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Quantification of the influence of NO_2, NO and CO gases on the determination of formaldehyde and acetaldehyde using the DNPH method as applied to polluted environments

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Abstract

Airborne aldehydes have a significant impact on human health, especially in confined spaces such as tunnels, vehicle depots, industrial and construction sites where combustion devices are in operation. The standard method for the measurement of aldehydes (formaldehyde and acetaldehyde) uses the 2,4-dinitrophenylhydrazine (DNPH) derivatisation method. However this method has been reported to be prone to interference from ozone and NO_2. The interference from these compounds have been viewed as chromatographic interferences on the quantification of formaldehyde. However, in these polluted environments, elevated levels of NO_2 along with NO and CO are normally present. This study quantifies the impact these gases have on the quantification of formaldehyde and acetaldehyde, by evaluating the chromatographic interferences, consumption of the DNPH during sampling, and the effect these gases have on the capture and retention of the aldehydes on the DNPH cartridge during sampling. For the first time, CO was shown to react with DNPH and interfere with the determination of acetone. The reaction product of CO with DNPH was determined to be a compound that could be mistaken for acetone-DNPH. It has been found that the presence of NO, NO_2 and CO in the sampled air consumes the DNPH cartridges, which results in the loss of formaldehyde and acetaldehyde during long-term sampling, and therefore extra capacity of DNPH is required for the measurement of formaldehyde and acetaldehyde in polluted environments. These findings reveal a potential risk of underestimation of formaldehyde and acetaldehyde measurements in a polluted workspaces such as a diesel engine operated environment where NO_x and CO concentration levels could be high.

Keywords: Aldehydes measurement, Formaldehyde measurement and monitoring, DNPH.

Abbreviations: DNPH – 2,4-dinitrophenylhydrazine; DEEE – Diesel engine exhaust emissions; VOC – Volatile organic compounds; GTL – Gas to liquid; HSE – Health and Safety Executive; TWA – Time-weighted average; FTIR – Fourier-transform infrared spectroscopy; SIFT-MS – Selected ion flow tube mass spectrometry; TDLS – Tuneable diode laser spectroscopy; HPLC – High performance liquid chromatography; GC-MS – Gas chromatography mass spectrometry; TD-GC – Thermal desorption gas chromatography; OSHA – Occupational Safety and Health Administration; UV – Ultraviolet; DNPA – 2,4-dinitrophenyl azide; PDA – Photodiode array.

1. Introduction

Aldehydes are carbonyls with the functional group in the terminal position. Airborne aldehydes are emitted through biogenic and man-made processes. The most abundant atmospheric aldehyde is formaldehyde, followed by acetaldehyde (Lee et al., 2001). Diesel engine exhaust emissions (DEEE) contain the products of combustion, including carbon dioxide (CO_2), carbon monoxide (CO), oxides of nitrogen (NO_x), oxides of sulphur (SO_x), various volatile organic compounds (VOCs) such as aldehydes. The concentrations of the DEEEs emitted will be influenced by the type of engine, maintenance of the engine, the fuel used, the workload of the engine, and the engine temperature (HSE, 2012a). 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 (Li et al., 2014). Using a gas-to-liquid (GTL) fuel showed a reduction in the aldehyde emission levels from gas turbine engines (Altaher et al., 2014). Aldehydes do not only come from combustion sources; new wood-based furniture and building materials in indoor environments also emit formaldehyde from particle boards bonded with urea-formaldehyde resin (Salthammer et al., 2010). Preservatives in museums and disinfectants in medical laboratories also contain formaldehyde which increase exposure (Salthammer, 2013; Salthammer et al., 2010).

Aldehydes affect the environment as they are precursors of oxidants such as ozone, peroxyacyl nitrates, and other photochemical air pollutants (Sirju and Shepson, 1995). Aldehydes are secondary pollutants as a result of photo oxidation of gas-phase hydrocarbons (Ban-Weiss et al., 2008; Lee et al., 2001). Exposure to aldehydes affect human health in the short term by causing symptoms such as nausea, headaches, coughing and irritation of the eyes, nose and throat (Wagner and Wyszyński, 1996). Formaldehyde, and acetaldehyde are suspected to be carcinogenic and mutagenic with long term exposure (Barro et al., 2009; Herrington and Hays, 2012).

Exposure to engine exhaust emissions, which include 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 (HSE, 2012b). The workplace exposure limits given by the Health and Safety Executive UK (UK HSE) are 2.5 and 37 mg/m^3 (8 h time-weighted average (TWA)) for formaldehyde and acetaldehyde, respectively, and are measured in the breathing zone of the worker (personal sampling) (HSE, 2018). Several methods have been developed to measure aldehydes, which include spectroscopic methods (Fourier-Transform Infrared Spectroscopy (FT-IR), Selected Ion Flow Tube Mass Spectrometry (SIFT-MS), Tuneable Diode Laser Spectroscopy (TDLS)) and chromatographic methods (High Performance Liquid Chromatography (HPLC), Gas Chromatography Mass Spectrometry (GC-MS), Thermal Desorption Gas Chromatography (TD-GC)) (Pal and Kim, 2007). Spectroscopic methods are expensive, suffer from high detection limits and are not suitable for personal monitoring, which requires light weight and portable devices.

A method based on the derivatisation of aldehydes with 2,4-dinitrophenyl hydrazine (DNPH) (ISO, 2011; Uchiyama et al., 2009), as shown in Figure 1, is commonly used for the measurement of aldehydes. The method is recommended by UK HSE (HSE, 2010), and the Occupational Safety and Health Administration (OSHA) of the United States (OSHA, 1988) for personal monitoring of workers' exposure to aldehydes in the workplace. Several studies have made use of the method to measure aldehydes in traffic tunnels (Ban-Weiss et al., 2008; Grosjean et al., 2001) and bus depots (De Andrade et al., 1998; Rodrigues et al., 2012).

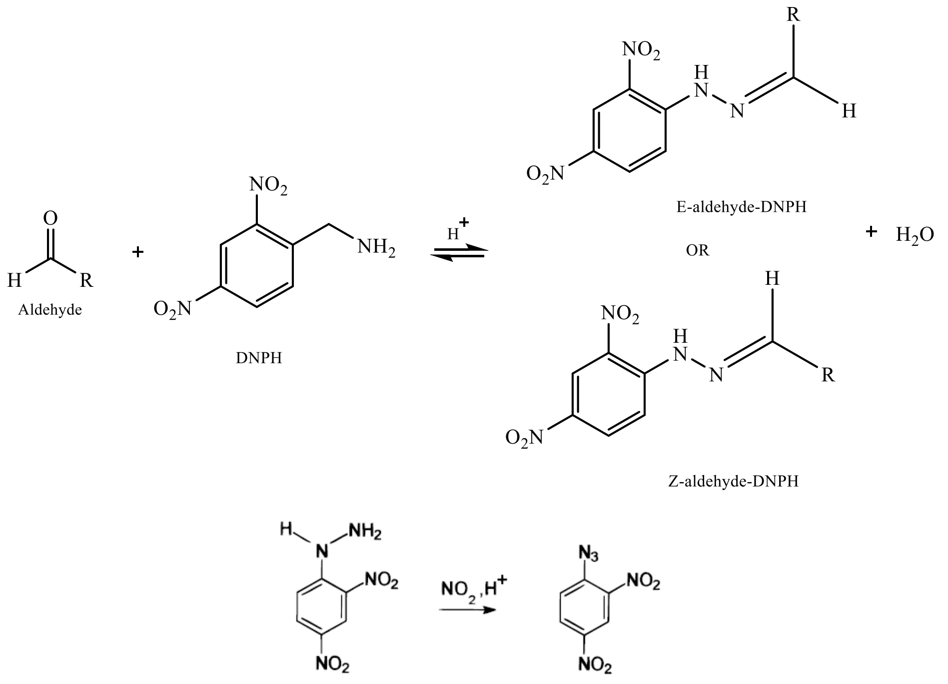

Figure 1: Reaction of aldehydes with DNPH(Uchiyama et al., 2009) and the reaction of NO_2 with DNPH to form DNPA (Pötter and Karst, 1996)

With the DNPH method, the sample is taken by pumping air through a cartridge containing a solid sorbent coated with DNPH, followed by desorption with a solvent and the resulting solution is analysed using HPLC with UV detection. The DNPH cartridge method has the advantage that it is compact, affordable and can be used to monitor multiple points simultaneously, and is thus widely used.

The method, however, is affected by interferences from ozone and NO_2, which have been extensively documented (Arnts and Tejada, 1989; Herrington and Hays, 2012; Szulejko and Kim, 2015; Vogel et al., 2000). Nitrogen dioxide reacts with DNPH to form 2,4-dintrophenyl azide (DNPA) (Pötter and Karst, 1996) (Figure 1), which may co-elute with formaldehyde-DNPH when analysing using HPLC-UV. A method using a dual-wavelength detection method to differentiate between the analyte and interferant was proposed by Pötter and Karst to overcome the co-elution problem (Pötter and Karst, 1996). Nitrogen monoxide has also been reported to react with DNPH to form the DNPA, but to a lesser extent (Karst et al., 1993).

However, the concentrations at which the interference from NO_x gases becomes a problem has not been determined, which is an important factor when measuring aldehydes in polluted environments. The impact that NO_2 and NO have on the capture and derivatisation of the aldehydes by the DNPH-cartridge has also not been evaluated.

Carbon monoxide (CO) is another reactive compound found in combustion emissions, and may be present at higher concentrations than NO_x gases in some combustion equipment emissions and environments. CO may react with DNPH and therefore affect the measurement of aldehydes using the DNPH method. Interference from CO on the DNPH method has not been reported, and could be significant in a polluted environment. Similarly to NO_2, CO may react with DNPH during sampling and the reaction product could interfere with the measurement of the aldehydes. Furthermore, the reaction of CO with DNPH would also then reduce the capacity of the DNPH cartridge. It is, therefore, the complexity of combustion emissions, particularly the high NO_x emissions in polluted environments, which create the problems for the DNPH method.

The objective of this work is to investigate the impact of NO, NO_2 and CO on the capture and retention of formaldehyde and acetaldehyde with the DNPH-cartridge and how this affects the capacity of DNPH-cartridges in DEEE environments. The reaction products of NO, NO_2 and CO with DNPH are identified, and their interference on the HPLC method are assessed.

2. Experimental

2.1 Quantification of consumption of DNPH by NO, NO_2 and CO

To quantify the consumption of the NO_2, NO and CO gases have on the commercial DNPH cartridge, separate gas cylinders containing NO_2, NO and CO in nitrogen were purchased from BOC Limited. Each gas (NO_2, NO and CO) was pumped with an ESCORT Elf® Pump (Zefon International) through a cartridge containing a high purity silica adsorbent coated with 2,4-dinitrophenylhydrazine (LpDNPH S10, 350 mg silica gel, 0.29% DNPH loading (1 mg), SUPELCO Bellefonte, PA, USA) at 1 L/min for a specified amount of time. The consumption of the DNPH was calculated by subtracting the amount of unreacted DNPH on the cartridge that was exposed to the gas, from the amount of DNPH on an unused cartridge.

2.2 Determination of the effect of NO, NO_2 and CO on aldehyde capture by the DNPH cartridge

A glass gas sampling bulb (125 mL), with Teflon stopcocks (Supelco Analytical, Sigma-Aldrich) which were used as a gas inlet port, outlet port, and which contained a septum inlet was used as the gas chamber (Figure 2). The glass was silanised before use to avoid absorption of the compounds onto the walls of the bulb. A gas-filled Tedlar bag (Sigma, St Louis, MO, USA) filled with either NO, NO_2 or CO, was attached to the inlet of the gas sampling bulb so that a fixed volume of gas flowed into the gas chamber. A standard solution of about 250 mg/L formaldehyde and acetaldehyde (Sigma-Aldrich, St Louis, MO, USA) respectively, in acetonitrile (HPLC grade, Fisher Scientific, U.K. Limited) was prepared, and a known volume was injected through the septum inlet and vaporised. A DNPH cartridge was attached to the opposite end to the Tedlar bag, of the chamber. The aldehyde gas mixture along with the gas being evaluated (NO, NO_2 or CO from the Tedlar bag) was pumped through the DNPH cartridge with the personal sampling pump at 1 L/min for a specified amount of time. Nitrogen gas was used to flush the bulb between experiments to avoid contamination and carry-over. Figure 2 shows the schematic of the experimental setup.

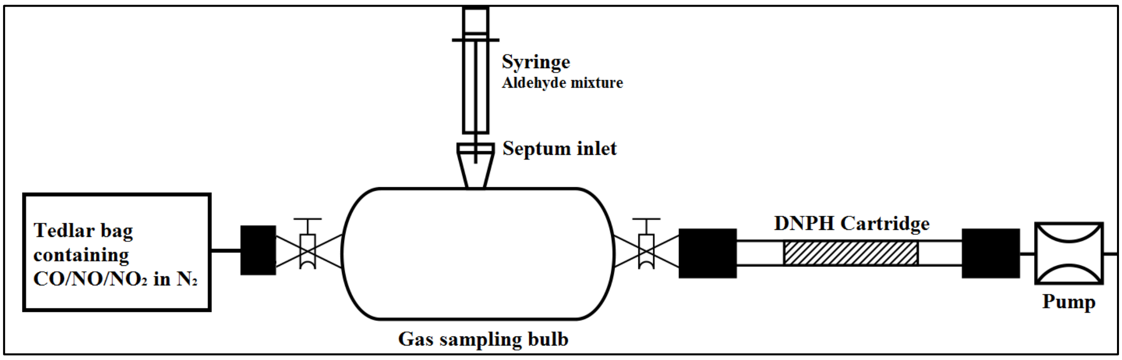

Figure 2: Gas mixing chamber with DNPH cartridge attachment

2.3 Determination of the effect of NO, NO_2 and CO on the retention of aldehydes on the DNPH cartridge

The effect of the gases on the retention of the aldehydes on the DNPH cartridge was determined by spiking a known volume of the aldehyde solution directly onto the DNPH cartridge, and left to react for 10 minutes. Each of the gases (NO_2, NO and CO) was pumped through the aldehyde-containing DNPH cartridge respectively, at 1 L/min using the personal sampling pump.

2.4 Sample Analysis

After each experiment was performed, each cartridge was eluted with 5 mL acetonitrile into a 5 mL volumetric flask. A second elution, with another 5 mL of acetonitrile was performed, to determine whether the 5 mL elution volume was sufficient for desorption of all the DNPH, derivatives and reaction products from the cartridge. Analysis of the second eluent was shown to be without any of these compounds, and therefore one elution of 5 mL was sufficient.

The cartridge extracts were analysed by injecting 10 µl into a high-performance liquid chromatography system (UltiMate 3000, Thermo Scientific, Waltham, MA, USA), equipped with a photodiode array detector (PDA). An Ascentis Express RP-Amide (2.7 µm, 10 cm x 4.6 mm) column was used to separate the DNPH-derivatives at 30 ℃. The gradient mobile phase consisted of acetonitrile (A) and water (B) (flow rate of 1.0 mL/min), which was set at 40 % A/60% B for 2 minutes, with a linear gradient to 85 % A/15 % B for 13 minutes, and returning to initial conditions in 0.5 minutes.

A certified aldehyde/ketone-DNPH calibration standard was purchased from Supelco (TO11/IP6A Aldehyde/Ketone-DNPH Mix, CRM4M7285, Supelco, Bellefonte, PA, USA), which was diluted into a calibration range of 0.10 – 15.0 µg/mL for formaldehyde and acetaldehyde.

2.5 Compound identification by GC-MS

Gas chromatography with mass spectrometry was used to identify the reaction products of NO, NO_2 and CO with DNPH using a Shimadzu GC-2010 Plus with GCMS-QP2010SE mass spectrometer equipped with an Agilent DB5-MS column (with dimensions 25 m x 0.25 mm I.D. x 0.25 µm). 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. Results and Discussion

3.1 Chromatographic interferences

Interferences seen on a chromatogram result from the co-elution of the interfering compounds, which have a UV response, with the aldehyde-DNPH compounds during HPLC analysis. The compounds may originate from the polluted environment, where one of the components of the polluting gases, such as NO, NO_2 or CO, is retained by the DNPH cartridge during sampling, which may react with the DNPH, and would elute along with the DNPH derivatives into the acetonitrile solution, and is subsequently analysed on HPLC. Therefore it is necessary to investigate the gases present in a polluted environment such as in an engine exhaust which include NO, NO_2, and CO.

Nitrogen dioxide is a major component of DEEE gases, 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, i.e. 0.2 ppm over 8 hours representing typical NO_2 concentrations in a polluted workplace (Hickman et al., 2018)), after which the cartridge was desorbed with acetonitrile, and the eluent was analysed on HPLC and GC. As previously reported by Pötter and Karst (Pötter and Karst, 1996), DNPA was the major product that had formed on the cartridge, and observed on the HPLC chromatogram at a retention time of 4.1 minutes (Figure 3). The DNPA peak was baseline separated from the formaldehyde-DNPH peak, using the current HPLC method. The baseline separation ensures that the formation of DNPA during sampling poses no chromatographic interference on the quantification of formaldehyde. The co-elution of the DNPA has previously been a problem (Pötter and Karst, 1996), and seems to have been resolved using the smaller particle size column, which has increased resolving power. The identity of the peak at 4.1 minutes was confirmed to be DNPA with GC-MS analysis.

The GC-MS analysis also identified 4-nitrobenzoic acid and 1,3-dinitrobenzene (also a reaction product of ozone with DNPH (Achatz et al., 1999)) in the sample, as reaction products of NO_2 with DNPH, but at much lower levels than the DNPA in the sample. Two small peaks were observed on the HPLC chromatogram marked d and e (Figure 3). The peaks labelled d or e could either be assigned to the 4-nitrobenzoic acid or 1,3-dinitrobenzene. At sufficient quantities of NO_2, the peak at e will interfere with the quantification of formaldehyde-DNPH, resulting in an overestimation of the formaldehyde quantities in the sample.

The DNPH cartridge exposed to 0.123 mg NO (equivalent to 0.26 mg/m^3 or 0.2 ppm NO over 8 hours) gas did not show any products from the reaction of NO with DNPH. Both the HPLC and GC-MS analyses 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 of the NO with DNPH occurred. However, NO can be oxidised to NO_2 when passing through the KI cartridge used for ozone removal during sampling (Herrington and Hays, 2012). The newly formed NO_2 therefore will react with the DNPH on cartridge to form DNPA, as already described.

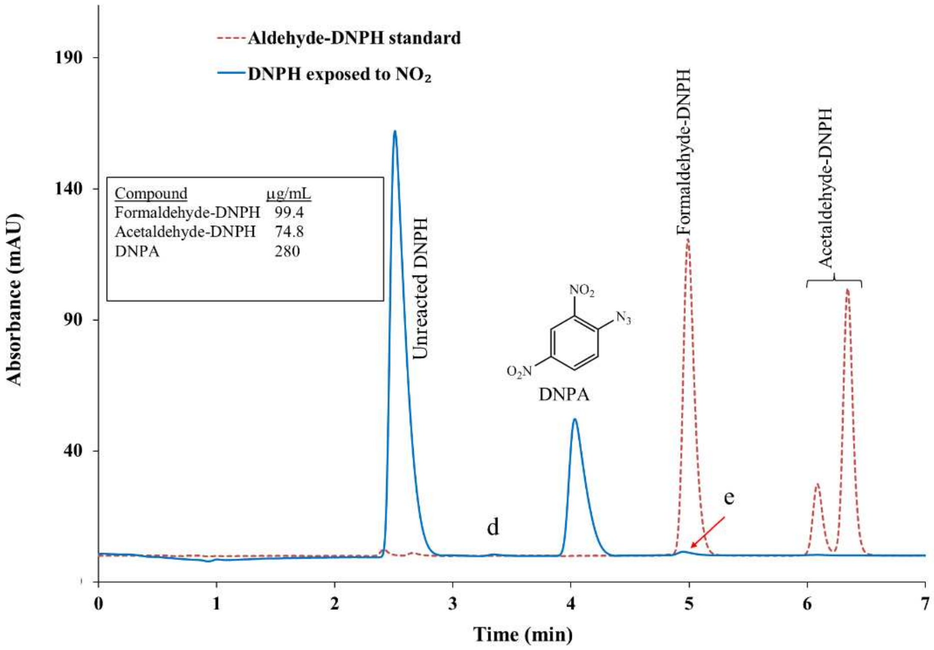

Figure 3: HPLC chromatogram of the reaction products of NO_2 with DNPH, DNPA (d and e could be assigned either 4-nitrobenzoic acid or 1,3-dinitrobenzene, respectively)

Carbon monoxide is present in the combustion product because of incomplete combustion processes. Carbon monoxide is a reactive compound, and therefore could have an effect on the sampling of aldehydes using the DNPH method.

On exposure of a DNPH cartridge to 0.23 mg carbon monoxide gas (equivalent to 0.48 mg/m^3 or 0.4 ppm over 8 hours), it was observed that the yellow DNPH on the cartridge turned white, which indicates a reaction of the DNPH with the carbon monoxide. 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 the chromatogram in Figure 4. 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 unreacted DNPH peak were detected in the sample. The UV spectra of the acetone-DNPH and the CO-DNPH reaction product were compared (Figure 5) and are also almost identical.

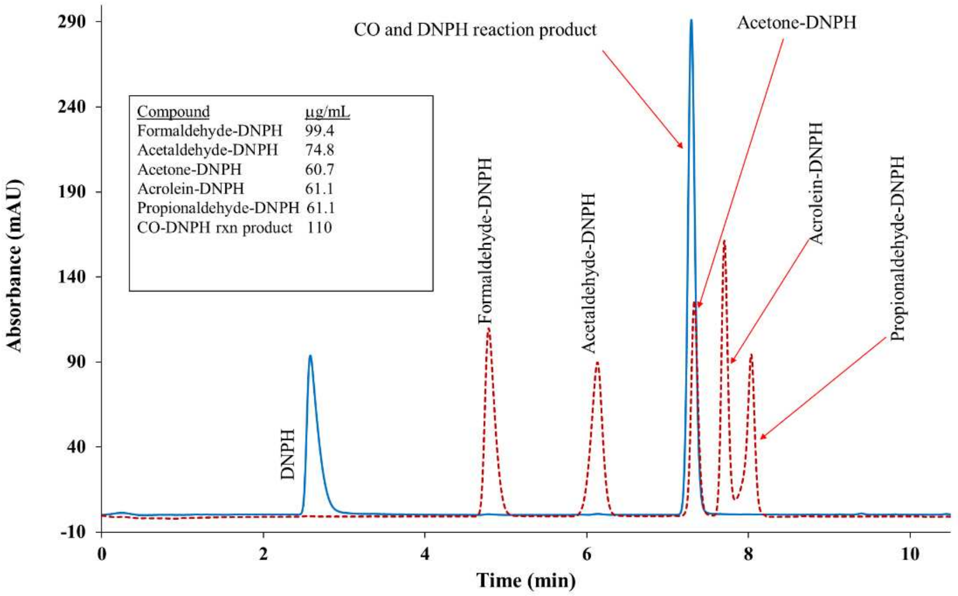

Figure 4: HPLC chromatogram of CO and DNPH reaction product

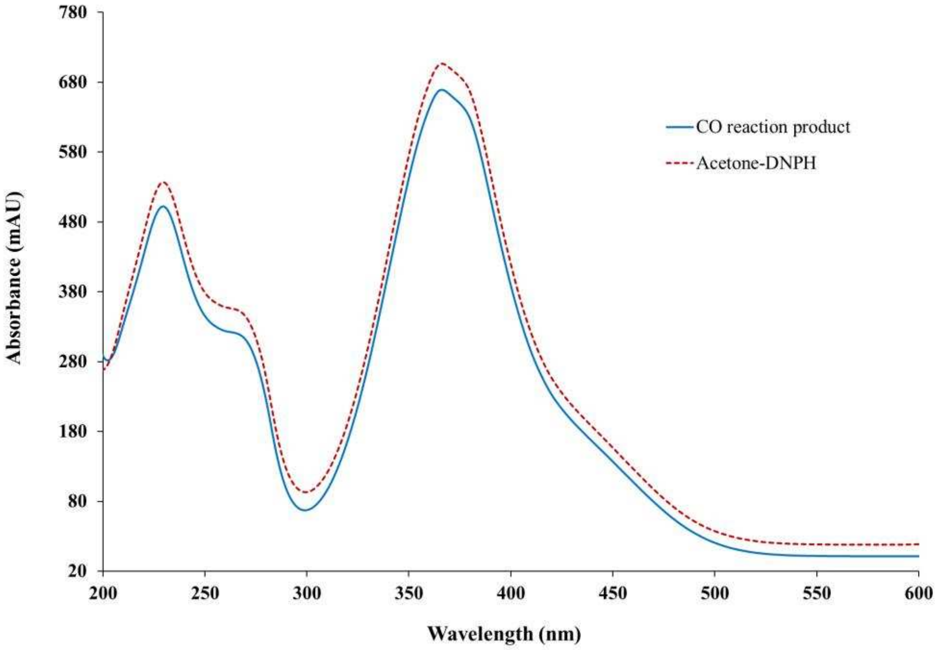

Figure 5: UV spectra comparison of Acetone-DNPH with the CO and DNPH reaction products

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 peak is shown in Figure 6, and the fragmentation pattern compares well with the fragmentation pattern of acetone-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.

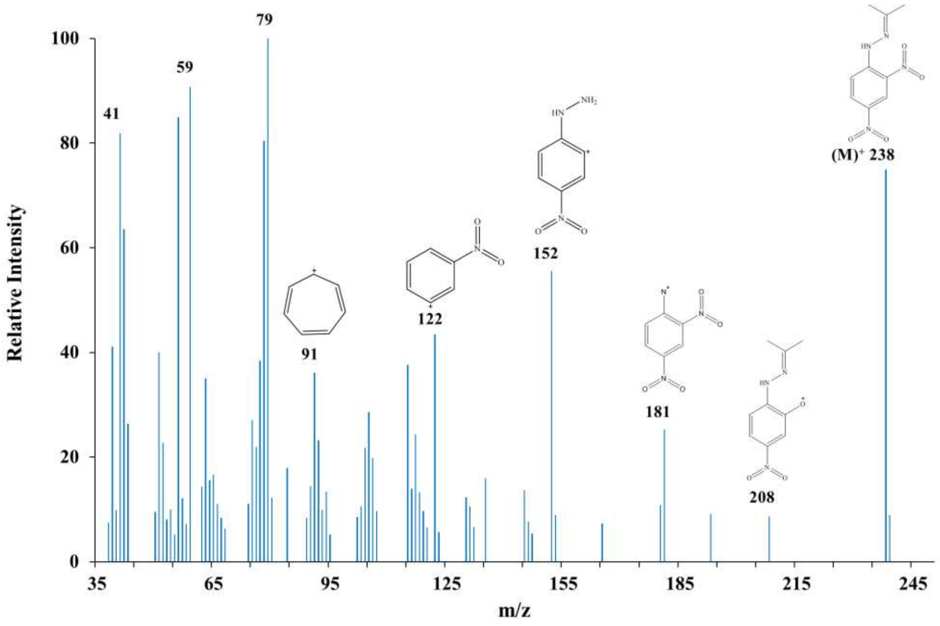

Figure 6: MS spectrum for the reaction product of CO and DNPH

NO_2 and CO react with DNPH to form reaction products that are visible on the HPLC chromatogram. The reaction of these gases with DNPH also reduces the capacity of the cartridge for aldehyde capture and retention, which was also investigated.

3.2 Effect of NO, NO_2 and CO on the quantification of aldehydes with DNPH

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 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 the already formed aldehyde-DNPH from the cartridge. The gases could also 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.

3.2.1 Effect of NO, NO_2 and CO on aldehyde capture and retention on the cartridge

To determine the effect that each individual gas has on the capture of the aldehydes, the gas mixing chamber was used, with each gas (NO, NO_2 and CO, respectively) 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.

$$Method\ recovery = \frac{Aldehyde\ on\ the\ cartridge\ by\ mass}{Aldehyde\ loaded\ into\ bulb\ by\ mass} \times 100\ \% \qquad [1]$$

The results are presented in Figure 7. In the absence of any NO, NO_2 and CO gases, only using nitrogen, the recoveries for both formaldehyde and acetaldehyde were 99 %.

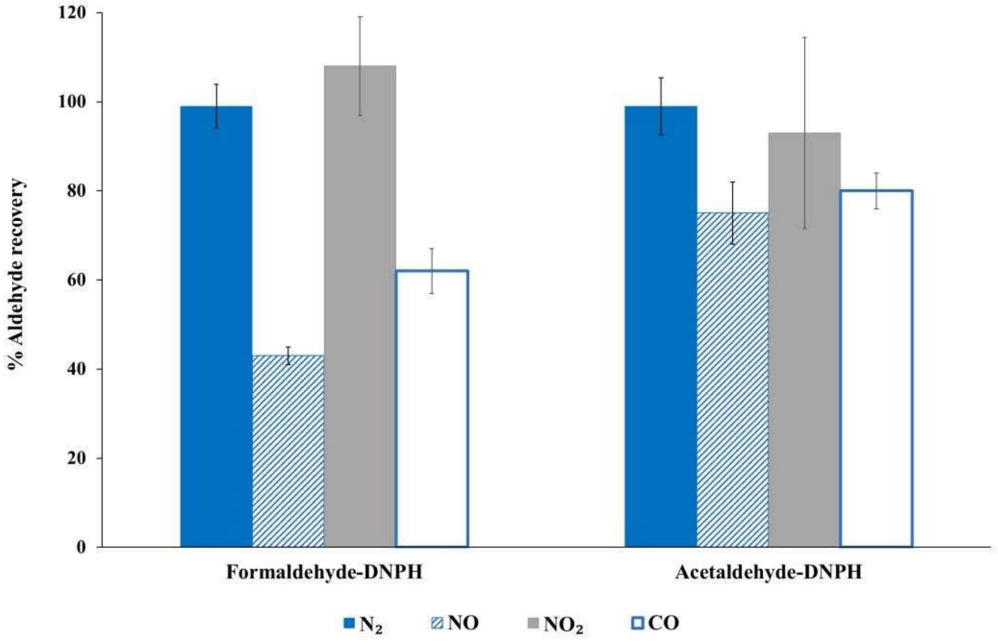

Figure 7: Effect of NO, NO_2 and CO gas on aldehyde capture

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 3.1) it is not due to a lack of the DNPH capacity, and therefore NO is competing with formaldehyde for adsorption sites on the silica substrate during sampling. The NO may also be displacing the formaldehyde-DNPH from the cartridge, although this is less likely as formaldehyde-DNPH is not very volatile.

Carbon monoxide also reduced the amount of formaldehyde recovered, for similar reasons as stated for nitrogen oxide, by competing with the capture of formaldehyde, or by displacement of the formaldehyde-DNPH from the cartridge. However, carbon monoxide does react with DNPH, 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 other reaction products, including 4-nitrobenzoic acid (Section 3.1) 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 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 was pumped through a cartridge containing the aldehyde-DNPH derivatives respectively. The cartridges were eluted with acetonitrile and prepared for HPLC analysis. Figure 8 shows the results for the experiment.

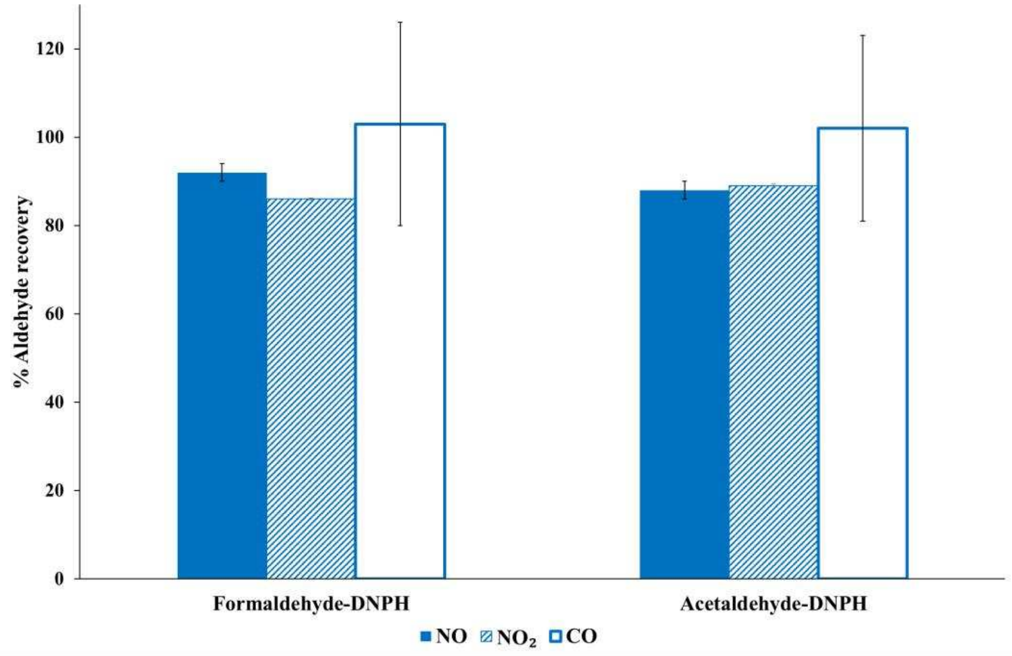

Figure 8: Effect of NO, NO_2 and CO gases on displacing aldehyde derivatives captured on cartridge

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 indicate that 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 are not very volatile. However, the derivatisation reaction is reversible, as is seen in Figure 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, 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 absorption.

3.2.2 Consumption of DNPH by diesel engine exhaust gases

One of the identified mechanisms for interference of the DNPH method, is the reaction of the 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 3.1 were used to calculate the amount of DNPH consumed. The results are presented in Figure 9, 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.

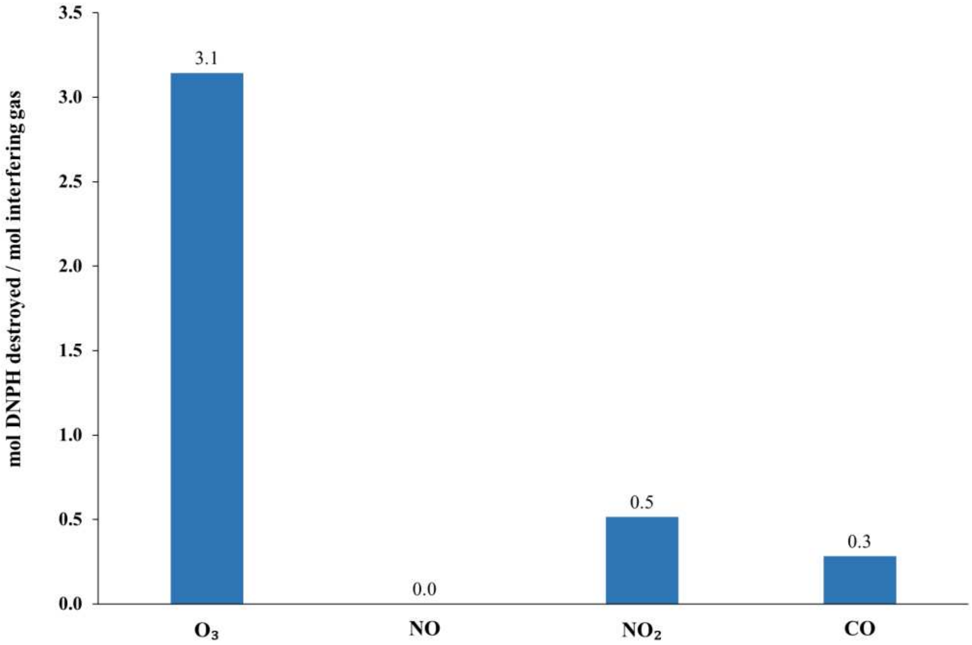

Figure 9: DNPH consumed per mol gas

From these results it seems that the ozone would have the largest impact on the DNPH cartridge capacity 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 (ISO, 2011). 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, was calculated from this data (**Table 1**).

Table 1: Amount of DNPH consumed by interfering 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 required (mg)	0	21.9	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 popular size choice of DNPH cartridge contains 350 mg of silica that coated with 1 mg DNPH. 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 formaldehyde and acetaldehyde in a polluted environment is given Equation 2 below.

$$m_{DNPH} = 396V_{sample}\left[\left(\frac{C_{CO}}{Mr_{CO}} \times a\right) + \left(\frac{C_{NO}}{Mr_{NO}} \times b\right) + \left(\frac{C_{NO_2}}{Mr_{NO_2}} \times c\right) + \left(\frac{C_{Form}}{Mr_{Form}}\right) + \left(\frac{C_{Acet}}{Mr_{Acet}}\right)\right] \qquad [2]$$

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 gas (mg/m^3)

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

a, b, c = 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. Conclusion

The DNPH method has been shown to be subject to chromatographic interference from the reaction products from NO_2 and CO. The reaction product of NO_2 with DNPH, DNPA, is formed when the DNPH cartridge is exposed to NO_2, however it does not interfere with formaldehyde-DNPH peak on the chromatogram. However, 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 NMR, is required to positively identify the compound. This compound does not interfere with the quantification of formaldehyde or acetaldehyde.

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 reacting with the acid catalyst on the cartridge, and subsequently allowing the reversing of the derivatisation reaction.

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, the capacity is of the cartridge is severely affected by CO, although the reactivity with DNPH is lower than for NO_2. In DEEE environments it is therefore necessary to take into account the concentrations 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.

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