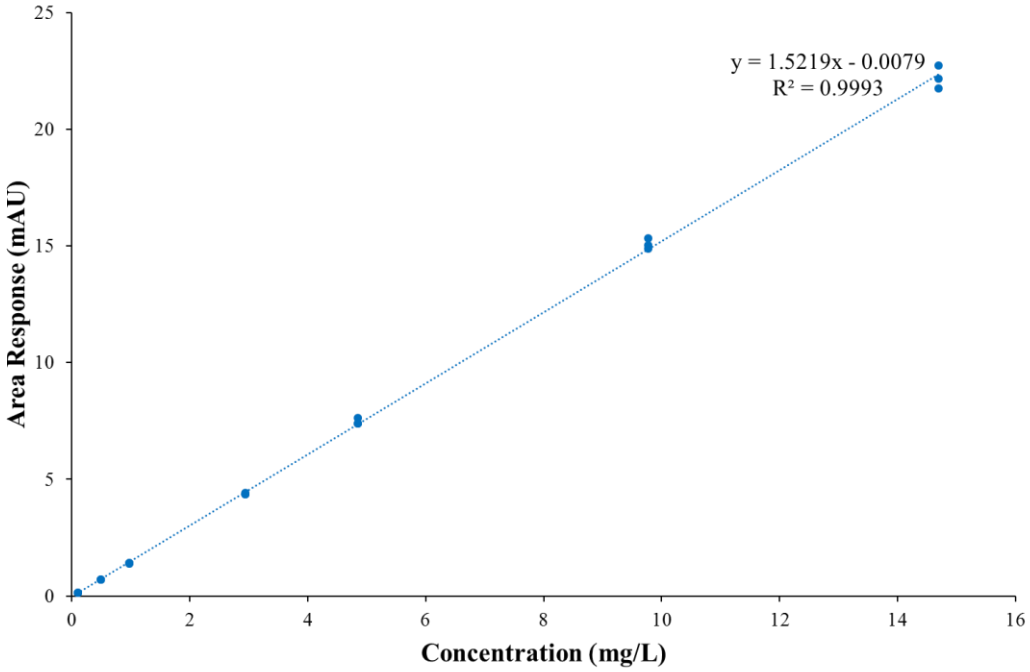

Figure A.2: Calibration curve for acetaldehyde-DNPH

A.2 PFPH

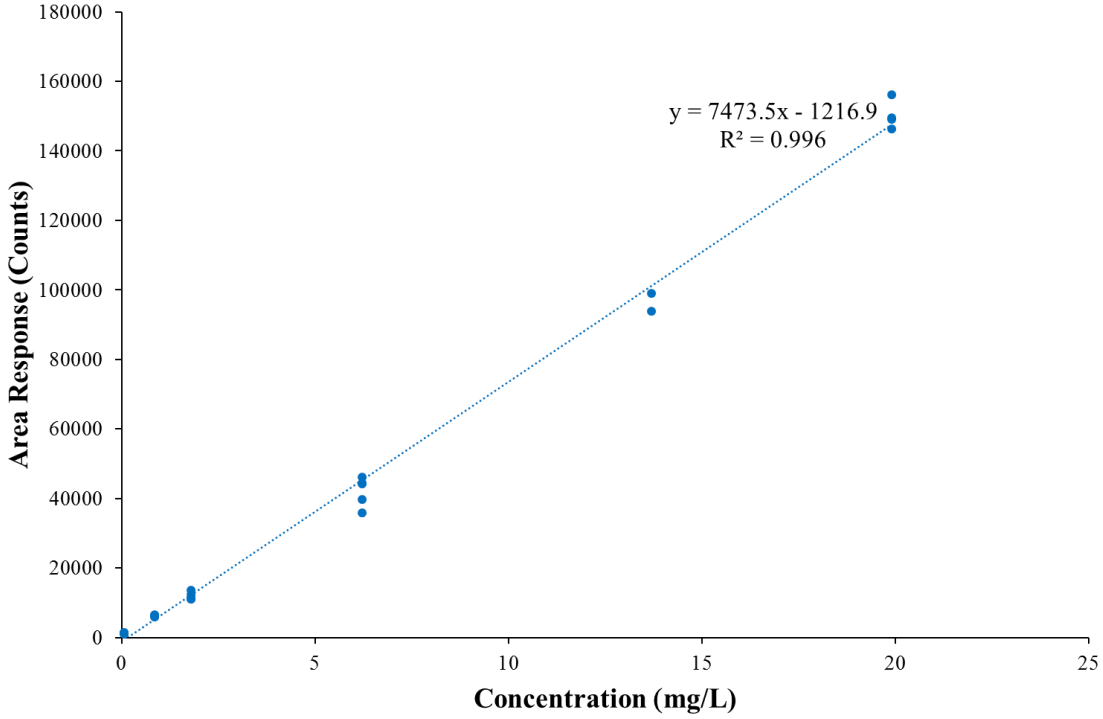

Figure A.3: Calibration curve for formaldehyde-PFPH

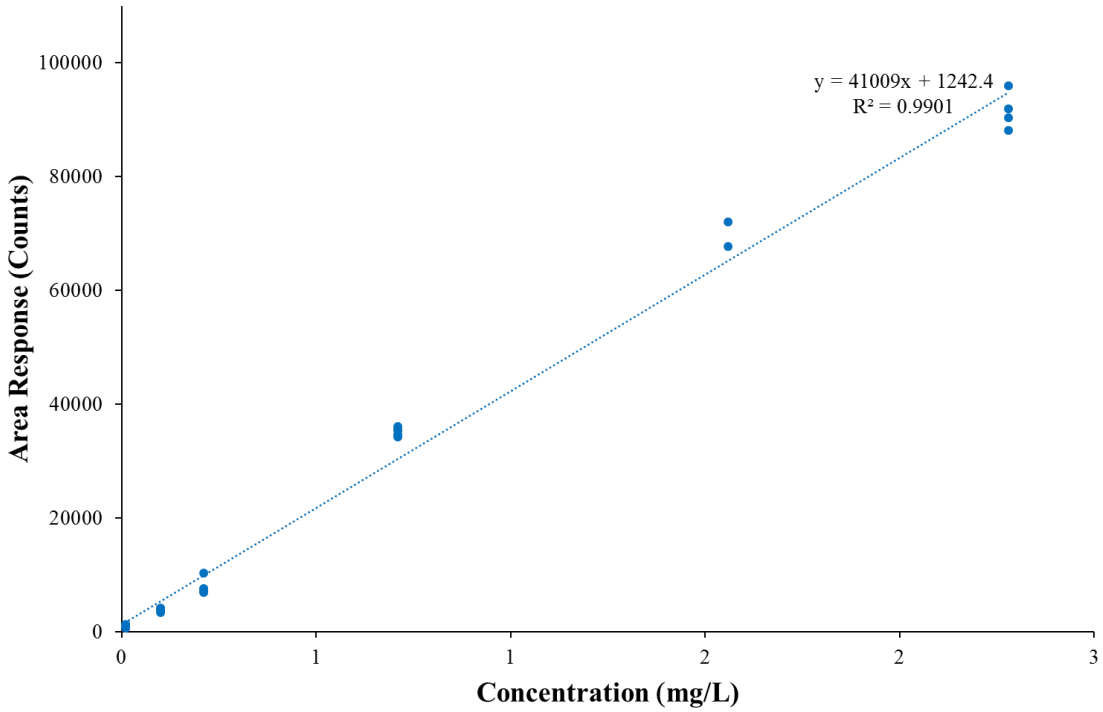

Figure A.4: Calibration curve for acetaldehyde-PFPH

A.3 PFBHA

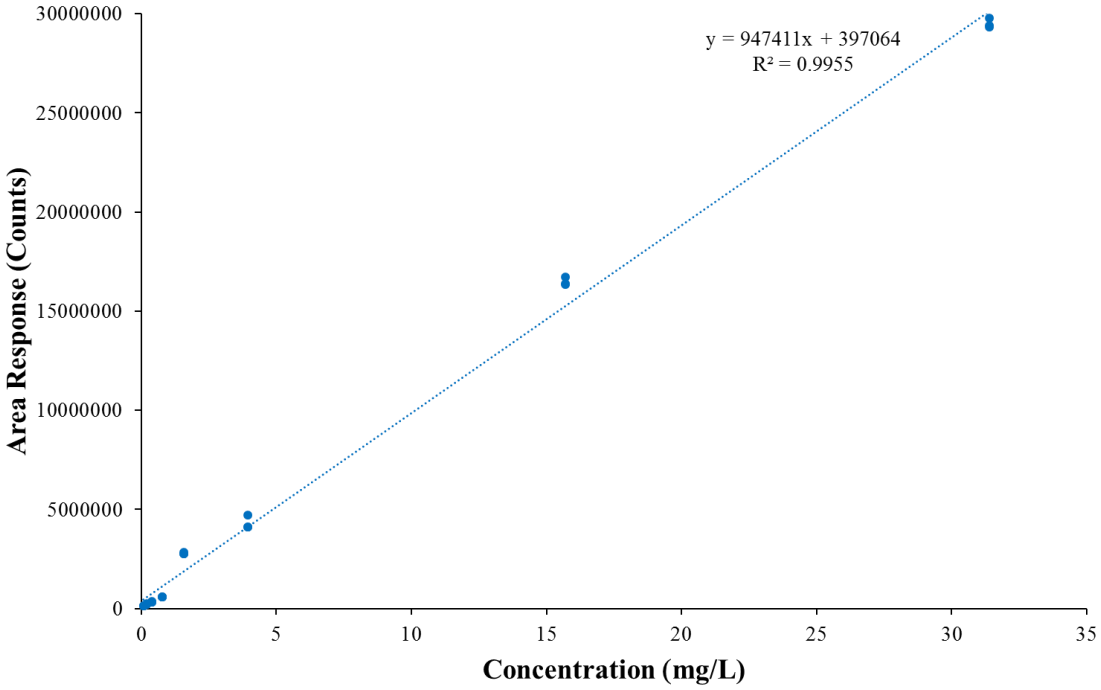

Figure A.5: Calibration curve for formaldehyde-PFBHA

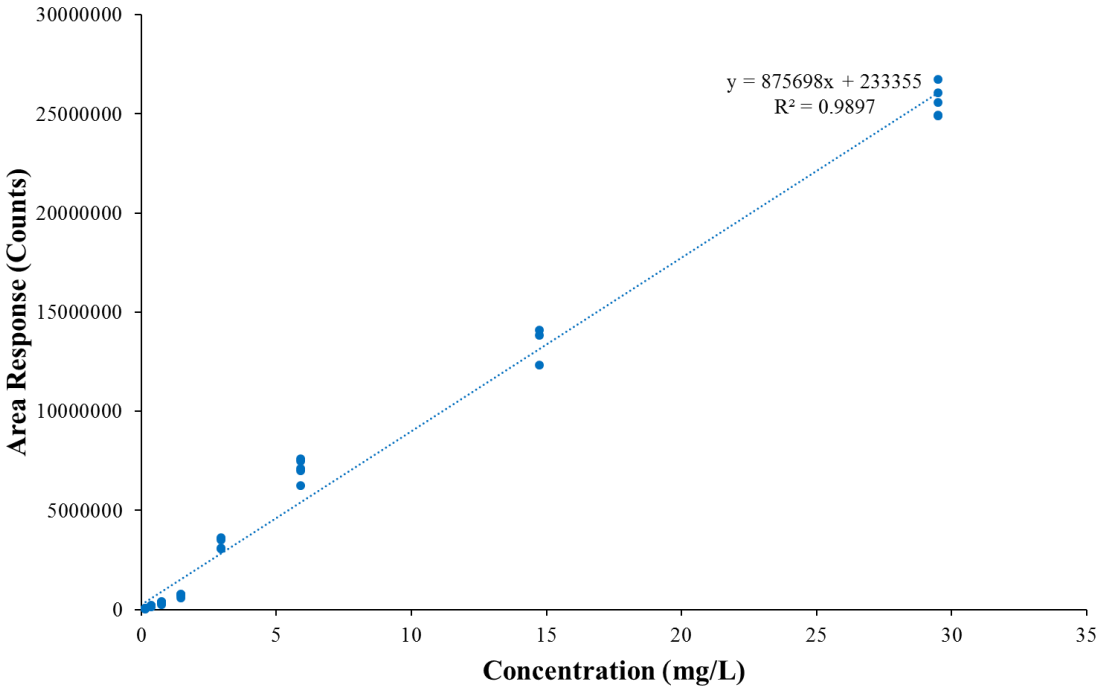

Figure A.6: Calibration curve for acetaldehyde-PFBHA

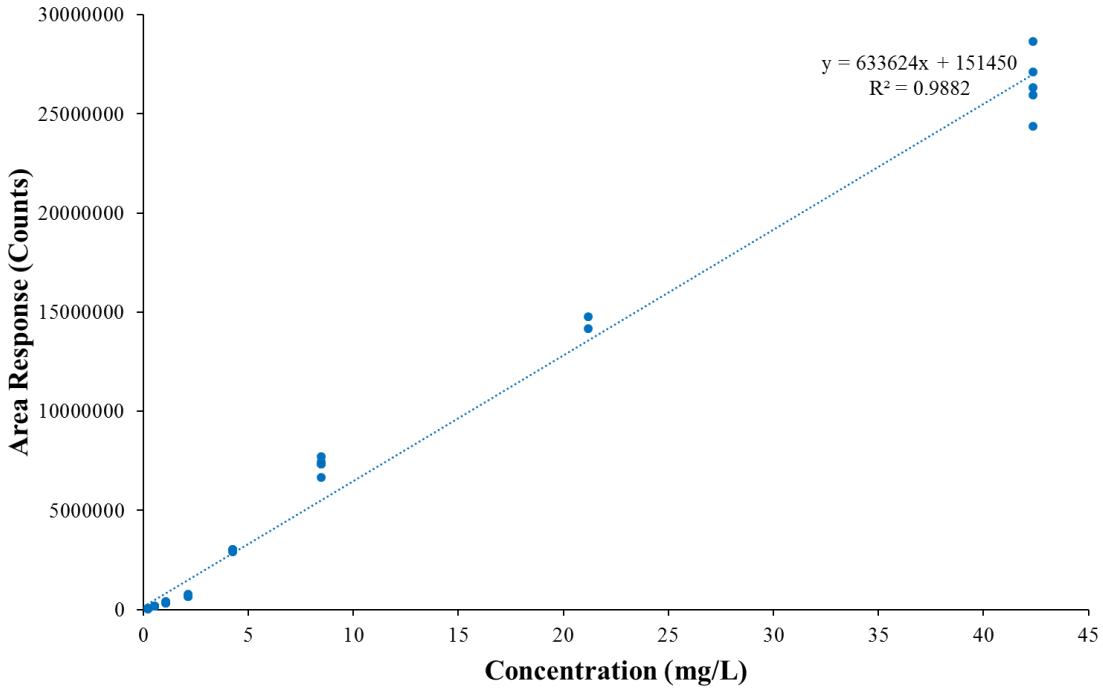

Figure A.7: Calibration curve for acrolein-PFBHA

A.4 MBTH

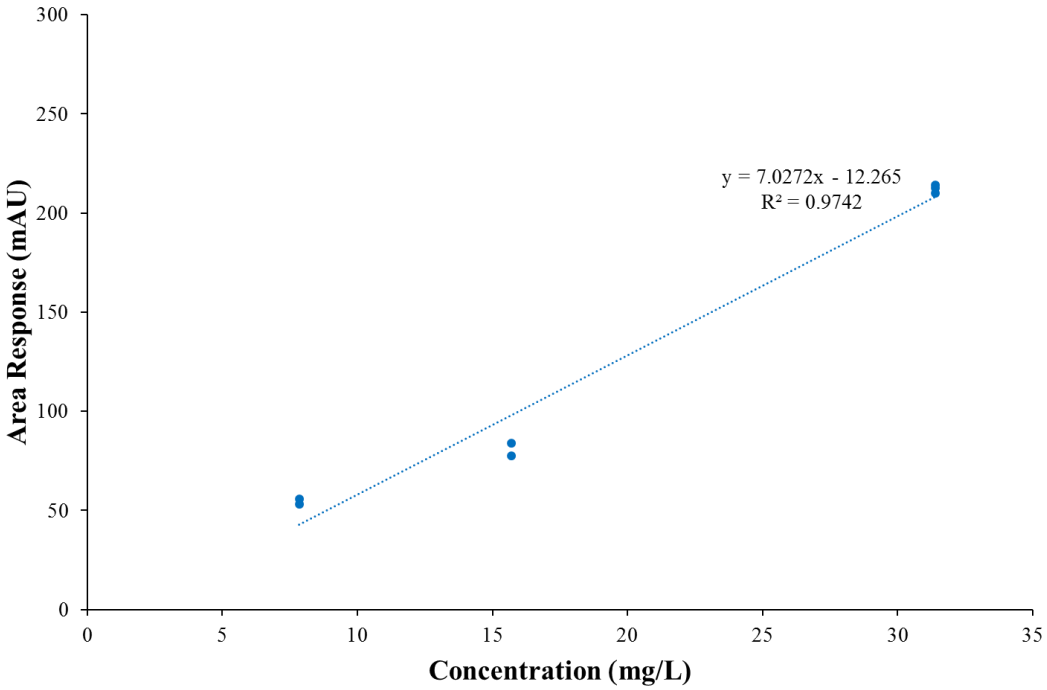

Figure A.8: Calibration curve for formaldehyde-MBTH

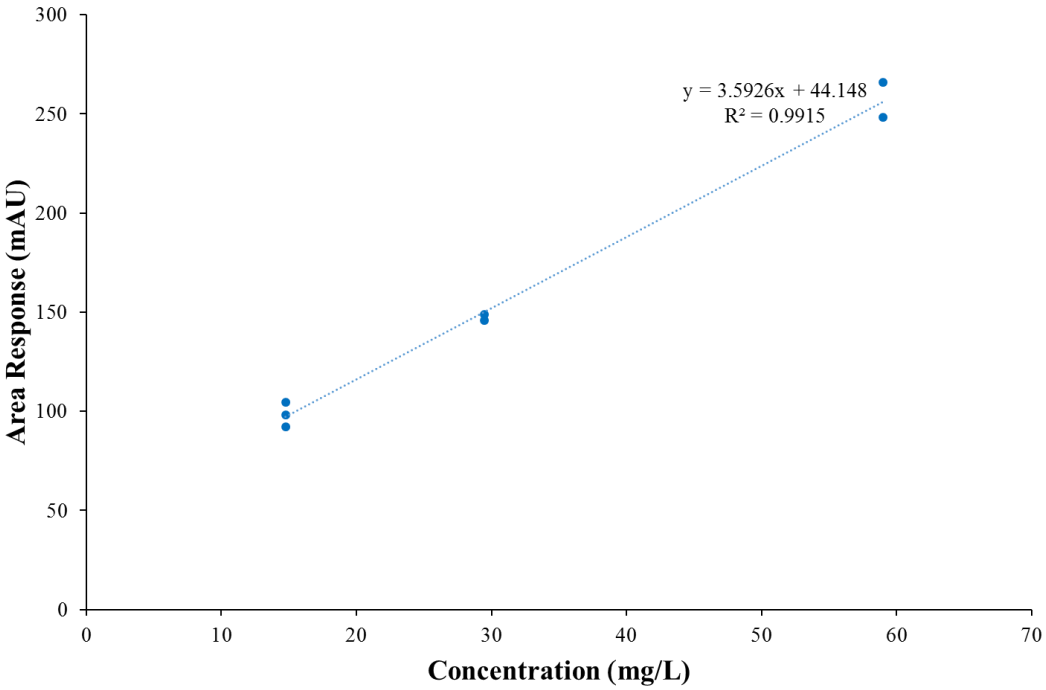

Figure A.9: Calibration curve for acetaldehyde-MBTH

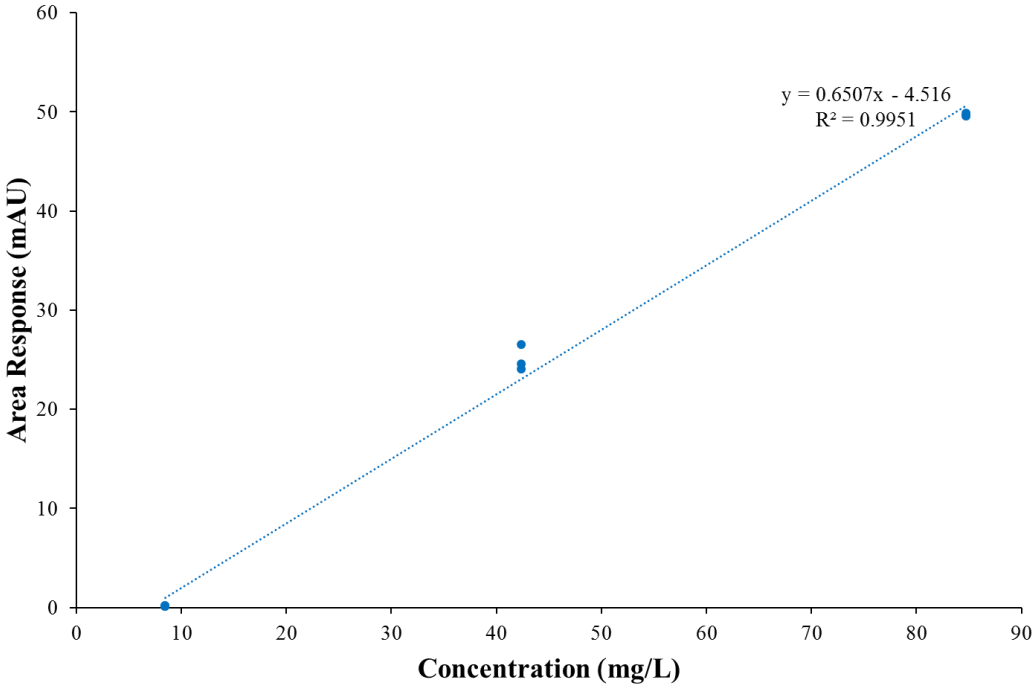

Figure A.10: Calibration curve for acrolein-MBTH

A.5 PFBHA and hydroquinone

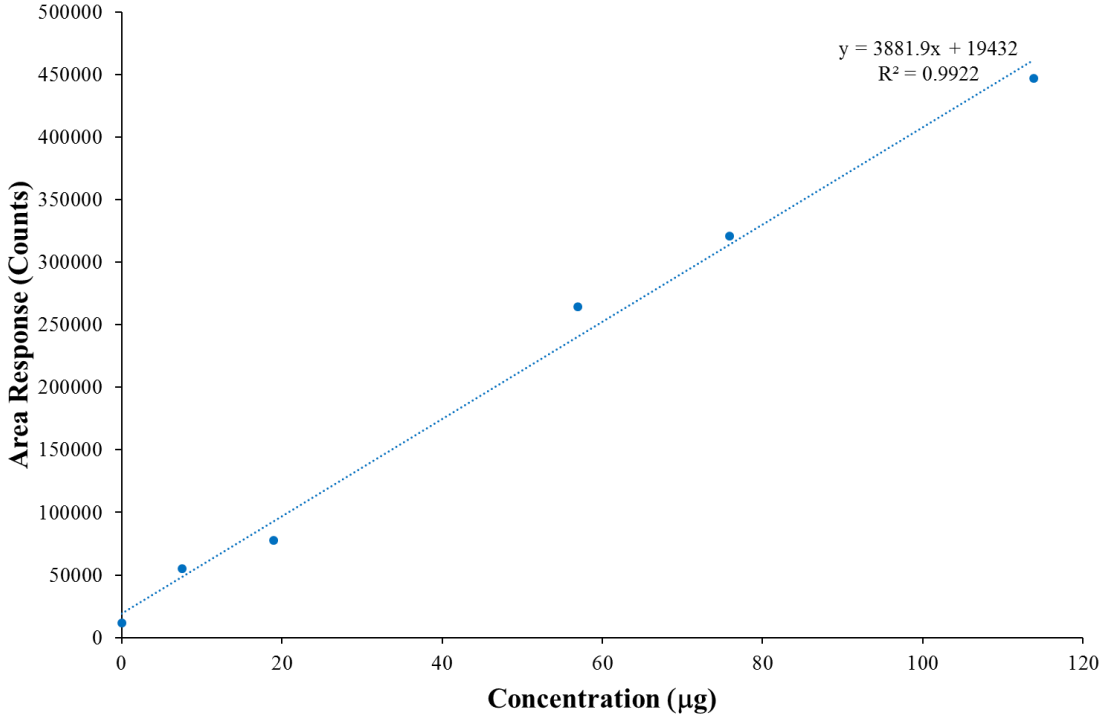

Figure A.11: Calibration curve for formaldehyde-PFBHA in presence of hydroquinone

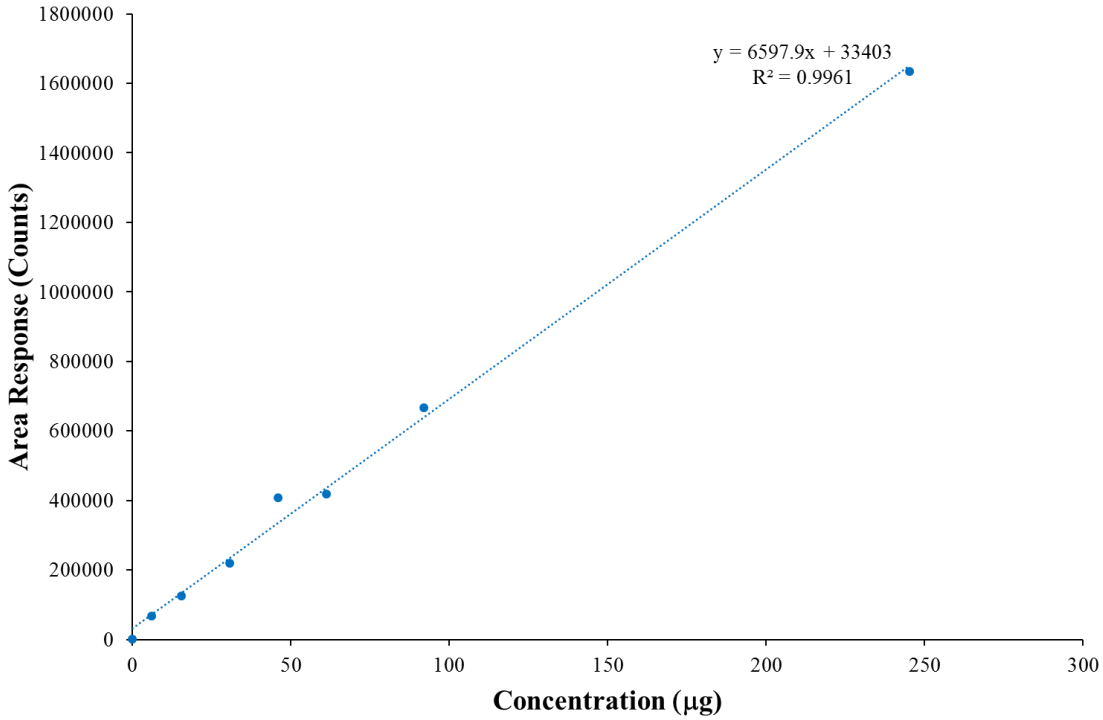

Figure A.12: Calibration curve for acetaldehyde-PFBHA in presence of hydroquinone

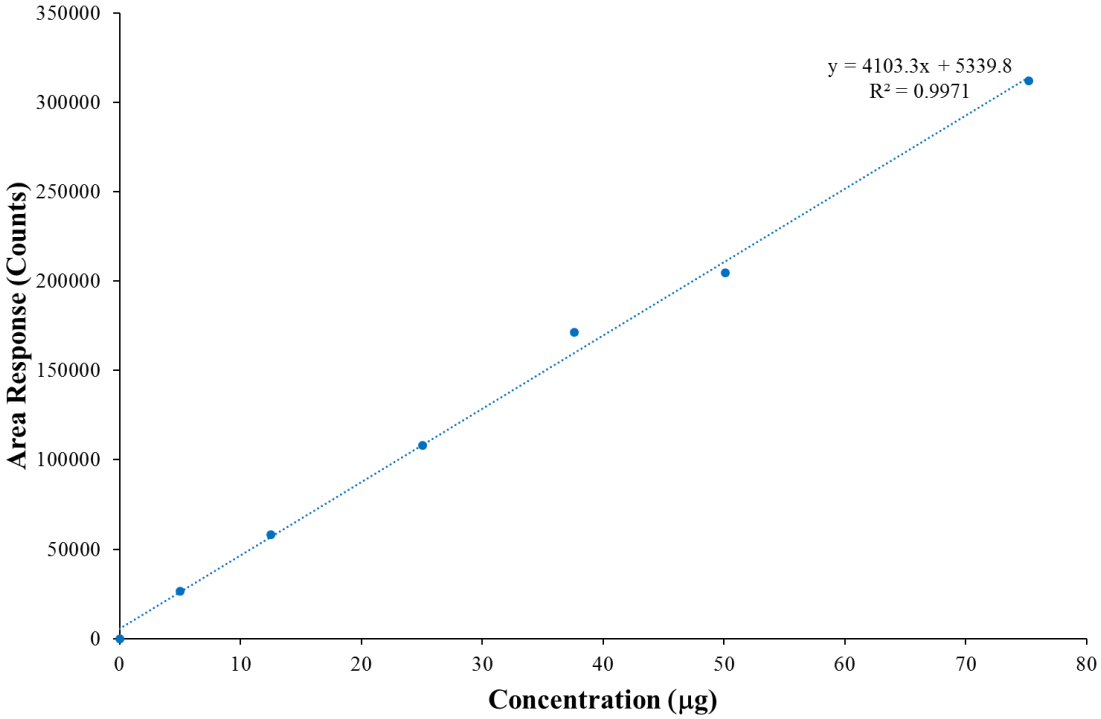

Figure A.13: Calibration curve for acrolein-PFBHA in the presence of hydroquinone

A.6 DAIH

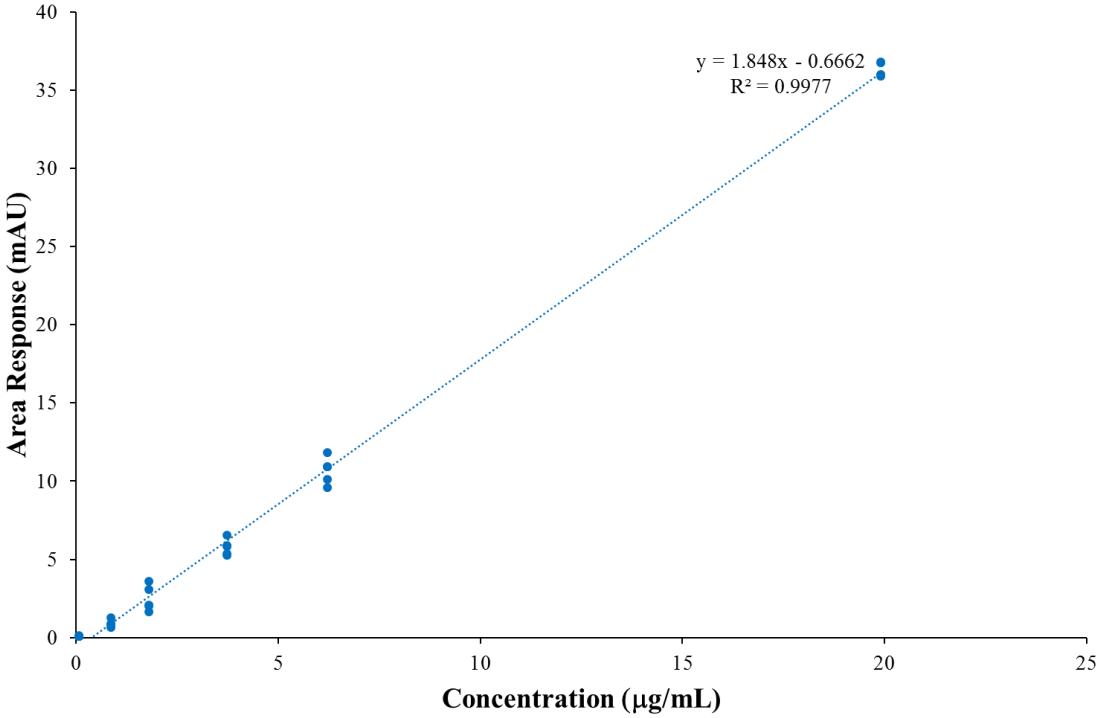

Figure A.14: Calibration curve for formaldehyde-DAIH

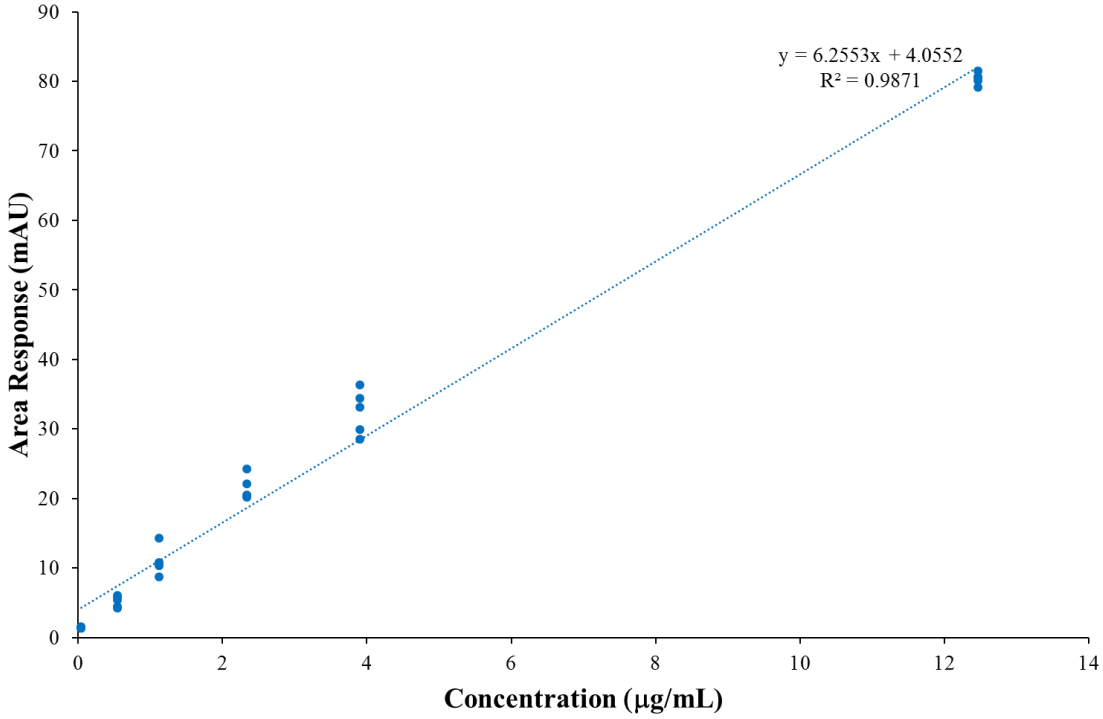

Figure A.15: Calibration curve for acetaldehyde-DAIH

A.7 Carboxylic acids on IC

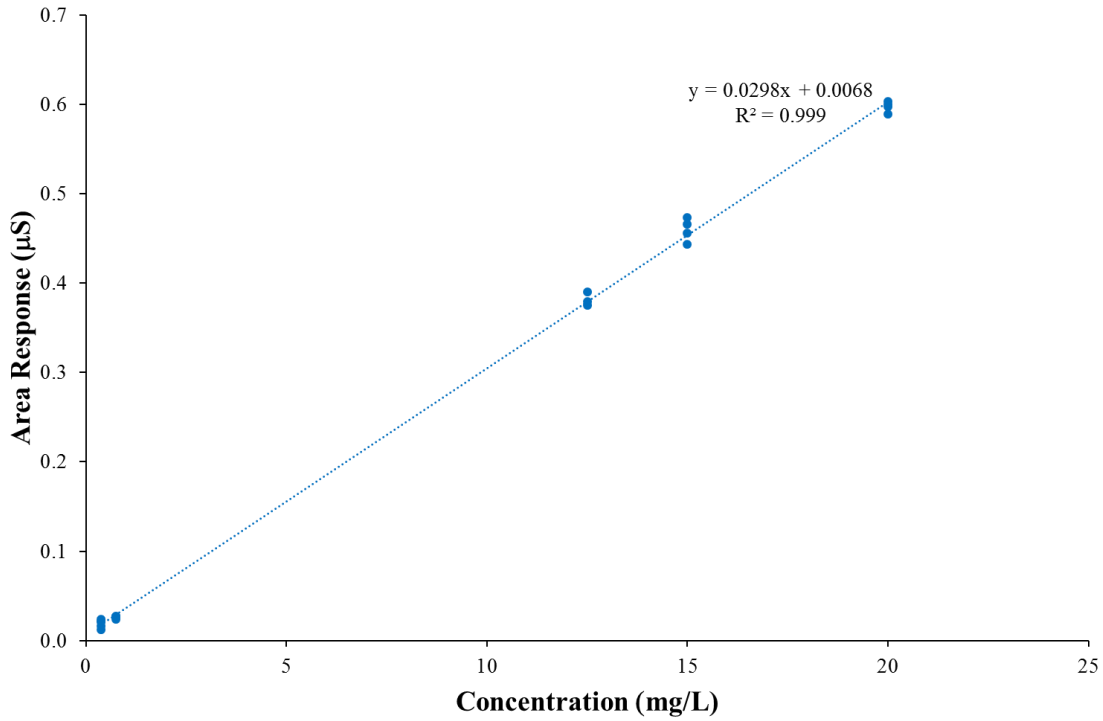

Figure A.16: Calibration curve for formic acid

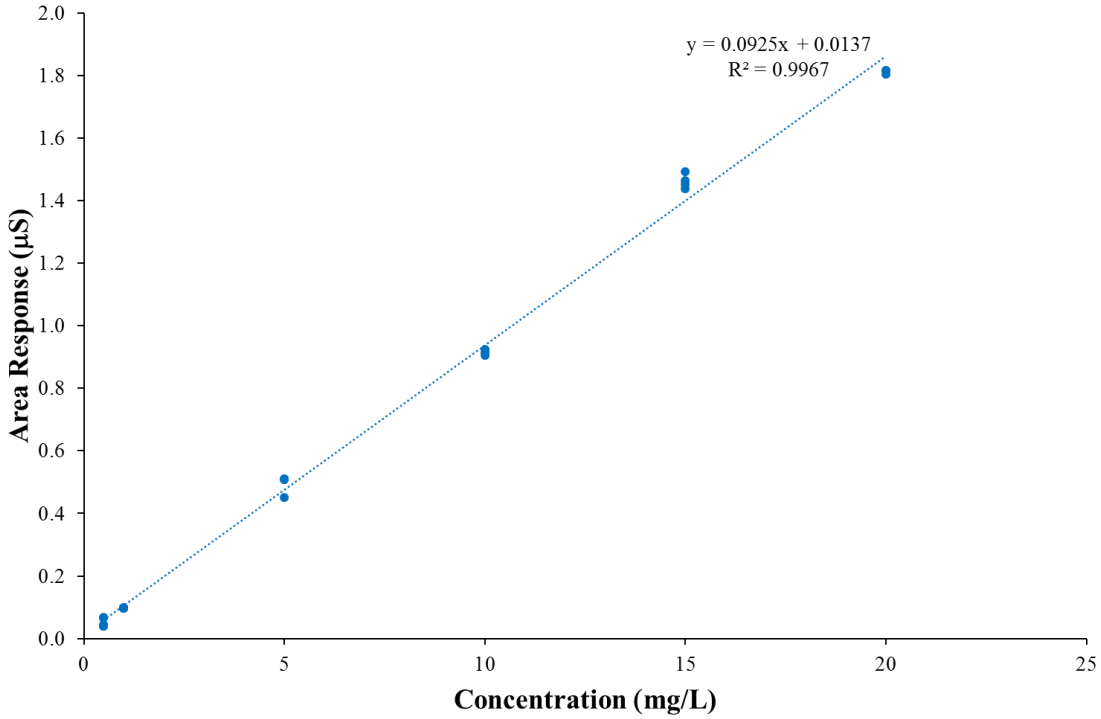

Figure A.17: Calibration curve for acetic acid

A.8 Method detection and quantification limits

Table A.1: Method detection and quantification limits

Derivatisation reagent/method	Formaldehyde		Acetaldehyde		Acrolein	
	LOD (µg/m^3)	LOQ (µg/m^3)	LOD (µg/m^3)	LOQ (µg/m^3)	LOD (µg/m^3)	LOQ (µg/m^3)
PFPH	8.13	24.58	1.48	4.38	-	-
MBTH	44.87	136.0	69.72	211.3	101.5	307.5
DAIH	5.42	16.46	8.13	24.38	-	-
Ion chromatography (carboxylic acids)	5.83	17.50	8.75	26.67	-	-

Appendix B
Mass spectra of identified compounds

B.1 DNPH

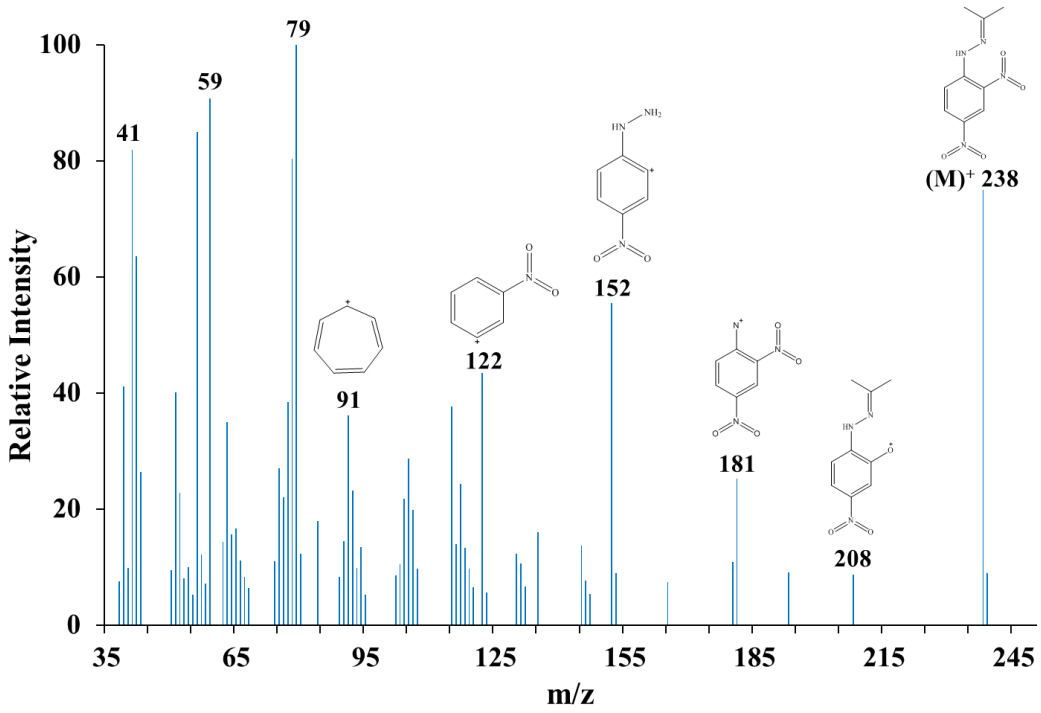

Figure B.1: Mass spectrum for the reaction product of CO with DNPH

B.2 MBTH

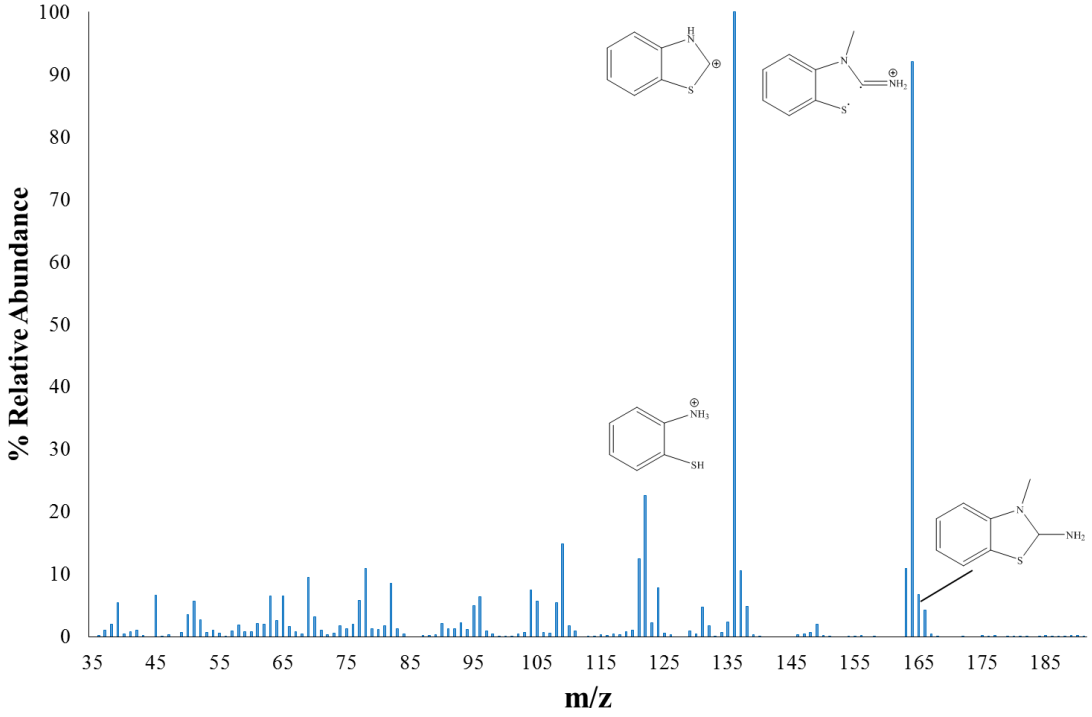

Figure B.2: Mass spectrum for the reaction product of NO_2 with MBTH (1)

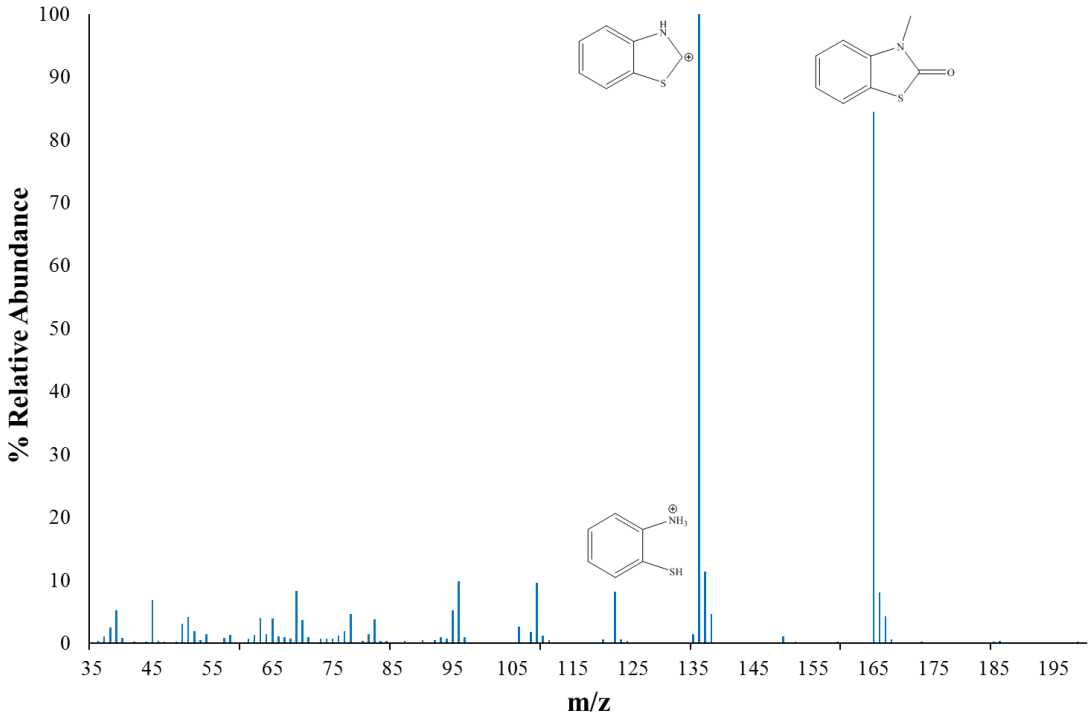

Figure B.3: Mass spectrum for the reaction product of NO_2 with MBTH (2)

B.3 PFPH

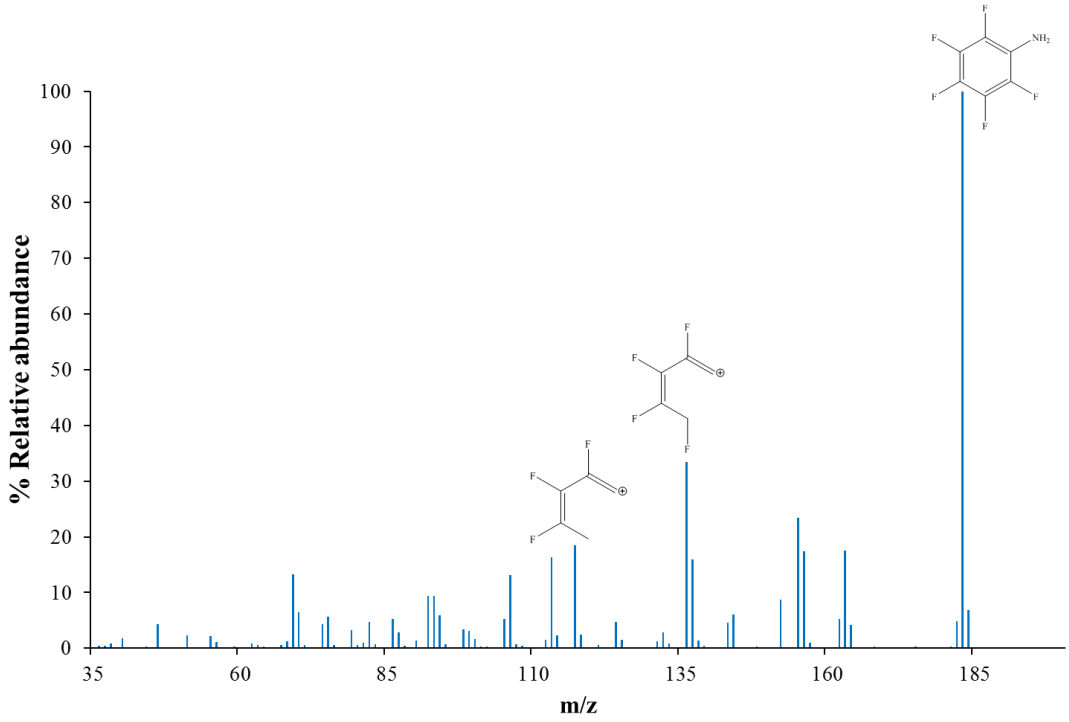

Figure B.4: Mass spectrum of reaction product of NO_2 with PFPH

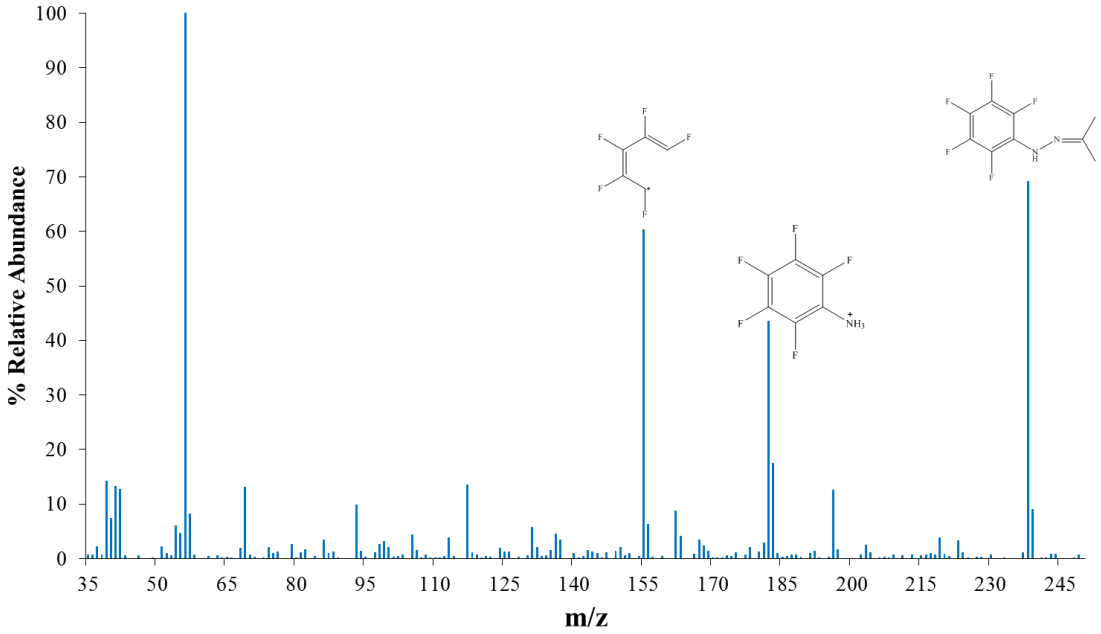

Figure B.5: Mass spectrum of reaction product of CO with PFPH (1)

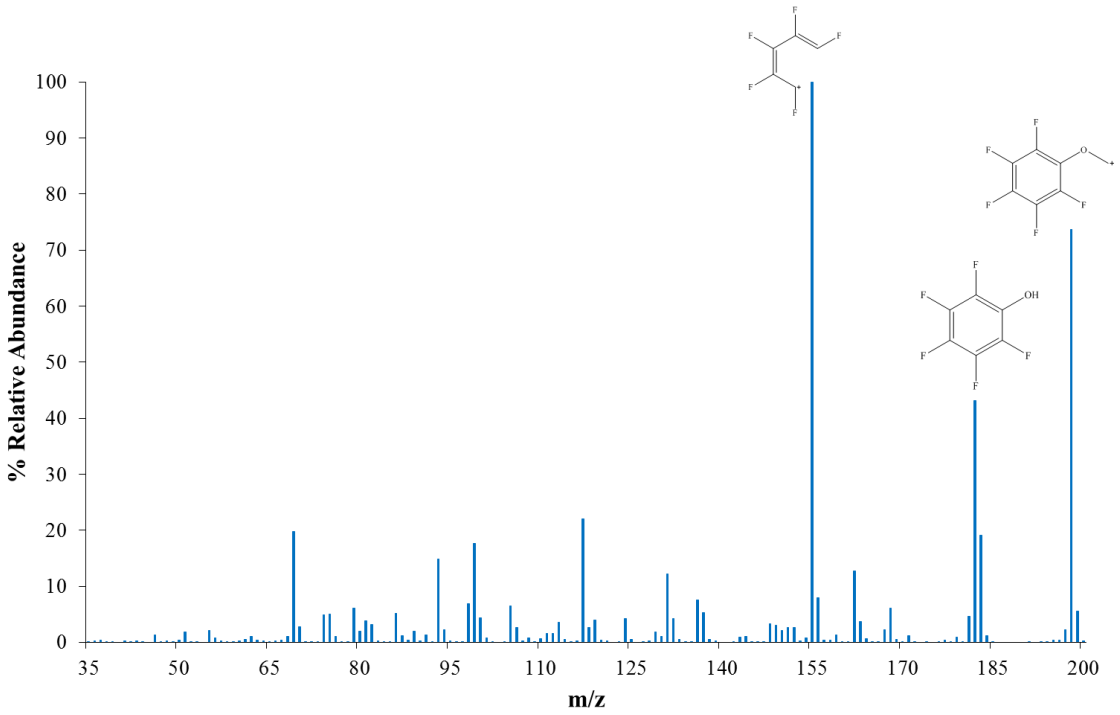

Figure B.6: Mass spectrum of reaction product of CO with PFPH (2)

B.4 PFBHA

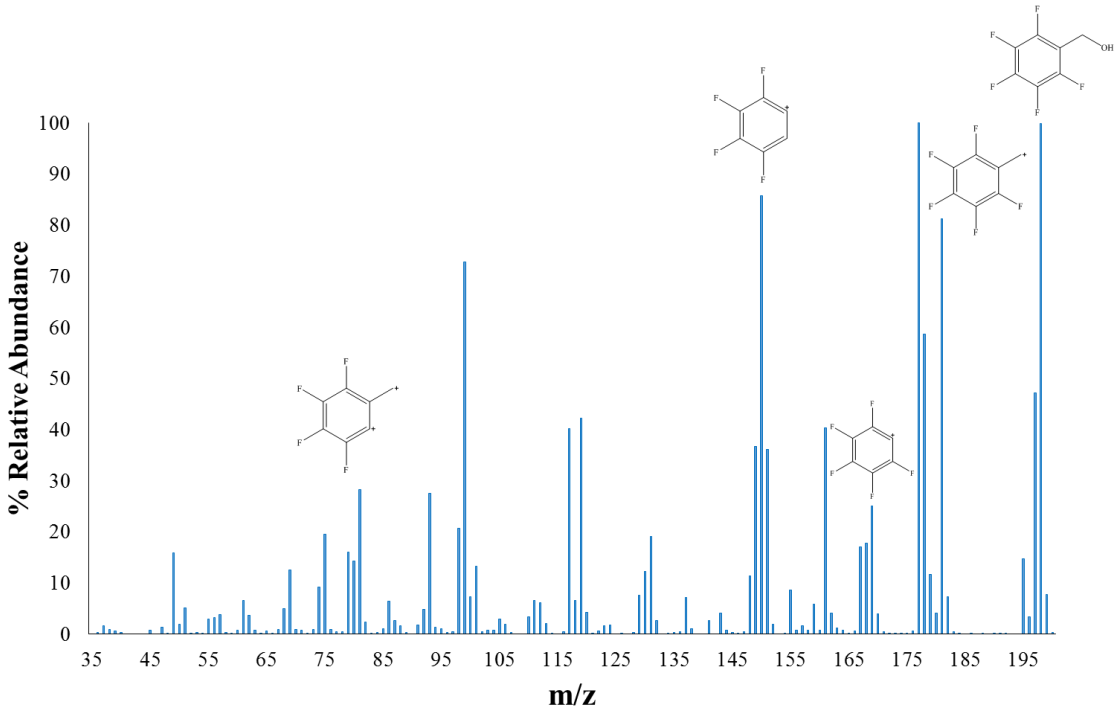

Figure B.7: Mass spectrum of reaction product of PFBHA with NO_2

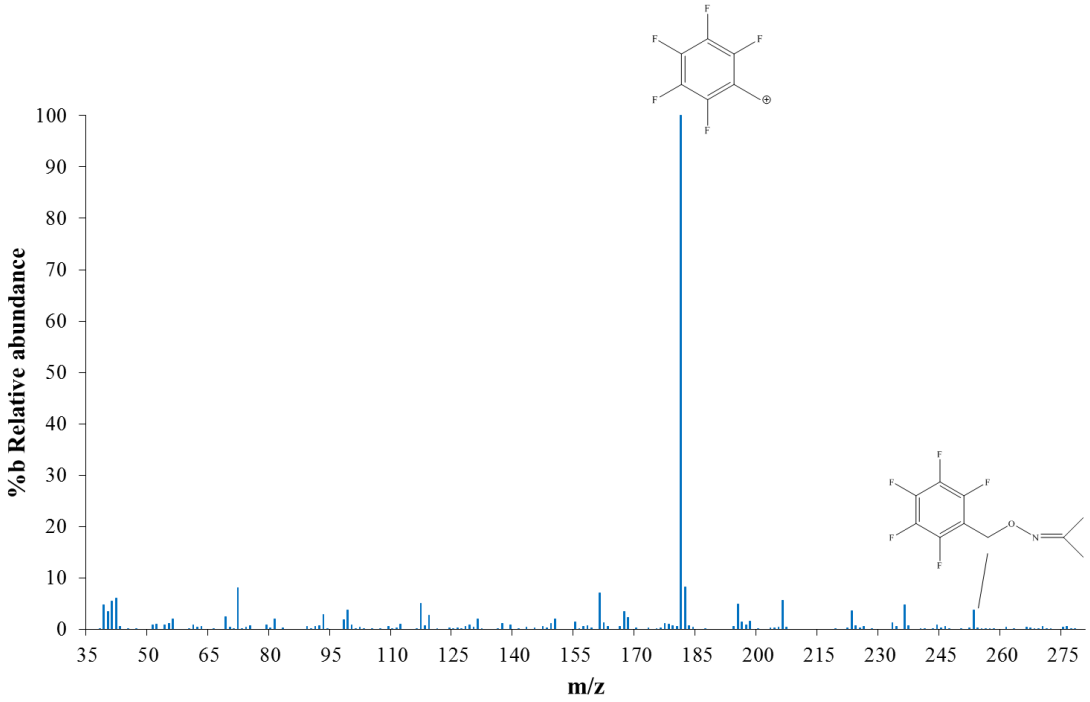

Figure B.8: Mass spectrum of reaction product of PFBHA with CO