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**Core Activity on Aldehyde Measurement and
Analysis**

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Science Group: **Health Improvement**

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EXECUTIVE SUMMARY

Objectives

1. To evaluate alternative reagents for measurement of aldehyde exposure.
2. To revisit the method for measurement of acrolein with a view to improving it.
3. To evaluate the ISO method 16000-3 as a possible basis for a section procedure.
4. To undertake quality assurance and other ad hoc work.
5. To evaluate a direct reading portable monitor.

Main Findings

1. Alternative reagents to dinitrophenylhydrazine (DNPH) were evaluated in an attempt to improve the analytical method. Two reagents, Dimethylamino naphthalene sulphonyl hydrazine (dansyl hydrazine) and N-methyl nitrobenzoxodiazolyhydrazine (MNBDH) were evaluated and found to be unsuitable on grounds of stability. N-methyl dinitrophenylhydrazine (MDNPH) showed satisfactory stability and was therefore subjected to a more detailed evaluation in a standard atmosphere of formaldehyde and glutaraldehyde. It was found to give better immunity from interference in the case of glutaraldehyde but this may be offset by the inconvenience of obtaining the reagent.
2. Initial investigations of the new reagent's (MDNPH's) performance to determine acrolein showed that it provided no clear advantage because, as with DNPH, a number of products were formed.
3. The review of the measurement of acrolein showed that, while the DNPH based method does measure acrolein, it would be worth investigating other means to measure it, in particular, Automated Thermal Desorption (ATD), should be further investigated.
4. After discussion with UKAS it was decided to develop a hybrid of current HSL practice and the ISO method. This will permit an extension of the scope of the HSL accredited analysis (currently for glutaraldehyde) to other aldehydes, and also to simplify procedures.
5. HSL has maintained Category 1 performance in the WASP scheme for the measurement of formaldehyde on filters, and UKAS accreditation for glutaraldehyde analysis.
6. A general aldehydes method based on ISO method 16000-3 has been written and issued as OMS-006 to replace the glutaraldehyde method.
7. The new method has been audited and has gained UKAS accreditation. Additional OMS staff have been trained in the use of the method and have obtained satisfactory results as participants in the WASP proficiency testing (PT) scheme.
8. A direct reading monitor was briefly evaluated in test atmospheres of formaldehyde and glutaraldehyde and, while it was quick and easy to use, it was found to over read by as much as 111%.

Recommendations

1. MDNPH should be used where it is more suitable than DNPH, i.e. where only glutaraldehyde is to be measured and there are other materials present that would interfere with one or other of the isomer peaks (e.g. succinyl dialdehyde). Succinyl dialdehyde is used in some disinfectant products, but it would be unusual for both of these compounds to be used at the same time.
2. The method based on hydroxymethyl piperazine should be used for measuring acrolein where the accuracy of quantitation is paramount. Where semi-quantitative analysis is required the method based on DNPH can be used. The DNPH method will be particularly favoured where other aldehydes are also being measured.
3. The new procedure OMS-006, based on the ISO standard will be employed for all routine aldehyde analysis.
4. HSL will maintain procedure OMS-006 and participate in the WASP QA scheme to demonstrate the quality of our work.
5. The direct reading instrument should only be used where a rough indication of the concentration is required and where ease of use outweighs the fact that it over-reads. Given that formaldehyde has a WEL these circumstances will be comparatively rare. There may be a case for using it to demonstrate that formaldehyde is absent.
6. Further work should be undertaken to provide an improved method for acrolein. In particular, it would be useful to examine the use of ATD-GC/MS for this analyte because sorbents and analytical equipment have improved since this technique was last examined. In particular, ATD would offer the prospect of a less labour intensive and more sensitive analysis than the hydroxymethyl piperazine method. It would also allow acrolein to be monitored using the same sampling device as other volatile organic compounds, thus negating the need for dual samplers in such instances.

1 INTRODUCTION

Aldehydes constitute a large and diverse group of chemicals and are widely encountered in the workplace. Some are utilised as industrial raw materials, others are generated as by-products. A few, most notably formaldehyde, can occur in both situations. Aldehydes vary in their toxicity and other properties but, from an occupational hygiene perspective, are commonly classified as irritants and, sometimes, as asthmagens and/or suspect carcinogens. In tonnage terms, by far the most common aldehyde is formaldehyde. In 1980 UK production was estimated as 15000 tonnes with tens of thousands of workers potentially exposed.

This report summarises the findings from a number of work areas investigated in Project Number JS2002668 - Core activity on aldehyde measurement. The justifications for the various areas of work are summarised below but, overall, the main aim was to provide a better service to HSE and others in terms of cost, turn-round time and accuracy.

1.1 NEW REAGENTS

There are a number of reagents used for the determination of aldehydes. The most commonly used has been dinitrophenyl hydrazine (DNPH), which has been HSL's preferred reagent for some years now, but does suffer from the following shortcomings.

- It is adversely affected by the presence of oxidants in the air (Potter & Karst, 1996) such as ozone (Helmig, 1997) and the oxides of nitrogen;
- It gives rise to two isomeric derivatives with many aldehydes (Rietz, 1985);
- It gives a series of derivatives with acrolein.

These all make chromatographic interpretation more difficult and increase the risk of interference from other materials present. Work was carried out to identify and assess alternative reagents that might avoid these difficulties.

1.2 ACROLEIN

Acrolein produces a number of different products when reacted with the standard DNPH reagent and this makes analysis and interpretation more difficult. HSL have used an alternative reagent, hydroxymethyl piperazine (HMP), but this is slow to react and a large excess of the reagent is required. The excess reagent has been found to cause problems with the gas chromatography and several blank (solvent) analyses are required between each sample analysis.

In order to avoid this we undertook some testing out to see if any of the new reagents (see 1.1) could be recommended as a replacement for HMP in the analysis of acrolein. Initial trials were also undertaken to assess the use of automated thermal desorption- gas chromatography- mass spectrometry (ATD/GCMS) as an alternative analytical approach

1.3 QUALITY AND ISO 16000-3

When this work was started HSL use differing sets of analytical conditions to measure acrolein, glutaraldehyde and the other aldehydes. This made documentation more complex and the adoption of standardised procedures difficult. We were also aware that ISO were producing a standard on the measurement of aldehydes in air so we took the opportunity to rationalise our procedures and have one method, based on ISO16000-3, for all aldehydes. In order to ensure

that HSL provides a high quality, reliable service it is essential that staff are trained in the new procedure, and also that the ability to deliver quality results is confirmed by their participation in Quality assurance scheme.

1.4 DIRECT READING MONITOR

Laboratory methods for determination of contaminants are generally more accurate than those undertaken on site, but the latter are often more convenient for occupational hygienists, consultants, Health and Safety advisers and workers to use. They also can carry the message to workers in a more convincing manner than getting results back from the lab some days later.

With this in mind the Direct reading monitor for formaldehyde was assessed alongside the analytical methods employing the new reagents.

2 NEW REAGENTS

2.1 INTRODUCTION

For some time HSL has used methods based on OSHA (Occupational Health and Safety Administration) Method 64 for measurement of aldehydes. This involves sampling onto a GF/A glass fibre filter coated with a mixture of DNPH and phosphoric acid (as a catalyst). The filters are returned to the laboratory, desorbed in 2 ml of acetonitrile and the solution analysed by high performance liquid chromatography (HPLC). The analyte is detected and measured by UV absorbance at 360 nm and, because a diode array detector is used, the identification, based on retention time, can be confirmed by UV spectroscopy. We have also used a diffusive sampling method, but this is much less commonly used.

The HSL methods have been published in the Methods for the Determination of Hazardous Substances (MDHS) series as MDHS 78 (diffusive sampling of formaldehyde) and MDHS 93 (pumped sampling of glutaraldehyde). For most other aldehydes the same sampling medium was used with slightly different sets of analytical conditions.

For acrolein, which gives a number of derivatives with DNPH, a method based on NIOSH (National Institute for Occupational Safety and Health) 2501 is used. This samples onto tubes containing HMP supported on XAD, a polymer. These are then desorbed and the solution analysed using GC with a nitrogen-phosphorus detector (NPD). Because the analyte reacts slowly with the HMP a large excess is used. This causes problems because the excess reagent contaminates the GC injector and repeated injections of solvent are required to remove it

Clearly, having 3 different methods is not ideal. With a view to improving the efficiency, robustness and economy of the analysis, as well as simplifying HSL's standard procedures, we looked at a selection of alternative reagents that, ideally, would have the following characteristics:-

- Be applicable to all (or as wide a selection as possible) of the aldehydes analysed at HSL;
- Be immune to interference from other materials in the atmosphere, in particular NO₂ and ozone;
- Be detectable by fluorescence as well as by UV (this is rather less important than the other two)

2.2 REAGENTS INVESTIGATED

After searching the literature, the following three candidate compounds were selected for further evaluation:-

- Dimethylamino naphthalene sulphonyl hydrazine (DNSH);
- N-Methyl-4-hydrazino-7-nitrobenzofurazan (MNBDH);
- N-Methyl dinitrophenylhydrazine (MDNPH).

No attempt was made to investigate the toxicity of any of these reagents. However, it seems reasonable to assume that they will be comparable to DNPH in this respect and should be treated accordingly.

2.2.1 Dimethylamino naphthalene sulphonyl hydrazine

Dimethylamino naphthalene sulphonyl, or dansyl, hydrazine (DNSH) was investigated because it is commercially available as a reagent for aldehydes. DNSH derivatives are fluorescent which offers the prospect of more sensitive and selective detection. The chemical structure of DNSH is shown in Figure 1.

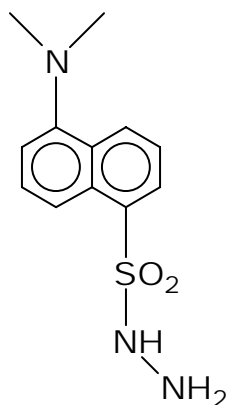


Figure 1: Chemical Structure of DNSH

2.2.2 N-Methyl-4-hydrazino-7-nitrobenzofurazan

The use of this reagent was put forward as a replacement for DNPH offering less susceptibility to interference by NO₂ (Buldt & Karst, 1997). Many NBD (nitrobenzoxadiazole) derivatives are fluorescent which would also offer a better sensitivity than DNPH. The reagent is not commercially available and had to be synthesised.

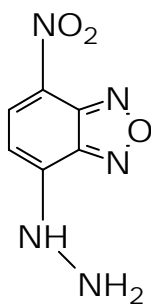


Figure 2: Chemical Structure of MNBDH

2.2.3 N-Methyl dinitrophenylhydrazine (MDNPH)

A third reagent (MDNPH), again based on methyl hydrazine, has also been suggested (Buldt & Karst, 1997). It too is less affected by NO_x and O₃. Again, this reagent is not commercially available and had to be synthesised.

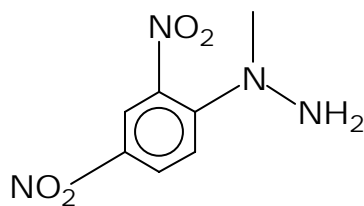


Figure 3: Chemical Structure of MDNPH

These were examined in more detail for their suitability and to compare them to the current reagent (DNPH), the chemical structure of which is shown in Figure 4.

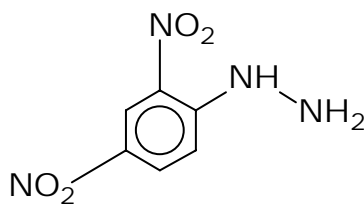


Figure 4: Chemical Structure of DNPH

2.3 EXPERIMENTAL

2.3.1 Reagents

Reagents were obtained from the following suppliers. HSL's use of these products should not be taken as an endorsement. Materials were analytical grade or equivalent except ethanol and acetonitrile, which were HPLC grade.

- DNSH Aldrich
- MDNPH Synthesised as per Appendix 1
- MNBDH Synthesised as per Appendix 2
- H₂SO₄ Aldrich
- Ethanol Fisher
- Acetonitrile Rathburns
- H₃PO₄ Aldrich
- Formaldehyde Aldrich
- Acetaldehyde Aldrich
- Propanal Aldrich
- Butanal Aldrich
- Pentanal Aldrich
- Acrolein Aldrich
- Glutaraldehyde Aldrich

2.3.2 Typical Analytical Conditions

Typical conditions for the analyses are given in Appendix 3

2.3.3 Dansyl Hydrazine (DNSH)

An attempt was made to produce the derivatives of formaldehyde, acetaldehyde, propanal, butanal, pentanal, acrolein and glutaraldehyde with dansyl hydrazine by reaction in acidified ethanol (Buldt et al., 1999). The derivatisation reaction is shown in Figure 5.

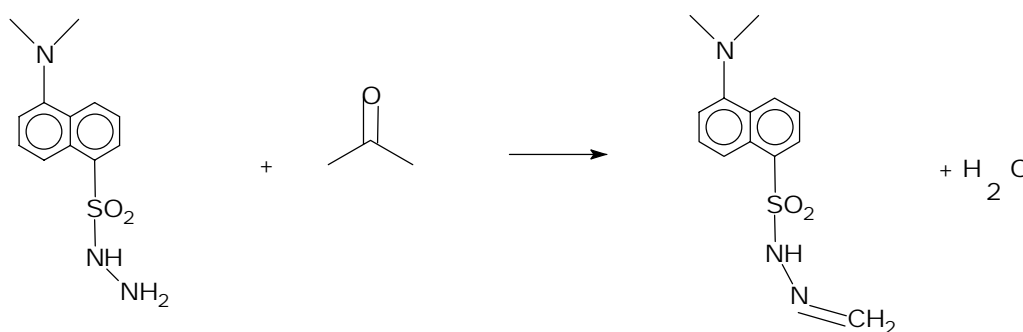


Figure 5: Derivatisation Reaction of Aldehydes with DNSH

A solution of 2.5 ml of sulphuric acid was prepared in 3.5 ml of water and added to 530 mg of DNSH dissolved in 18 ml of ethanol to give an approximately 0.33M solution. For each aldehyde 0.25 mMol were added to 1.85 ml of the 0.33M acidified DNSH solution (this represents an approximately 2.5 fold excess of reagent). The samples were left overnight to react at room temperature.

Following the reaction no crystalline derivative could be produced and HPLC analysis of the reaction mixtures showed them to be a mixture of products. This is consistent with the observation that, while the aldehydes can be derivatised in this way for direct analysis, the derivatives have limited stability (Gromping & Cammann, 1993). Because of the stability problems no further work was done on this reagent.

2.3.4 MNBDH

The reagent is not commercially available and was synthesised using the procedure described in Appendix 1. Essentially, the reaction is that of chloro nitrobenzoxadiazole (NDB chloride) with methyl hydrazine (see Figure 6).

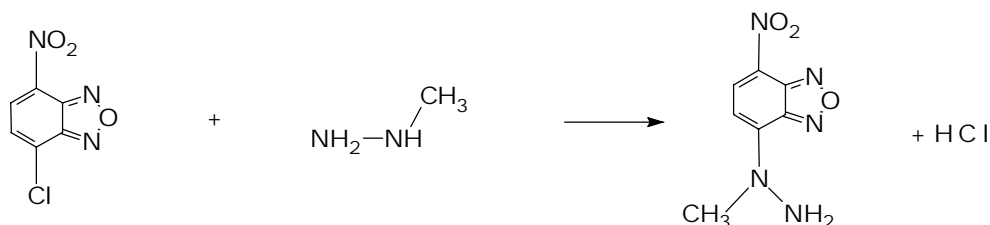


Figure 6: Formation of MNBDH

Crystalline MNBDH derivatives of glutaraldehyde and formaldehyde were obtained using the scheme illustrated, with formaldehyde, in Figure 7.

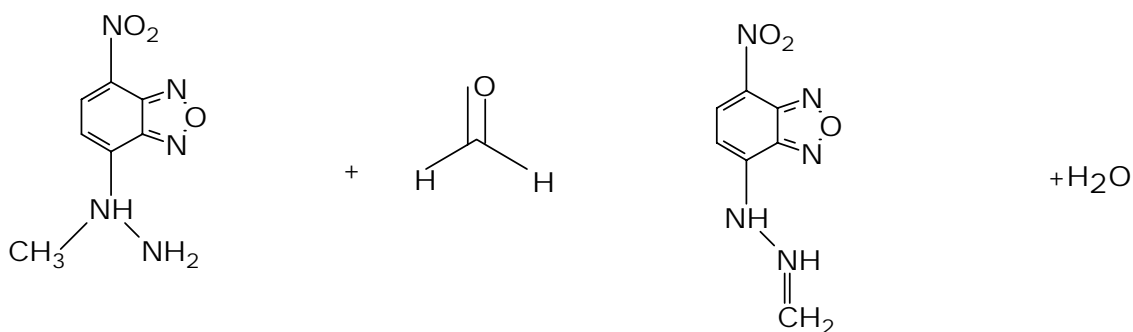


Figure 7: Reaction of Formaldehyde with MNBDH

100 mg of MNBDH was dissolved in a mixture comprising 0.7 ml of water, 0.5 ml of sulphuric acid and 2.5 ml of ethanol. A 50% molar excess of the aldehyde was added and the hydrazone filtered off. The resulting MNBDH derivatives was washed with water and recrystallised from acetonitrile/water. UV spectra of the derivatives were obtained and found to be a good match for those in the literature (Buldt et al., 1999).

The MNBDH derivatives were analysed by HPLC with UV detection and the calibration curves produced indicated that the sensitivity of the method was comparable to those of the equivalent DNPH derivatives. However, while several NDB derivatives are reported to fluoresce, no fluorescence was observed in any of these materials.

Tests were undertaken to assess sampling onto filters coated with this reagent. A solution containing 105.6 mg of the reagent and 0.5 ml 85% H₃PO₄ in 25 ml of acetonitrile was prepared and 0.5 ml aliquots of this were pipetted onto 37 mm glass fibre (GF/A) filters. These were left for the solvent to evaporate, resulting in a filter evenly coated with the reagent and an acid catalyst. It was hoped that these would serve as a sampling medium for the aldehydes. Unfortunately, the colour of the filters was observed to change with time over the course of several hours. It was thought that this might be due to decomposition of the reagent, so to test this a number of filters were prepared and stored under the following conditions:-

- In sealed bags on the bench;
- In a refrigerator at a nominal 4°C;
- In a dark cupboard.

Following storage the samples were analysed. The results of these analyses are summarised in Table 1, and clearly show evidence that the reagent is decomposing. After 4 days, even with cold storage, significant decomposition had taken place, whilst after 3 weeks in a polythene bag on the lab bench, only 9.43 % of the reagent remained on the filter.

Table 1: Decomposition of MNBDH Reagent Over Time

Time (days)	% of Reagent Remaining		
	Fridge	Cupboard	Bench
0	99.9	99.9	99.7
1	99.7	99.1	98.4
2	99.2	95.7	93.5
4	98.8	84.3	80.5
9	99.3	51.3	35.0
21	96.4	10.0	9.4

2.3.5 MDNPH

Of the three new reagents examined, MDNPH is the most similar to DNPH. The extra methyl group means that the effects of NO_x and O₃ are lessened because only one oxidation product is formed and this does not coelute with the analytes. The reagent is not commercially available and were synthesised using a published procedure given in Appendix 2 (Buldt & Karst, 1997).

Derivatives of formaldehyde, acetaldehyde, propanal, butanal, pentanal, acrolein and glutaraldehyde were prepared. 100 mg of MDNPH was dissolved in 0.5 ml of sulphuric acid and diluted with a mixture of 0.7 ml of water and 2.5 ml of ethanol. For each aldehyde, 0.7 mEquiv (respectively 21 mg, 31 mg, 41 mg, 50 mg, 60 mg, 39 mg and, for glutaraldehyde which is a dialdehyde, 0.35 mMol i.e. 35 mg) was dissolved in ethanol and added to the acidified MDNPH solution. Most of the aldehydes formed yellow crystals, however the pentanal derivative formed an oil.

HPLC conditions were optimised to allow analysis of both DNPH and MDNPH derivatives. These conditions are given in Appendix 3, and were used to prepare calibration data for the derivatives of formaldehyde and glutaraldehyde. These indicated similar levels of sensitivity between the MDNPH and DNPH derivatives. A useful aspect of the MDNPH reagent is that it seems only to produce a single compound with most aldehydes whereas DNPH gives rise to two isomers for all aldehydes except formaldehyde. This should result in a slight improvement in sensitivity and a considerable improvement in selectivity.

Figure 8 shows examples of chromatograms obtained from MDNPH and DNPH derivatives of formaldehyde and glutaraldehyde. A comparison of the two chromatograms produced the following observations:-

- Formaldehyde, being the unique, symmetrical, aldehyde, to give single peak at with both reagents (both at about 5 minutes);
- Glutaraldehyde gives a single MDNPH peak (at around 11 minutes), but two isomers of the DNPH derivative (at about 14 and 16 minutes).

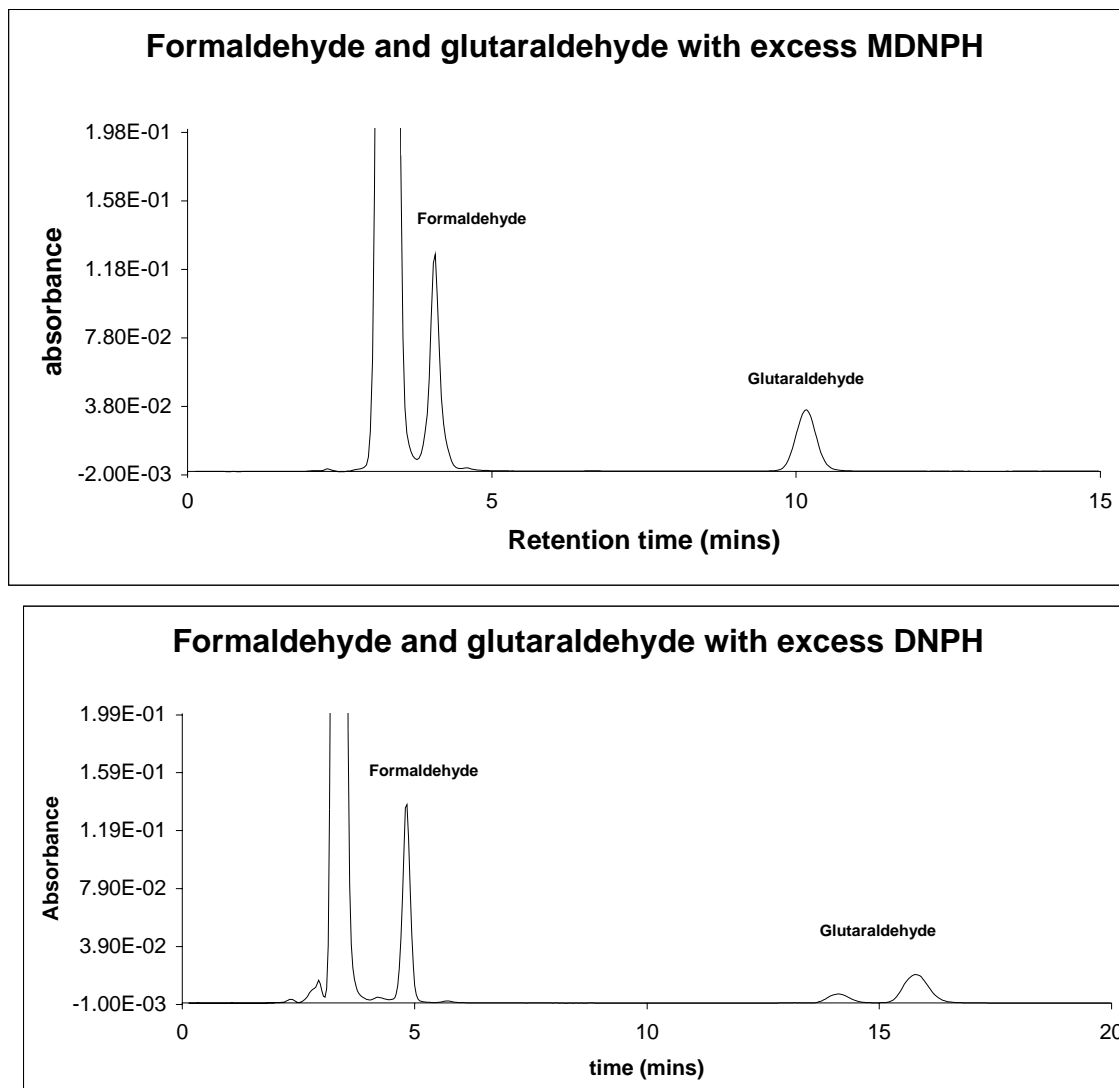


Figure 8: Chromatograms Showing MDNPH and DNPH Derivatives of Formaldehyde and Glutaraldehyde

2.4 COMPARISON OF THE REAGENTS FOR AIRBORNE SAMPLING

A test atmosphere system was assembled in which samplers could be exposed to known concentrations of both formaldehyde and glutaraldehyde in air at constant temperature and humidity. A schematic of the atmosphere system is shown in Figure 9.

In this system compressed air is fed through a set of three regulators (**M1**, **M2** and **M3**) to three needle valves (**V1**, **V2** and **V3**). The three controlled streams of air from these are used to supply glutaraldehyde (**V1**), formaldehyde (**V2**) and humidified air (**V3**) to the test chamber. The temperature of the air in the test chamber is controlled by a water bath circulating water through the jacket of the chamber and also a condenser through which the air passes just before entering the chamber. The humidified air stream (**V3**) is split into two by valves (**V4** and **V5**).

The airflow through **V5** is passed over water maintained at about 35°C and then recombined with that from **V4**. By varying the flow through the two valves the humidity of the air in the chamber can be adjusted. The formaldehyde air stream (**V2**) is passed over the tip of a fine tube through which formaldehyde solution is pumped. The solution evaporates and the formaldehyde is carried to the chamber. The glutaraldehyde air stream (**V1**) is directed through three wash bottles (**W1**, **W2** and **W3**) set in a thermostated bath maintained at 17°C. This is just below room temperature and prevents condensation in the flow meter. **W1** and **W2** contain glutaraldehyde solution (typically 2%) and **W3** acts as a spray trap.

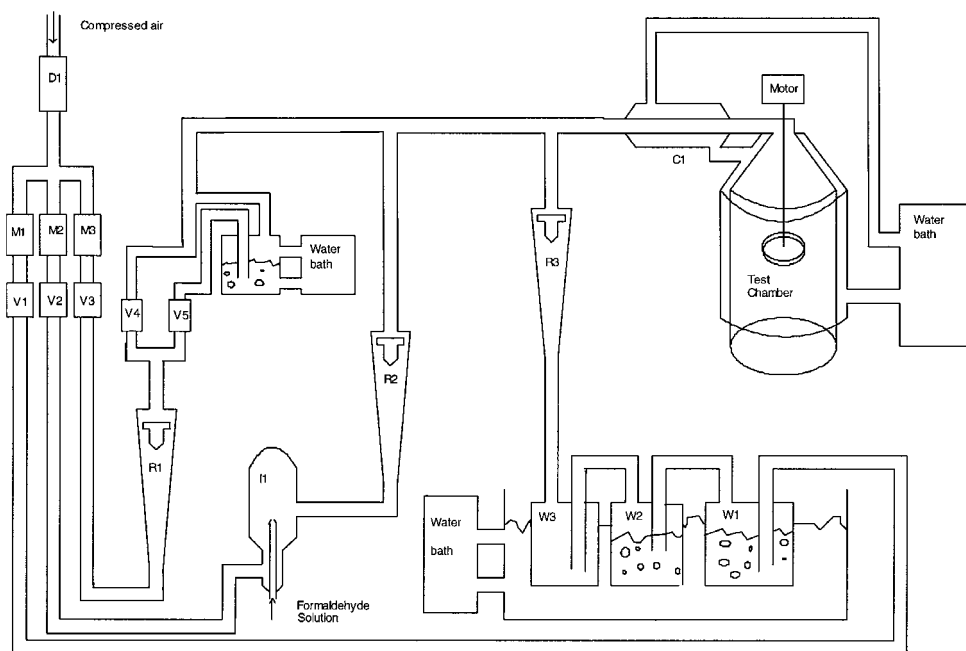


Figure 9: Schematic of Aldehyde Standard Atmosphere System

The test rig also includes three flow meters (**R1**, **R2** and **R3**) which measure the flow rates of the humidified air, formaldehyde and the glutaraldehyde respectively. In use, the flow rates are typically 20, 5 and 1 l/min respectively.

In order to reduce losses of the aldehydes all the parts of the apparatus through which aldehyde-bearing air pass were silanised. This was done by placing a wad of glass wool dipped in dichlorodimethyl silane in the formaldehyde injector and passing the vapour through the apparatus followed by passing methanol vapour through the apparatus in the same way to end-cap the silane. This process does not silanise the rotameters (**R1**) and (**R3**), however since the glutaraldehyde concentrations present in the two rotameters are either zero (**R1**) or high (**R3**), this lack of silanisation should not significantly affect performance. Also, silanisation would probably result in corrosion damage to the float inside the rotameter.

Comparisons were carried out of the MDNPH and the DNPH reagents under a variety of conditions of temperature, humidity, concentration, and duration of exposure. Atmospheres contained both formaldehyde and glutaraldehyde, allowing both components to be studied at the same time.

2.5 RESULTS

2.5.1 Effect of Relative Humidity at 20°C

The effect of relative humidity (RH) on sampling efficiency was examined by carrying out a set of sampling tests at relative humidities of 25%, 50% and 75%. The three experiments were conducted at constant temperature, nominally 20°C, in air containing a nominal concentration of 2.5 mg/m³ of formaldehyde and 0.2 mg/m³ of glutaraldehyde.

The results of the experiments are summarised in Table 2, and show the apparent airborne concentrations, in mg/m³, of the two aldehydes, as measured using the two reagents. The mean and standard deviation are for sets of 3 replicate samples. The full data are presented in Appendix 4.

Table 2: Effect of Relative Humidity at 20°C

RH (%)	DNPH (mg/m ³)				MDNPH (mg/m ³)			
	Formaldehyde		Glutaraldehyde		Formaldehyde		Glutaraldehyde	
	Front	Back	Front	Back	Front	Back	Front	Back
25	1.97 ± 0.22	0.18 ± 0.24	0.084 ± 0.014	N/D	2.81 ± 0.31	0.57 ± 0.31	0.127 ± 0.018	0.010 ± 0.018
50	2.58 ± 0.10	0.02 ± 0.00	0.209 ± 0.009	N/D	3.09 ± 0.11	0.05 ± 0.08	0.214 ± 0.008	N/D
75	2.11 ± 0.07	N/D	0.126 ± 0.007	N/D	2.09 ± 0.04	0.08 ± 0.01	0.172 ± 0.003	N/D

Over the humidity range tested, the data in Table 2 show no consistent effect of relative humidity on the capture of either aldehyde. However, the data do appear to show some difference in capture efficiency, with the MDNPH sampler giving significantly higher concentration readings than the DNPH samplers, at least at the two lower relative humidities. It is unclear whether this is a 'real' effect, due to changing relative humidity, or is due to a higher than usual degree of experimental error, particularly with regard to calibration.

2.5.2 Effect of Temperature

The effect of temperature on sampling efficiency was examined by carrying out a set of sampling tests at temperatures of 10°C, 20°C and 30°C. The three experiments were conducted at a constant relative humidity, nominally 50%, in air containing a nominal concentration of 2.5 mg/m³ of formaldehyde and 0.2 mg/m³ of glutaraldehyde.

The results of the experiments are summarised in Table 3, and show the apparent airborne concentrations, in mg/m³, of the two aldehydes, as measured using the two reagents. Once again the mean and standard deviation are for sets of 3 replicate samples. The full data set is presented in Appendix 4.

Over the temperature range tested, the results show no consistent effect of temperature on the capture of formaldehyde or glutaraldehyde. However, once again the data do appear to show a difference in capture efficiency, with the MDNPH sampler giving significantly higher concentrations than the DNPH sampler at all three test temperatures.

The full data set in Appendix 4 show that two of the DNPH results for glutaraldehyde at 10°C were below the limit of detection. It is suspected that this may have been due to pump failure.

Table 3: Effect of Temperature at 50% RH

Temp (°C)	DNPH (mg/m ³)				MDNPH (mg/m ³)			
	Formaldehyde		Glutaraldehyde		Formaldehyde		Glutaraldehyde	
	Front	Back	Front	Back	Front	Back	Front	Back
10	3.06 ± 0.19	0.13 ± 0.00	0.182 ± 0.003	N/D	3.96 ± 0.11	0.57 ± 0.05	0.194 ± 0.010	N/D
20	2.58 ± 0.10	0.02 ± 0.00	0.209 ± 0.009	N/D	3.09 ± 0.11	0.05 ± 0.08	0.214 ± 0.008	N/D
30	2.88 ± 0.18	0.07 ± 0.02	0.162 ± 0.007	N/D	3.44 ± 0.04	0.08 ± 0.13	0.185 ± 0.016	N/D

2.5.3 Effect of Sampling Duration

Two experiments were conducted to establish the effect of sampling time. For the 8-hour formaldehyde samples three filters were used in series, and the “front” result is a sum of the first two filters. This is because an 8-hour sample at the MEL and running at 200 ml/min would overload the samplers. The results of these experiments are given in Table 4 (with the full data set presented in Appendix 4).

Table 4: Effect of Sampling Duration

Duration	DNPH (mg/m ³)				MDNPH (mg/m ³)			
	Formaldehyde		Glutaraldehyde		Formaldehyde		Glutaraldehyde	
	Front	Back	Front	Back	Front	Back	Front	Back
15-min	2.58 ± 0.10	0.02 ± 0.00	0.209 ± 0.009	N/D	3.09 ± 0.11	0.05 ± 0.08	0.214 ± 0.008	N/D
8-hr	2.36 ± 0.04	0.47 ± 0.03	0.121 ± 0.006	N/D	2.80 ± 0.05	0.44 ± 0.06	0.134 ± 0.002	N/D

The data in Table 4 appear to show, under the test conditions, no significant difference between short term and long term samples. Once again however, the MDNPH samplers consistently give higher results than their DNPH equivalents, particularly for formaldehyde.

2.6 SUMMARY OF NEW REAGENTS

2.6.1 Preparation and Availability

DNPH is clearly the easiest of the reagents to obtain, being a commercially available product. However, the material, as supplied, has been found to contain traces of the formaldehyde derivative and of other materials that might interfere with the analysis. These need to be removed before use by recrystallisation.

Dansyl hydrazine is also commercially available, albeit at a higher price than DNPH.

MNBDH is not commercially available and synthesis would add significantly to the cost of the analysis. Also, while the synthesis is not difficult, it does require the use of methyl hydrazine, which is a carcinogen.

MDNPH suffers the same problems as MNBDH.

2.6.2 Stability

DNPH and its derivatives are known to be stable over a period of years. Even when subjected to poor storage conditions they have shelf lives that are long enough to permit easy stock handling.

Dansyl hydrazine derivatives are not stable. It had been hoped that they would be stable enough to permit sampling and analysis, but unfortunately this was not the case.

MNBDH and its derivatives were found to be unstable; even over a period of a few days, the decomposition was too great to permit reliable analysis.

MDNPH and its derivatives are stable over the period examined, sufficiently so that the reagent is usable.

2.6.3 Analytical Performance

The performance of the dansyl and NBD hydrazines was not examined in detail because of their limited stability.

UV spectra obtained from various derivatives of formaldehyde and glutaraldehyde are illustrated in Figure 10.

The UV spectrum of the MNBDH derivative shows absorbance at relatively long wavelength of 478 nm. This would give good selectivity as few other compounds absorb at this wavelength, however, unfortunately, the stability of the reagent was inadequate.

Comparison of the two DNPH based reagents shows that they give derivatives with similar spectra, examples of which are shown in Figure 10. The MDNPH derivatives, with their additional methyl group, absorb at slightly longer wavelength of 369 nm (compared with 356 nm for the DNPH derivatives). Generally, this will reduce the interference by other materials, however the effect will be small. The intrinsic sensitivity of the two compounds will be similar since in each case due to the similarity of the chromophores.

More importantly, the methylated reagent (MDNPH) forms just one isomeric product with most of aldehydes rather than the cis and trans forms obtained with DNPH. By concentrating all of the product into one peak there is an improvement in sensitivity and, also, less likelihood of interference.

2.6.4 Test Sampling

Only the two reagents that gave stable products (DNPH and MDNPH) were tested in parallel in a known atmosphere. This indicated no significant difference between the two reagents.

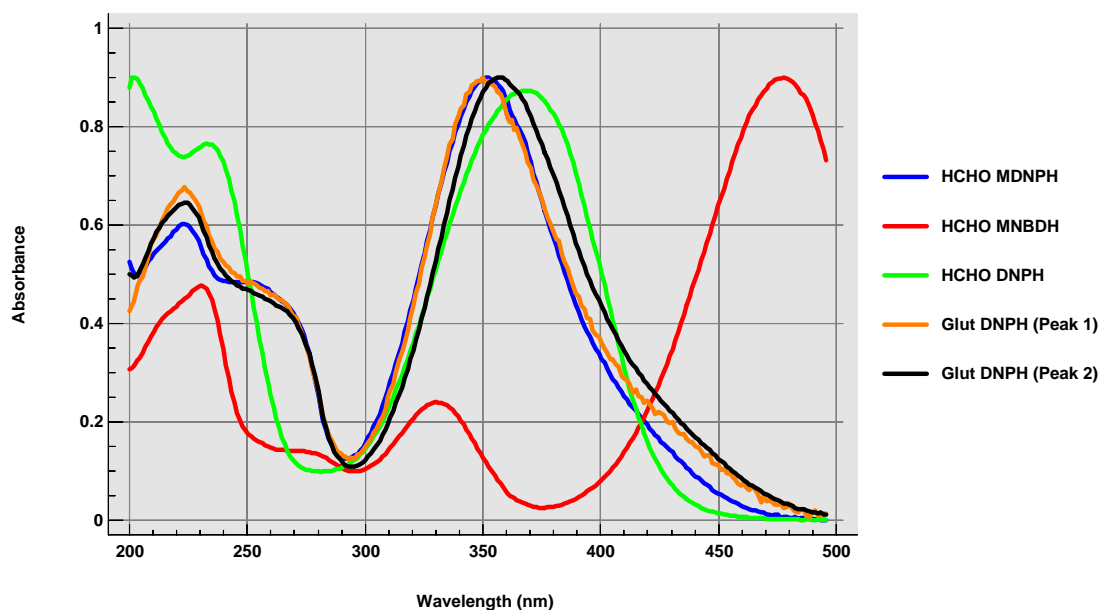


Figure 10: UV Spectra of Formaldehyde & Glutaraldehyde Derivatives

2.7 CONCLUSIONS

The results of the various experiments produced the following conclusions:-

- Two of the potential new reagents (DNSH and MNBDH) were found to be unsuitable because they were not stable in air.
- MDNPH is stable and offers the advantages of less interference by atmospheric oxidants and slightly reduced risk of interference. However, this is offset by the fact that it is not commercially available and its production requires the use of hazardous materials.
- Overall, the advantages of MDNPH would only outweigh this if there were known to be a problem that couldn't easily be solved by other means (for example, using a potassium iodide (KI) scrubber to remove oxidants).

3 ACROLEIN

3.1 INTRODUCTION

Acrolein is a special case of the aldehydes. It has a double bond conjugated to the carbonyl group which gives rise to additional complexity in its reactions. In particular, the reaction with DNPH is complex and gives rise to a number of products. These make the interpretation of analytical results more difficult, particularly with respect to calibration. They also mean that there is an increased risk of interference both with measuring acrolein and with measuring other aldehydes in its presence. For these reasons, HSL has, in the past, used another method based on OSHA Method 52 for acrolein measurement. The method is based on the reaction of aldehydes with hydroxymethyl piperazine coated onto XAD-2 to give a derivative that is subsequently analysed by GC using an NPD.

While this method is effective, it is more labour intensive and less sensitive than the DNPH based method used for the other aldehydes. The greater complexity of the method makes it more expensive and it also requires somewhat more unusual equipment. This can mean that there are problems with availability of equipment and this in turn can mean the turn-round time is adversely affected. Acrolein commonly occurs as a by-product along with the other aldehydes and it would be an advantage if a single sampling and analysis system could be used for all the aldehydes. With a view to addressing these problems and other, less significant ones, some work was undertaken to investigate the reaction of acrolein with the proposed new reagent. Unfortunately, the reaction of acrolein with MDNPH was found to be similarly complex and so no clear advantage would follow from replacing DNPH with MDNPH. Some preliminary work was performed to look at the use of ATD-GC/MS to measure acrolein.

Acrolein commonly gives rise to a number of products with reagents. Many reagents give derivatives containing a CN double bond and the geometry of the molecule can be cis- or trans- at this bond as illustrated, in the case of acetaldehyde, in Figure 11.

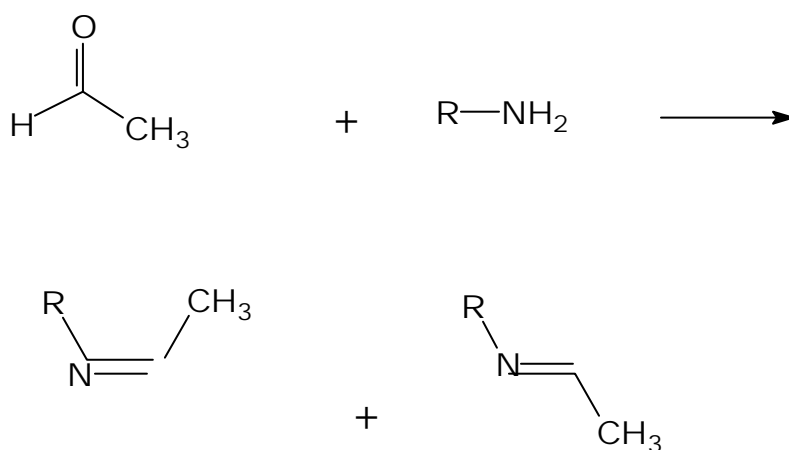
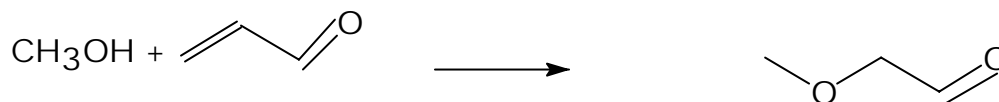


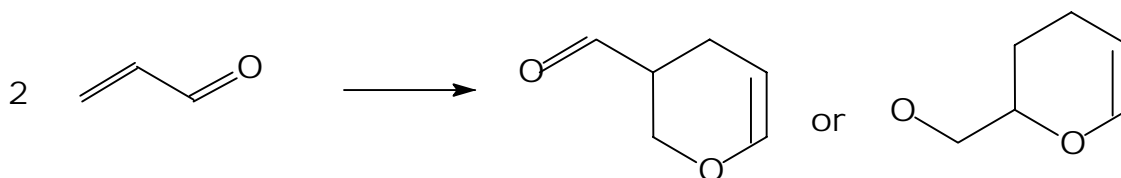
Figure 11: Reagent of acetaldehyde with amine reagent

This sort of reaction can occur with any aldehyde (apart from formaldehyde) and gives rise to the pair of peaks as seen in the glutaraldehyde-DNPH chromatogram (see Figure 8).

In addition, there is potential for side reactions with the solvent to occur at the double bond, for example;



and for the acrolein to dimerise before reacting.



These reactions give rise to a number of products which, in turn, makes quantification difficult.

3.2 EXPERIMENTAL

3.2.1 HPLC

A pair of solutions was prepared containing MDNPH or DNPH and phosphoric acid at concentrations corresponding to a desorbed filter. These were then spiked with a solution of acrolein and the mixture was analysed. The resulting chromatograms are shown in Figure 12.

In each case there are a group of 3 products. The UV spectra of the peaks indicate that they are (in order) the expected acrolein derivative and the 2 isomers of the hydroxypropanal derivative. The hydroxypropanal is formed by hydrolysis of the acrolein by moisture present in the air.

Additionally, the DNPH solution contains the 2 peaks from the dimer of acrolein near 19 minutes. These are absent from the MDNPH solution for reasons that are unclear.

In a real sample there are likely to be other peaks that co-elute with these 3 materials making accurate measurement more complex.

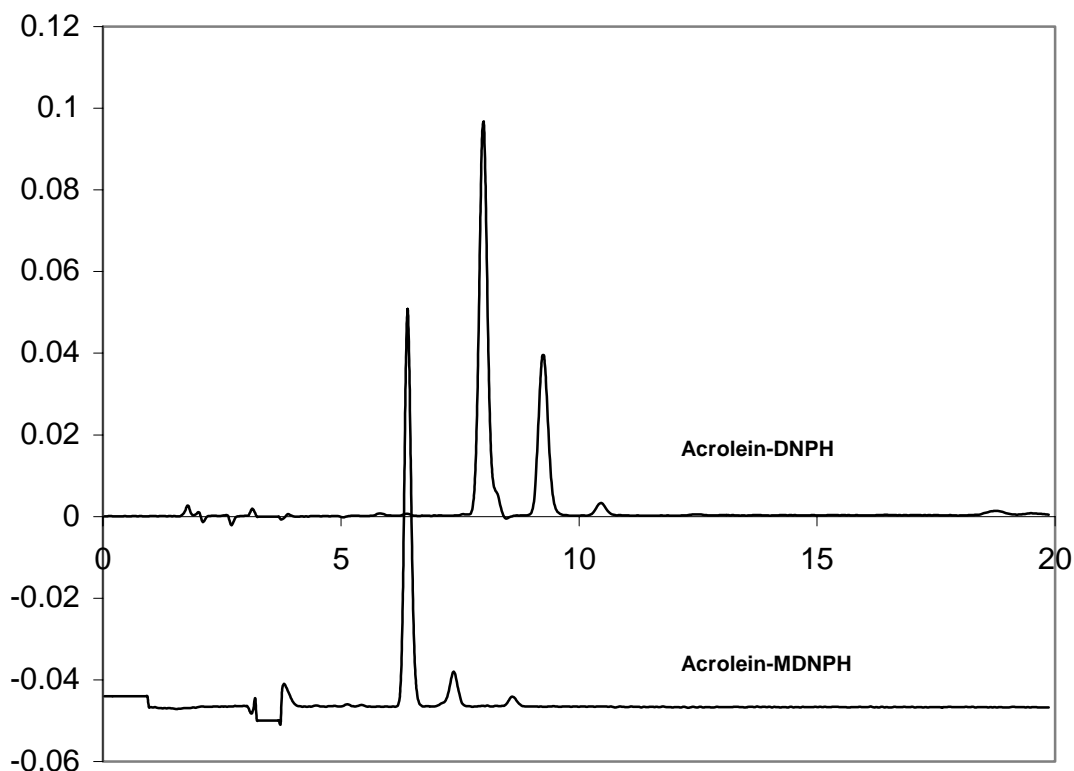


Figure 12: MDNPH and DNPH Derivatives of Acrolein

3.2.2 Automated Thermal Desorption

A brief investigation was carried out into the possibility of using Automated Thermal Desorption (ATD) for analysis of acrolein was also carried out. The main benefit of using an ATD-based sampling/analytical procedure is that it is quicker and easier than the HPLC-based technique, and can also be used for determination of other, non-carbonyl, components. Acrolein was spiked onto ATD tubes containing the following sorbents - Tenax, Chromosorb-106, Carboxen-1000 and Air Toxics. The spiked tubes were then analysed by thermal desorption and gas chromatography-mass spectrometry. The purpose of this experiment was to gather some initial information on the reproducibility and stability of the various ATD sampling media.

Figures 13 and 14 show MS chromatograms obtained from ATD analysis of Tenax and Chromosorb-106 tube, both spiked with acrolein, methyl, ethyl ketone and methyl isobutyl ketone. Because these tubes were spiked from the vapour phase the dimer is not seen in these chromatograms. The Chromosorb tube gives both a better peak shape than Tenax (see inset in Figure 14) and a larger response for the acrolein. Whilst the responses for MEK and MIBK are similar for both sorbents, that for acrolein on Tenax is only about 40% of that on Chromosorb. Two other sorbents, Carboxen-1000 and Air Toxics were found to give recoveries of 88% and 79% for acrolein, although the Carboxen tubes showed very poor recoveries for the other two test compounds.

Further tubes analysed after a period of one week gave good recoveries from Chromosorb. Because the ATD system is more robust and simpler than the current GC/NPD method more work should be done to investigate this technique, specifically to investigate the absolute recovery and storage stability.

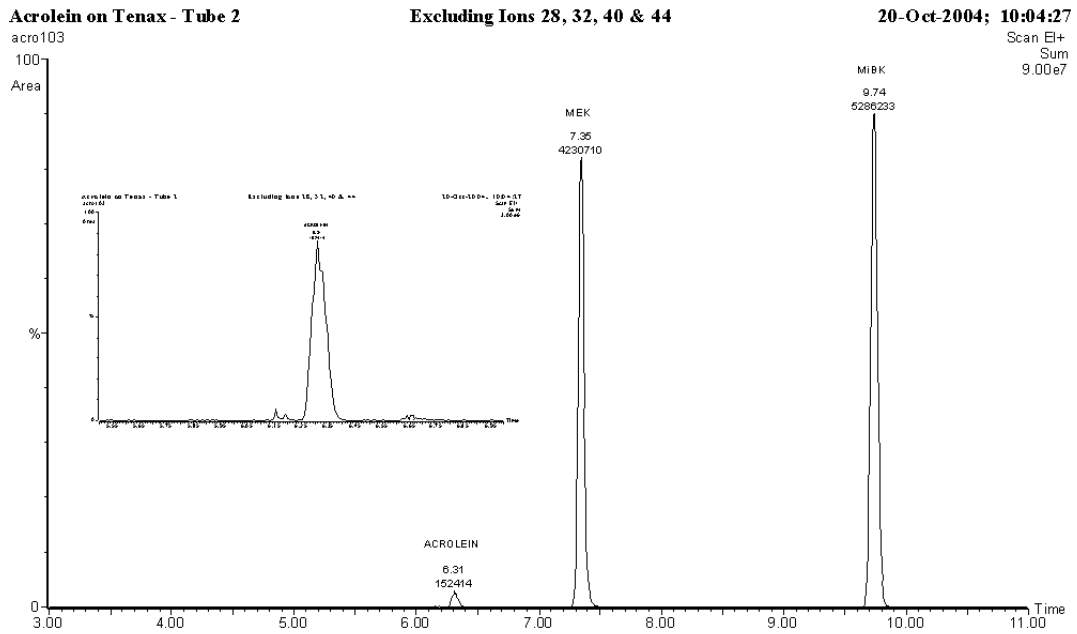


Figure 13: Acrolein on Tenax ATD tube (by GC-MS)

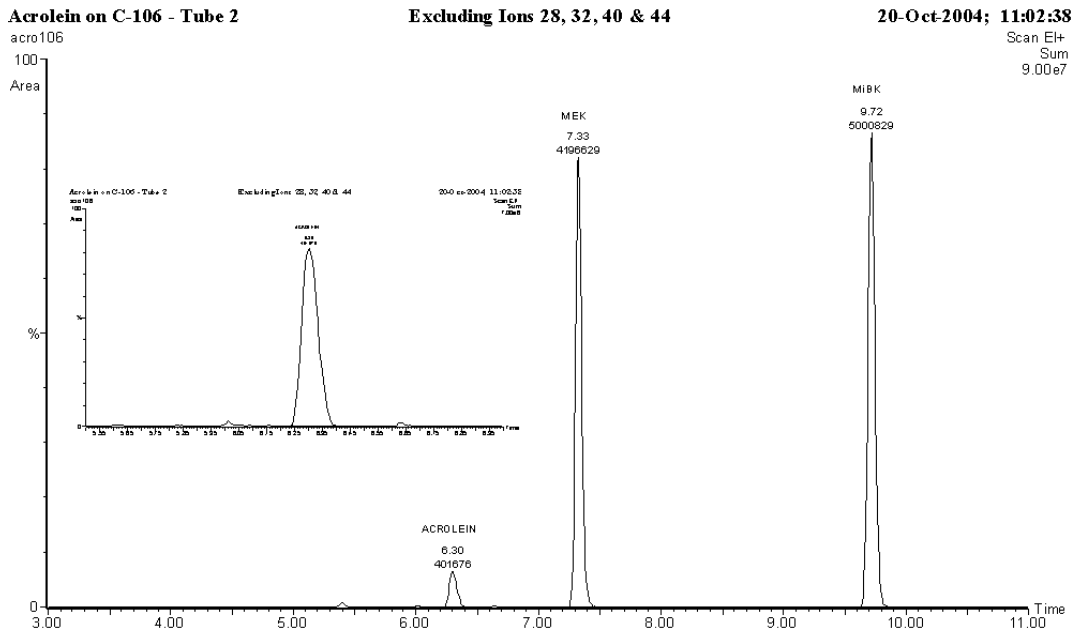


Figure 14: Acrolein on Chromosorb-106 ATD tube (by GC-MS)

3.3 RESULTS AND DISCUSSION

The data, while limited in their extent, show that ATD may be a suitable technique for analysis. This involves less sample preparation than the HPLC method and is more automated so it would be quicker and more economical. They also show that Chromosorb 106 is the best choice of sorbent and that the samples are stable for a week.

3.4 CONCLUSIONS

The results of these initial tests look quite encouraging. Consequently, it is recommended that a fuller investigation of the use of ATD as a measurement technique for acrolein be carried out.

There may also be scope for investigating the technique for measurement of other unsaturated aldehydes such as methacrolein, crotonaldehyde, etc.

4 ISO 16000-3:2001

4.1 INTRODUCTION

For some years, HSL has maintained UKAS accreditation for method OMS-006; analysis of glutaraldehyde by HPLC. HSL are often called on to analyse samples for other aldehydes and it would be better accreditation covered a wider range of aldehydes. Additionally, it would be beneficial to align the HSL method with an internationally recognised standard. ISO 16000-3:2001 is such a standard for the determination of formaldehyde and other carbonyl compounds in air.

Much of the standard refers to specific sampling materials and there is less to gain from standardising these. On the other hand, it is useful to adopt the analytical side of the standard. In addition to standardising our procedure, this would simplify it, as we currently use different conditions for glutaraldehyde compared to the other aldehydes. Adopting the standard would be an opportunity to improve the service we offer in terms of compatibility and quality.

4.2 PROGRESS

An in-house method for aldehydes analysis based on the analytical aspects of ISO 16000-3:2001, but using our sampling equipment has been developed and written up as a draft procedure. The procedure has now been written up as OMS-006 and has been accredited and audited by UKAS.

The new method has been validated in that it has been used to analyse two sets of WASP samples with satisfactory results

The new method has been validated in that it has been used to analyse two sets of quality control samples supplied as part of the Workplace Analysis Scheme for Proficiency (WASP) scheme. Both sets of samples achieved satisfactory results.

The new method is uses a C₁₈ column because of the greater robustness compared to cyano columns and to provide compatibility with the ISO method. The analysis is performed at an elevated temperature to improve the resolution. Otherwise the analysis is essentially the same as the previous method but has been calibrated for a greater range of analytes. Provision has also been made for the inclusion of other aldehydes as required.

4.3 CONCLUSIONS

The new method has met the requirements of the ISO standard, and should be adopted as the standard method of analysis for aldehydes in HSL.

5 QUALITY CONTROL

5.1 DISCUSSION

HSL has a reputation for producing work of exceptional quality. This is maintained by a policy of continued improvement and is demonstrated by our taking part in quality assurance and proficiency testing schemes where possible.

HSL both runs, and participates in, the Workplace Analysis Scheme for Proficiency (WASP). This is a quality assurance scheme where participants receive samples spiked with analytes. They analyse the samples and return their results to the organisers. The results are then compared against the known values and the proficiency of the participating laboratory is assessed on this basis. Among the analytes that are offered in this scheme is formaldehyde as the DNPH derivative. The derivative is spiked at a level corresponding to 3 to 60 micrograms per sample.

Four members of the Organic Measurement Section staff have been trained to carry out the formaldehyde analysis and have gained satisfactory results in WASP.

Over the duration of this project HSL has taken part in the formaldehyde scheme and has consistently maintained Category 1 status (see Table 6). The full set of historical data for the past 10 years are presented in Table 5. The mean result is the ratio of HSL's result to the mean of the results of the WASP participants.

Table 5: Past Performance in WASP

Round Number	Round Date	Mean Result [†]	Ranking [‡]	Category*	Comments
29	Mar-96	0.96	N/A	-	
30	Apr-96	0.88	N/A	-	
31	Jun-96	0.99	N/A	-	
32	Dec-96	0.90	4 of 6	2	Possibly affected by bias of other labs
33	Feb-97	1.40	5 of 8	2	Data transposed. Without that error would have been 0.98 and Cat 1
34	May-97	0.74	8 of 9	2	Miscalculated- would have been 0.98. This brought about a change in sign-off procedures and the "countersigning sheet".
35	Jul-97	0.93	10 of 11	2	
36	Nov-97	0.99	9 of 10	2	
37	Feb-98	0.97	11 of 12	2	
38	May-98	0.96	3 of 15	1	Errors from Rounds 33 & 34 drop out of the calculation
39	Jun-98	0.88	4 of 12	1	
40	Nov-98	1.03	4 of 15	1	
41	Feb-99	1.01	3 of 16	1	
42	May-99	1.01	8 of 17	1	
43	Jul-99	1.01	4 of 16	1	

[†] = Mean Standardised Result; [‡] = Ranking of Laboratory; * = Performance Category

Table 5: Past Performance in WASP (continued)

Round Number	Round Date	Mean Result [†]	Ranking [‡]	Category*	Comments
44	Dec99	1.01	1 of 15	1	
45	Apr-00	1.02	1 of 23	1	
46	Oct-00	1.03	2 of 24	1	
47	Nov00	0.99	1 of 25	1	
48	-	-	-	-	No data on file
49	May-01	1.05	5 of 28	1	
50	Aug-01	1.01	9 of 29	1	
51	Nov-01	1.03	9 of 31	1	2nd analyst
52	Mar-02	1.01	10 of 30	1	
53	Jul-02	1.13	13 of 30	1	
54	Sep-02	1.04	8 of 31	1	
55	Jan-03	1	8 of 27	1	3rd analyst
56	Mar-03	1.05	11 of 29	1	
57	Jun-03	1	8 of 33	1	
58	Sep-03	1.04	7 of 31	1	
59	Dec-03	0.94	9 of 33	1	
60	Mar-04	0.98	10 of 33	1	
61	-	-	-	-	No data on file
62	Sep-04	1.02	5 of 31	1	
63	Dec-04	1.02	1 of 34	1	4th analyst
64	Mar-05	1.02	1 of 30		
65	Jun-05	1.04	3 of 30	1	
66	Sep-05	1.04	4 of 34	1	
67	Dec-05	1.02	5 of 34	1	1 st analyst again

† = Mean Standardised Result; ‡ = Ranking of Laboratory; * = Performance Category

Table 6: Definitions of WASP Performance Categories

Scheme	Performance Category (RPI*)		
	1 (Best)	2	3 (Worst)
Formaldehyde	< 79	79 – 330	> 330

* = Running Performance Index

6 DIRECT READING MONITOR

6.1 INTRODUCTION

From time to time new equipment comes on the market for measuring organic pollutants in air. HSE accepts that real-time monitoring of pollutants is a valuable way of showing employers and employees how compliance with limits can be achieved and is also useful in demonstrating compliance. In general, portable real-time monitors are less sensitive and selective than laboratory based analyses, however they still serve a purpose. For these reasons, and to maintain our background knowledge, it is sometimes useful for HSL assesses such equipment.

During this work we took the opportunity to evaluate a commercial direct reading monitor for formaldehyde. This monitor is based on an updated version of the well-known Direct reading tube in which contaminated air is drawn through a glass tube containing a colour indicator. Contaminants in the air affect the indicator and change its colour. The length of the stain produced is an indicator of the amount of the contaminant. This monitor takes this a step further by automating the measurement of the stain length and providing a digital output. In addition, a number of tubes are combined into a plastic cartridge which enables ten analyses to be made. The cartridge also carries calibration information so the monitor can be used for a number of different analytes, by using different cartridges.

6.2 EXPERIMENTAL

The direct reading monitor was used to measure airborne formaldehyde concentration in the test chamber during the experiments to evaluate the two derivatisation reagents (see Section 2.5).

Table 7: Results using Direct reading Monitor to Measure Formaldehyde

Conditions	Indicated Concentration (ppm)	% of True Concentration	Mean (%)
2.45 ppm HCHO [†] 10.4°C 44.6% RH	>5	>197	145
	3.40	134	
	2.99	118	
	3.30	130	
3.00 ppm HCHO [†] 14.4°C 35.6% RH	3.70	123	129
	4.20	140	
	2.57	87	
	>5	167	
1.75 ppm HCHO [†] 27.8°C 52.3% RH	3.9	223	211
	3.8	217	
	4.5	257	
	3.2	183	
	3.1	177	
1.32 ppm HCHO [†] 19.9°C 70.9% RH	1.71	130	151
	1.74	132	
	2.64	200	
	1.89	143	
1.32 ppm HCHO 20.2°C 69.8% RH	2.13	161	137
	1.70	129	
	1.70	129	
	1.67	127	

[†] = Atmosphere also contains approximately 0.2 mg/m³ of glutaraldehyde

6.3 RESULTS AND DISCUSSION

The results of the tests are summarised in Table 7. Whilst disparity between these results is rather large, it is possible that part of this may be due to the presence of glutaraldehyde as well as formaldehyde in the test atmosphere. However, the quantity of glutaraldehyde is small and these data seem likely to indicate a real inaccuracy. Furthermore, the final two sets of data are taken with and without the addition of glutaraldehyde respectively. The difference caused by the glutaraldehyde is not statistically significant.

6.4 SUMMARY AND CONCLUSIONS

In conclusion, our tests appear to show that the Direct reading to over-read formaldehyde concentrations. While this is not ideal, it does mean that the instrument fails on the safe side. Despite the inaccuracy of the calibration, the equipment is easy to use and gives an almost real-time indication of formaldehyde. This might be useful in some circumstances, for example to demonstrate the absence of formaldehyde following a spillage.

7 OVERALL CONCLUSIONS

The possible new reagents tested do not generally provide any advantage over DNPH. In some cases, where a large number of different aldehydes need to be identified individually the methylated reagent MDNPH might offer better separation because it generally only forms a single isomer of the derivative. This needs to be offset against the difficulty and cost of preparing the reagent. While this could be obtained by contract synthesis we felt it was more appropriate for us to prepare the material in house where we have the facilities for dealing with the carcinogenic and sensitising precursors

The current method for acrolein, while problematic, can be used. The other reagents did not offer any particular advantage. The ATD approach to this analysis should be examined in more detail. In particular, ATD offers the prospect of a less labour intensive and more sensitive analysis than the hydroxymethyl piperazine method, and would also allow acrolein to be monitored using the same sampling device as other volatile organic compounds, thus negating the need for dual samplers in such instances.

HSL now has a formally documented procedure for analysis of aldehydes as their DNPH derivatives, accredited by UKAS. This procedure should be used for analysis of samples.

HSL has also maintained expertise and understanding of aldehyde issues. By expanding the number of trained and competent staff, quality service cover will be maintained.

The Direct Reading monitor apparently over-reads the formaldehyde concentration but, in doing so, it "fails safe". It would certainly be useful in some instances.

8 APPENDICES

APPENDIX 1: MDNPH SYNTHESIS

Methyl-DNPH reagent was prepared by the reaction of chlorodinitrobenzene with methyl hydrazine using the following procedure:-

- i) In a 500 ml flask fitted with a reflux condenser, 10.8 g potassium acetate was dissolved in 100 ml water. An addition funnel was fitted to the flask.
- ii) 20.2 g of chlorodinitrobenzene was dissolved in 100 ml warm ethanol and added to the flask
- iii) A 6 ml of methyl hydrazine was added to 25 ml of ethanol
- iv) This solution was added to the flask via the addition funnel and washed down with a few ml of ethanol.
- v) The mixture of water, ethanol, potassium phosphate and methyl hydrazine was heated on a water bath to reflux.
- vi) The solution of chlorodinitrobenzene was added to the addition funnel and then added to the refluxing mixture dropwise.
- vii) The solution was refluxed for 4 hours then left to cool overnight.
- viii) The product of the reaction was diluted with 100 ml water and the product filtered off.
- ix) The crystals were washed with ethanol and water then recrystallised from acetonitrile.
- x) This gave the product as yellow crystals. The identity and purity of the compound were confirmed by HPLC/UV/VIS spectroscopy

Important Safety Note:

It should be noted that the synthesis of MDNPH involves the use of methyl hydrazine which is volatile, toxic, and, most importantly, a suspected carcinogen. It is therefore essential to carry out a thorough risk assessment before undertaking any work with this material. The risk assessment should pay particular attention to the controls which should be in place for handling of methyl hydrazine. It is recommended that this synthesis is only carried out by those experienced in the use of this sort of toxic material.

APPENDIX 2: MNBDH SYNTHESIS

MNBDH was synthesised by the reaction of chloro nitrobenzoxadiazole (NBD chloride) and methyl hydrazine using the following procedure:-

- i) A solution of 2 g of NBDCI in 160 ml dichloromethane was prepared and heated to reflux in the apparatus described in Appendix 1.
- ii) A solution of 5 ml of methyl hydrazine in 100 ml dichloromethane was added and the mixture refluxed for 20 min.
- iii) The reaction mixture was cooled and 100 ml of water was added.
- iv) The lower layer was separated and then washed with 5% H_3PO_4 to remove excess methyl hydrazine.
- v) The solution was dried with sodium sulphate and the solvent removed under vacuum to recover the product.
- vi) The product was recrystallised from acetonitrile as very dark red crystals. The purity and identity of the product were confirmed by HPLC/ UV VIS spectroscopy.

Important Safety Note:

It should be noted that the synthesis of MNBDH involves the use of methyl hydrazine which is volatile, toxic, and, most importantly, a suspected carcinogen. It is therefore essential to carry out a thorough risk assessment before undertaking any work with this material. The risk assessment should pay particular attention to the controls which should be in place for handling of methyl hydrazine. It is recommended that this synthesis is only carried out by those experienced in the use of this sort of toxic material.

APPENDIX 3: OPTIMISED HPLC CONDITIONS

The optimised HPLC conditions used for analysis of the DNPH and MDNPH derivatives were as follows:-

1. Mobile phase

- Methanol + buffer (M/100 NaHPO₄ in 90 : 10 water : methanol).
- Mixed 70:30 for MDNPH and 75:25 for DNPH

2. Column

- 30 cm by 3.9 mm 5 µm C18 Resolve™

3. Flow rate

- 1 ml/min

APPENDIX 4: RAW DATA

Tables A4.1 – A4.3 present the full results from the experiments described in Section 2.5 of this report.

Table A4.1: Effect of relative humidity at 20°C

RH (%)	DNPH (mg/m ³)				MDNPH (mg/m ³)			
	Formaldehyde		Glutaraldehyde		Formaldehyde		Glutaraldehyde	
	Front	Back	Front	Back	Front	Back	Front	Back
25	2.15	0.05	0.094	N/D	2.73	0.43	0.130	N/D
	1.73	0.46	0.068	N/D	2.55	0.93	0.107	0.031
	2.04	0.04	0.089	N/D	3.16	0.36	0.143	N/D
50	2.59	0.02	0.200	N/D	2.96	0.14	0.196	N/D
	2.48	0.02	0.209	N/D	3.15	N/D	0.214	N/D
	2.67	0.02	0.217	N/D	3.16	N/D	0.210	N/D
75	2.07	N/D	0.133	N/D	2.05	0.17	0.085	N/D
	2.19	N/D	0.121	N/D	2.13	0.17	0.082	N/D
	2.06	N/D	0.122	N/D	2.09	0.18	0.075	N/D

Table A4.2: Effect of temperature at 50% RH

Temp (°C)	DNPH (mg/m ³)				MDNPH (mg/m ³)			
	Formaldehyde		Glutaraldehyde		Formaldehyde		Glutaraldehyde	
	Front	Back	Front	Back	Front	Back	Front	Back
10	2.89	0.18	0.135	N/D	4.08	0.62	0.183	N/D
	3.03	0.18	0.128	N/D	3.90	0.56	0.197	N/D
	3.27	0.18	0.130	N/D	3.89	0.52	0.201	N/D
20	2.59	0.02	0.200	N/D	2.96	0.14	0.196	N/D
	2.48	0.02	0.209	N/D	3.15	N/D	0.214	N/D
	2.67	0.02	0.217	N/D	3.16	N/D	0.210	N/D
30	2.71	N/D	0.156	N/D	3.40	N/D	0.181	N/D
	2.87	0.04	0.159	N/D	3.49	0.23	0.203	N/D
	3.07	N/D	0.170	N/D	3.43	N/D	0.172	N/D

Table A4.3: Effect of sampling duration

Duration	DNPH (mg/m ³)				MDNPH (mg/m ³)			
	Formaldehyde		Glutaraldehyde		Formaldehyde		Glutaraldehyde	
	Front	Back	Front	Back	Front	Back	Front	Back
15-min	2.59	0.02	0.200	N/D	2.97	0.14	0.204	N/D
	2.48	0.02	0.209	N/D	3.16	N/D	0.219	N/D
	2.67	0.02	0.218	N/D	3.16	N/D	0.219	N/D
8-hr	1.26*	0.46	0.122*	0.004	1.53*	0.41	0.135*	N/D
	1.06**		0.003**		1.28**		0.001**	
	1.29*	0.45	0.112*	0.002	1.56*	0.51	0.132*	N/D
	1.10**		0.003**		1.29**		0.000**	
	1.34*	0.50	0.121*	0.002	1.55*	0.40	0.133*	N/D
	1.04**		0.003**		1.21**		0.001**	

* = Front filter (of 3); ** = Middle filter (of 3)

APPENDIX 5: SUPPORTING DATA

Section	Book	Page	CD
2.2.1	Core activity on aldehydes (Book1)	5-7	-
2.2.2	Core activity on aldehydes (Book1)	28,51,54-60	14
2.2.3	Core activity on aldehydes (Book1)	2,3,8,9,33	-

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