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**Investigation of complex harmful substances  
call-off contract 2003/5**

**HSL/2006/106**

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Science Group: **Health Improvement**

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## EXECUTIVE SUMMARY

This report summarises the work carried out during 2003-2005 under the Investigation of Harmful Complex Substances Call-off contract. The main aims of this core activity work includes the following :

1. To ensure that HSL can maintain the necessary capability in order to continue to provide the science and technology services required by HSE to support its frontline mandatory activities and strategic aims under the FIT3 programme on disease reduction.
2. To support the ability for HSL to provide advice and representation according to HSE needs and disseminate information on relevant issues.

Aim 1 includes: Targeted analytical method developments to respond to current and anticipated enforcement and frontline requirements. This will ensure that exposures to, and risks associated with, chemical usage can be more accurately, reliably and easily determined and controlled. Maintenance of capability, quality assurance and staff competency so that information provided to HSE inspectors will stand up to scrutiny. Call-off components to allow for ad hoc support to underpin scientific investigations as required.

Aim 2 includes: Maintenance of expertise and representation of HSE's interests on appropriate committees and knowledge transfer into the public domain where appropriate, including input to HSE guidance and training initiatives.

### Main Findings

A wide range of diverse complex issues have been investigated, new capabilities have been developed and dissemination of knowledge has been achieved in response to HSE's requirements:

#### **Diesel engine exhaust emissions – Inter-laboratory sampling and analysis exercise at IGF Dortmund.**

The results show there was very good agreement between all the laboratories when measuring diesel particulate generated by an old design engine running on standard low sulphur diesel. However, when a modern turbocharged engine was used the agreement was not as good and the laboratories appeared to be dividing into two distinct groups. There was even less agreement between laboratories when the modern engine was run on a bio-diesel fuel and the two distinct groups became more apparent with one group of four laboratories recording EC levels more than twice those of the other group of five laboratories. This was attributed to the method of analysis employed and the high levels of organic carbon generated from bio-diesel.

#### **Coulomat carbon analysis of toner powder.**

The method used for measurement of diesel engine exhaust emissions is suitable for the measurement of carbon black content of printer toner. There was no indication that the polymer which formed the bulk of the toner would interfere with the analysis method through charring to form elemental carbon.

### **Rosin-free solders.**

These tests identified a number of aliphatic acidic components, particularly in the rosin-free products. In many cases, these additional components were the main components present. These components are also important as some, such as glutaric acid are listed as "irritants", and others, such as adipic acid, are suspected as possible causes of asthma.

### **Weld-thro' primers.**

This work provides information on test methods, analytical methods and sampling procedures for determination of thermal degradation products generated during welding involving weld-thro' products and coatings (JS223898). The information was used to aid completion of European Standard prCEN/ISO/TS 15011-5.

### **Glove permeation testing rig.**

This work was carried out in support of COSHH Essentials for Printers under the Skin Disease sub-programme to provide information on the suitability of the gloves used in this industry for protection against cleaning fluids.

A computer controlled glove permeation testing rig has been constructed and validated with a standard reference material. The system has been shown to be capable of making measurements in the range 10 to 35°C for a range of glove types and composition using a wide selection of organic solvents and complex mixtures including printing cleaning fluids.

### **Isocyanate (NCO) sampling and analysis.**

#### Hot melt glues

For the glues tested (HDI, MDI and TDI based) all were shown to be able to liberate appreciable NCO vapour at temperatures above 100 °C. No NCO was detected in the air during brushing, mixing and pouring operations. MDHS 25/3 has the required sensitivity to detect airborne NCO from very short-term tasks (~ 30 s or less).

#### Development of MDHS 25/3 (analytical method)

The use of a suitable internal standard greatly improves the reproducibility of the electrochemical (EC) detector. MP derivatized MDI on WASP filters has been found to be stable for ~ 2 years. This work corrects an anomalous earlier finding. Work on the EC response of mono, di- and tri- isocyanate MP derivatives has shown that the "equivalent response" assumption for the EC quantification of NCO is valid.

#### Development of MDHS 25/3 (Surface sampling method)

The feasibility of a surface sampling method based on the chemistry employed in MDHS 25/3 has been demonstrated.

#### Development of MDHS 25/3 (air sampling method)

Two alternative "solid state" sampling methods have been investigated and found to give acceptable correlation to the reference method MDHS 25/3 for the sampling of HDI based isocyanate aerosols. One method was judged to give better correlation with MDHS 25/3. These results suggest that for the sampling of aerosols produced during the spraying of slow curing HDI based paints, as in MVR work, sampling using this method is an acceptable alternative to the impinger/filter method described in MDHS 25/3. The use of an MP impregnated "thick" filter (GF/B) or two MP impregnated GF/A filters in an IOM head is a significantly more user friendly personal sampling device than the impinger/filter method.

## **Investigation of on-gun extraction in MVR**

When a sanding operation was carried out the photographic data recorded clearly showed the full extent of the dust cloud when the on-gun extraction was switched off. With the on-gun extraction switched on the lack of airborne dust clearly demonstrated the high efficiency of the extraction device. In addition to this, in the absence of Tyndall lighting the dust cloud was not visible under normal lighting conditions.

## **Smart Repairs**

The results show that SMART repairing does generate short term peak exposures above the workplace exposure limit (WEL). For each of the four given spraying scenarios, the time spent spraying was broadly the same but the highest and lowest results for a particular scenario varied by as much as factor of ten. Clearly atmospheric conditions have a considerable effect on the potential NCO exposure during SMART repair and that air-fed RPE is essential for ensuring adequate protection from airborne isocyanates.

## **Validation of cyanoacrylates samplers**

Two commercially available samplers were evaluated to BS EN 482. Both samplers performed effectively except at extremes of temperature and humidity.

## **Acrylamide in cooking fume**

Work was carried out in completion of an existing project (OMS/2004/10) on the investigation of acrylamide in cooking fume (JS2003162). Analytical method development and analysis of food samples for acrylamide were investigated.

## **Publications and Presentations**

A paper entitled "An assessment of occupational exposure to polycyclic aromatic hydrocarbons in the UK has been published by The Annals of Occupational Hygiene. The paper summarises the activity carried out by HSL for HSE over the past 15 years on exposure to polycyclic aromatic hydrocarbons. The main theme of the paper is concerned with an occupational hygiene survey carried out between 1998 and 2000 on 25 sites. The findings of the survey have subsequently informed HSE on the risks of exposure to coal tar pitch volatiles and polycyclic aromatic hydrocarbons in the workplace and has led to the introduction of a Biological Monitoring Guidance value (BMGV) in 2004 which is now being used to assess exposure from all routes (inhalation or skin absorption) in the workplace.

As part of a HSE session on isocyanates at the British Occupational Hygiene Society conference in 2004, HSL was asked to make a presentation on measuring personal exposure to airborne isocyanates. The presentation was well received and communicated the effective methods for appropriate sampling of isocyanates to a wide audience.

## **Quality**

The quality and validity of HSL's isocyanate analytical data generated during this project and in support of HSE's mandatory activities is demonstrated by effective performance in an external quality assurance (QA) scheme. Category 1 performance was achieved in the Workplace Analysis Scheme for Proficiency (WASP) for isocyanate and formaldehyde during the QA rounds analysed throughout this call-off contract.

UKAS accreditation has been maintained for aldehydes work (isocyanates method is not accredited at this time).

## **Recommendations**

Many of the sampling and analytical methods developed under this call-off contract are being applied to reactive, planned support and project work. OMS should continue to perform planned and ad-hoc development work using the call-off (or core-activity approach) in new areas of interest to HSE in support priority programmes and mandatory activities. This will allow HSL to be able to provide a modern and efficient service with robust and up to date data enabling HSE to effectively assess and control exposure to harmful complex substances. Specific recommendations for further work are made in each section of the report.

# **1 DIESEL ENGINE EXHAUST EMISSIONS – INTERLABORATORY SAMPLING AND ANALYSIS EXERCISE AT IGF DORTMUND**

## **1.1 INTRODUCTION**

In April 2004, a European Standard BS EN 14530:2004 titled '*Workplace atmospheres – Determination of diesel particulate matter – General requirements*' was issued. The Technical Committee CEN TC137/WG2 ad hoc group 'European Co-ordination Group on Diesel Soot Exposure (ECDSE)' had prepared the document and HSL were represented on this committee and had played an important role in developing this standard.

The standard specifies the sampling and analytical requirements for the determination of exposure to diesel engine exhaust particulate emissions in workplace atmospheres. Time weighted average particulate mass concentrations of organic carbon (OC), elemental carbon (EC) and total carbon (TC) are determined and EC is used as the surrogate measure of exposure to diesel engine exhaust emissions (DEEEs).

The standard enables users to select a procedure to determine occupational exposure to DEEEs according to a uniform approach and to obtain directly comparable results.

Whilst developing the standard, members of the committee participated in five inter-laboratory round robins, with each laboratory using their own particular analytical method to determine the carbon content of diesel particulate samples. For the first three Round Robins, replicate samples were obtained by one of the laboratories involved and the samples sent out to the other laboratories for analysis. However, in the last two Round Robins a unique diesel sampling facility at IGF in Dortmund, Germany was used. This facility allowed each laboratory to both collect their own samples in parallel with the other laboratories and to then analyse them using their own specific method within the scope of the standard. This allowed excellent comparative data to be obtained which considered both the sampling and analytical errors.

Reported here are HSL's sampling details and results from Round Robin 5, which was carried out over four days in May 2004 at IGF, Dortmund.

## **1.2 EXPERIMENTAL**

### **1.2.1 The Diesel Sampling Facility at the Institut für Gefahrstoff-Forschung (IGF)**

The diesel exhaust sampling chamber at IGF in Dortmund is a modified concrete room/bunker with approximate dimensions of 3.3 m X 2.5 m X 2.8 m (total volume ~ 23 m<sup>3</sup>). External to the chamber is a large extract fan with a maximum throughput of about 200 m<sup>3</sup>/min and which provides about 8 gas exchanges per minute in the chamber. In the diagonally opposite corner of the room to the fan and about midway between the floor and ceiling was another opening which connected into a 21 m long, 0.5 m diameter steel tube that was open at the end. Access to the room was through a single door.

The sampling chamber was empty except for five vertical chains fixed from floor to ceiling. On four of these chains and at two heights were fastened metal cross-bars and on the central chain was fastened one cross bar providing 18 sampling locations in all. Onto either end of these bars participants fastened sampling heads and pumps for each of the sampling runs.

Diesel exhaust was introduced axially about 2 m into the open end of the long steel tube and was drawn into the chamber, along with an excess of air, by the extract fan. The amount of exhaust introduced into the steel tube was controlled by a butterfly valve, with the excess being exhausted to the outside.

### 1.2.2 SAMPLING

There were nine sampling runs in total and eighteen sampling positions within the chamber. Nine laboratories took part in the study (table 1.1), with each laboratory deploying six samplers in each run. To eliminate the possibility of non-homogeneity of the particulate concentration in the chamber, each laboratory deployed their samplers in separate groups of three and after each run these were moved around the chamber to a previously determined statistical plan. At the end of the nine sampling runs each laboratory had deployed three samplers at each of the eighteen sampling positions within the chamber.

**Table 1.1** Participants and sampling details

Institute	Sampler	Pump	Flow rate (l/min)
Health & Safety Laboratory, UK	Casella Cyclone	SKC	2.2
Bundesanstalt für Arbeitsschutz und Arbeitmedizin (BAuA), Germany	Casella Cyclone	Gilian PP5	2.0
Berufsgenossenschaftliches Institut für Arbeitssicherheit (BIA), Germany	FSP-10	2 x SG-10 4x Aircon2	10.0 10.0
Institute for Occupational Health Sciences (IST), Switzerland	Casella Cyclone	'Home Made'	2.2
Institut für Gefahrstoff Forschung (IGF), Germany	Casella Cyclone	GSA 2000	2.0
Institute for Applied Environmental Research. Stockholm University, (AIER), Sweden	GK 4.2 (still a prototype and no name yet)	BGI 400S	10.0
Laboratory for Industrial Toxicology (LIT), Belgium	Casella Cyclone	Gilian GilAir 5	2.2
Institut für Gefahrstoff Forschung (IGF), Germany	Casella Cyclone	GSA 2000	2.0
SUVA, Switzerland	Casella Cyclone	SKC 224	2.0

## 1.3 RESULTS

### 1.3.1 HSL OC and EC Results

HSL's OC and EC data for all nine runs are presented in Tables 1.2a – 1.2c. The mean, standard deviation (SD) and coefficient of variation (CV) for each run are calculated.

Note the large reduction in particulate EC concentration between the modern VW diesel engine running on low sulphur diesel, see Table 1.2b when compared with the old Mercedes Benz engine using the same fuel, see Table 1.2a. For each type of engine the OC values are similar or even slightly higher with the modern engine but the particulate EC concentration, calculated as a mean over the three runs, is ~85% lower with the modern engine. This demonstrates just how much cleaner modern engines are when compared to engines from 15 or 20 years ago. However, there are concerns that the size distribution of particles from modern engines may be much smaller than from older design engines and it could be that the risk to health from exposure to the exhaust emissions from modern engines may be just as high or even higher than for older engines where particles were larger. This is one area that will need investigating in the future.

The particulate EC concentration is reduced a further 33% when the VW engine is run on bio diesel fuel, see Table 1.2c. However, the particulate OC concentration is more than twice that measured when the engine is run on low sulphur diesel fuel. Consequently the particulate OC to EC ratio is very much higher for bio diesel fuel than for low sulphur diesel fuel. In this case, the particulate OC/EC for the VW engine running on bio diesel is 12.6 compared to 3.5 when running on low sulphur fuel.

**Table 1.2a.** HSL OC & EC Results from Runs 1 – 3  
Old Mercedes Benz Diesel Engine - Low Sulphur Diesel Fuel

Run	Mean Flow Rate (l/min)	Sampling Time (mins)	Sample Vol. (m <sup>3</sup> )	OC Conc. (µg/m <sup>3</sup> )	EC Conc. (µg/m <sup>3</sup> )	Run Statistics					
						OC (µg/m <sup>3</sup> )	EC (µg/m <sup>3</sup> )				
1	2.217	150	0.333	250.1	606.5	<b>Mean =</b>	243.6	606.5			
	2.176	150	0.326	251.1	606.9						
	2.206	150	0.331	247.1	596.4				<b>SD =</b>	12.5	8.2
	2.198	150	0.330	246.8	602.0				<b>CV% =</b>	5.1	1.3
	2.176	150	0.326	248.0	621.0						
	2.221	150	0.333	218.4	606.0						
2	2.193	150	0.329	193.8	490.3	<b>Mean =</b>	189.9	499.4			
	2.207	150	0.331	193.8	494.5						
	2.221	150	0.333	189.6	491.5				<b>SD =</b>	4.5	8.7
	2.201	150	0.330	188.3	502.0				<b>CV% =</b>	2.4	1.7
	2.217	150	0.332	191.8	511.0						
2.206	150	0.331	181.8	507.4							
3	2.183	75	0.164	212.4	385.4	<b>Mean =</b>	197.2	371.3			
	2.197	75	0.165	213.4	374.5						
	2.211	75	0.166	202.4	372.1				<b>SD =</b>	15.5	9.7
	2.188	75	0.164	197.2	355.2				<b>CV% =</b>	7.8	2.6
	2.210	75	0.166	180.8	371.1						
	2.196	75	0.165	177.0	369.7						

**Table 1.2b.** HSL OC & EC Results from Runs 4 – 6  
Modern Turbocharged VW Diesel Engine – Low Sulphur Diesel Fuel

Run	Mean Flow Rate (l/min)	Sampling Time (mins)	Sample Vol. (m <sup>3</sup> )	OC Conc. (µg/m <sup>3</sup> )	EC Conc. (µg/m <sup>3</sup> )	Run Statistics		
						OC (µg/m <sup>3</sup> )	EC (µg/m <sup>3</sup> )	
4	2.201	150	0.330	248.9	77.2			
	2.214	150	0.332	237.8	87.6	Mean =	229.9	79.9
	2.233	150	0.335	235.8	74.9	SD =	17.0	6.0
	2.174	150	0.326	227.4	87.4	CV% =	7.4	7.5
	2.228	150	0.334	198.6	74.5			
	2.203	150	0.330	231.1	77.8			
5	2.195	150	0.329	221.0	68.3			
	2.198	150	0.330	242.0	66.4	Mean =	247.1	69.6
	2.223	150	0.333	233.8	68.0	SD =	19.9	4.3
	2.166	150	0.325	262.8	73.5	CV% =	8.1	6.2
	2.228	150	0.334	276.4	76.3			
	2.197	150	0.329	246.9	65.2			
6	2.190	150	0.329	281.8	70.3			
	2.204	150	0.331	299.4	68.0	Mean =	281.8	67.5
	2.219	150	0.333	278.7	64.0	SD =	19.1	3.0
	2.159	150	0.324	285.2	64.5	CV% =	6.8	4.5
	2.228	150	0.334	247.0	66.7			
	2.210	150	0.332	298.5	71.5			

**Table 1.2c.** HSL OC & EC Results from Runs 7 – 9  
Modern Turbocharged VW Diesel Engine – Bio diesel Fuel

Run	Mean Flow Rate (l/min)	Sampling Time (mins)	Sample Vol. (m <sup>3</sup> )	OC Conc. (µg/m <sup>3</sup> )	EC Conc. (µg/m <sup>3</sup> )	Run Statistics		
						OC (µg/m <sup>3</sup> )	EC (µg/m <sup>3</sup> )	
7	2.197	150	0.329	526.2	38.5			
	2.204	150	0.331	552.2	37.2	Mean =	524.2	38.1
	2.226	150	0.334	530.6	41.0	SD =	24.9	2.0
	2.225	150	0.334	543.4	39.2	CV% =	4.8	5.2
	2.205	150	0.331	509.7	37.2			
	2.208	150	0.331	483.0	35.3			
8	2.192	52	0.114	970.2	46.4			
	2.195	52	0.114	998.4	63.9	Mean =	982.2	60.8
	2.230	52	0.116	1022.4	73.2	SD =	30.3	9.3
	2.254	52	0.117	989.4	58.8	CV% =	3.1	15.2
	2.224	52	0.116	932.0	56.1			
	2.223	52	0.116	980.7	66.5			
9	2.186	150	0.328	567.1	37.5			
	2.190	150	0.328	511.4	42.3	Mean =	523.9	45.2
	2.227	150	0.334	487.2	45.2	SD =	32.9	5.7
	2.257	150	0.339	551.6	43.4	CV% =	6.3	12.6
	2.225	150	0.334	535.7	48.8			
	2.208	150	0.331	490.2	54.0			

### 1.3.2 Results from all laboratories

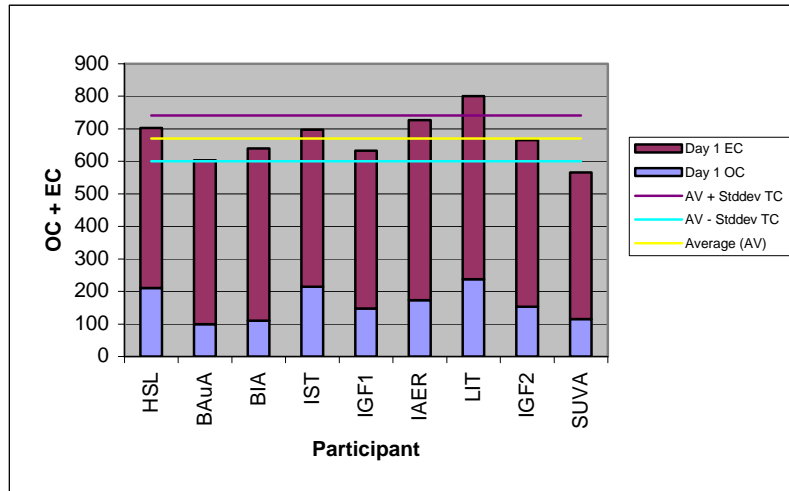
The total carbon (OC and EC) results for each laboratory and averaged over each day are presented in Figures 1.3a – 1.3c and similarly the particulate EC results are presented in Figures 1.4a – 1.4c.

Considering runs 1 – 3, the old Mercedes Benz engine running on low sulphur fuel. The total carbon results (OC + EC) in Table 1.3a show reasonably good agreement between all the laboratories (CV = 10%) with HSL very close to the mean of all the laboratories. When only the EC data is considered, see Figure 1.4a, then the agreement between the laboratories is even better (CV = 7%).

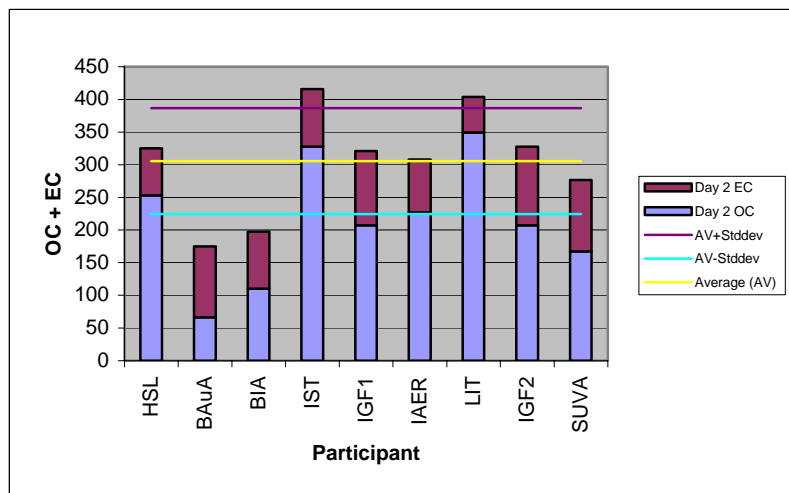
For runs 4 – 6, modern VW engine running on low sulphur fuel, the agreement between the laboratories is not so good with a CV of 26% for the total carbon data. These data in Figure 1.3b show large variability, with some laboratories measuring more than twice that of other laboratories. Five laboratories are fairly close to the mean value for all the laboratories, including HSL, but two laboratories appear to have high results and two others low results. The elemental carbon data in Figure 1.4b shows a similar pattern with only a slightly improved CV of 23%. The HSL result is below the mean for all the laboratories but is within one standard deviation of the mean. From these data there appears to be two groups of results, one group of four laboratories with EC values in the range 110 to 120  $\mu\text{g}/\text{m}^3$  and a group of five laboratories with EC values in the range 55 to 88  $\mu\text{g}/\text{m}^3$ . As will be seen this disparity is even more evident in the next series of runs when bio diesel fuel is used.

For runs 7 – 9, modern VW engine running on bio diesel fuel, the agreement between the laboratories is poor with a CV of 36% for the total carbon data and a CV of 54% for the EC data. The total carbon data in Figure 1.3c show two of the laboratories with very low values when compared to the other seven laboratories. One laboratory with a high total carbon and the other six, including HSL, in the range 720 to 820  $\mu\text{g}/\text{m}^3$ . However, when the EC data are considered in Table 1.4c the disparity hinted at in runs 4 – 6 above becomes very apparent with the laboratories splitting into two distinct groups. Four laboratories with EC values in the range 144 to 174  $\mu\text{g}/\text{m}^3$  and five with EC values in the range 48 to 76  $\mu\text{g}/\text{m}^3$ . Three laboratories, including HSL, measured exactly the same EC concentration of 48  $\mu\text{g}/\text{m}^3$ .

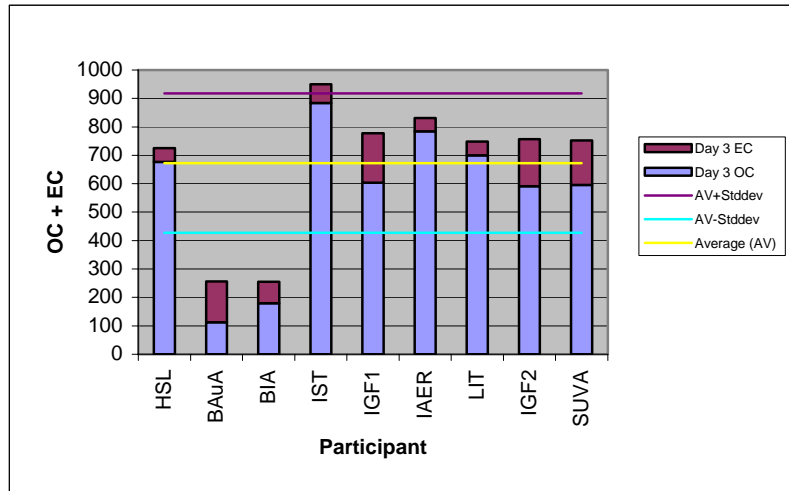
**Figure 1.3a.** Runs 1 to 3 the average OC and EC data for all labs.



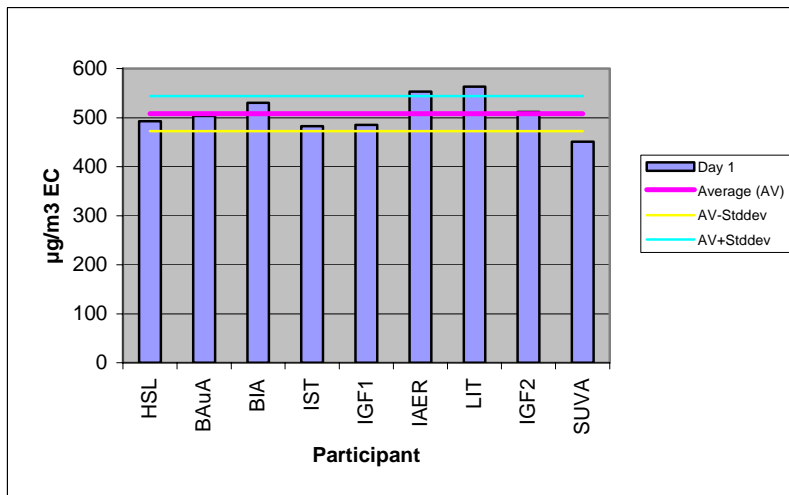
**Figure 1.3b.** Runs 4 to 6 the average OC and EC data for all labs.



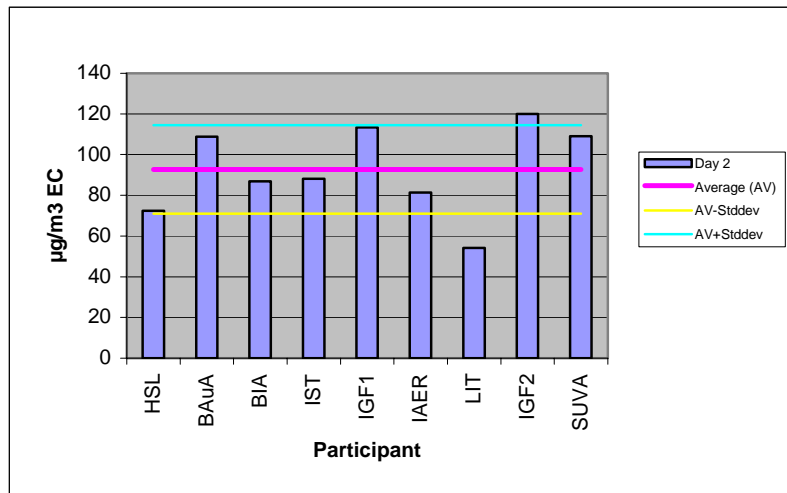
**Figure 1.3c.** Runs 7 to 9 the average OC and EC data for all labs



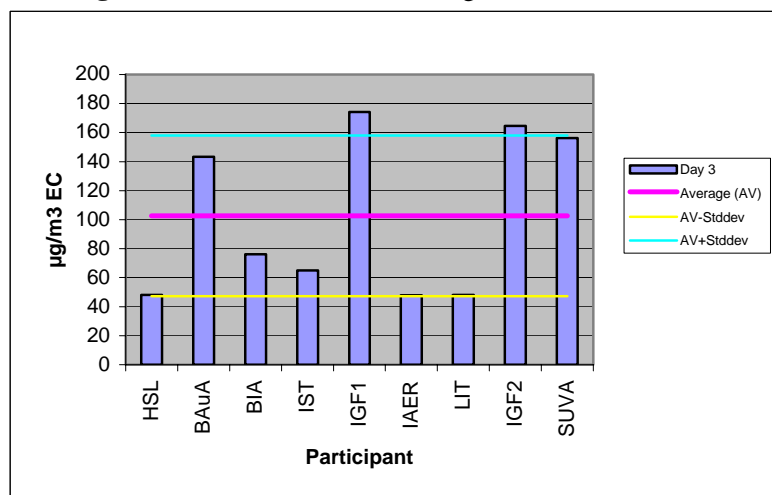
**Figure 1.4a.** Runs 1 to 3 the average EC data for all labs.



**Figure 1.4b.** Runs 4 to 6 the average EC data for all labs.



**Figure 1.4c.** Runs 7 to 9 the average EC data for all labs.



### 1.3.3 Meeting in Brussels 17<sup>th</sup> November 2004

A meeting with representatives from all the laboratories took place at the CEN headquarters in Brussels on the 17<sup>th</sup> November 2004. The meeting focussed on the serious disparity in the results between laboratories when the modern engine was used and especially when running on bio diesel fuel. In previous inter-laboratory studies the samples analysed had been derived from older design engines and there had always been good agreement between the laboratories and on the strength of this the European standard was developed and published. These data here cause concern because obviously modern engines are more relevant for the future and older design engines will be phased out with bio diesel being used more and more as a blend with standard low sulphur diesel to reduce emissions. The evidence here suggests that there are serious limitations with the method when using modern engines and bio diesel fuel and the reasons for this need to be addressed.

After much discussion and statistical analysis of the data it was still not obvious what was causing the two disparate groups of EC results. There were no obvious differences between laboratories in one group, or the other, but first thoughts were that it could be the quartz or glass fibre filters, which were from several different suppliers. It may be that some filters were better at collecting the finer particulate than others and IGF agreed to carry out some further sampling in the diesel chamber using a range of different makes of filters to check this theory. However, if HSL's results from runs 7 – 9 are considered then the EC data is low compared with some of the laboratories, suggesting that the quartz filters used don't trap all the particulate. But the total carbon result is very much in line with most of the other laboratories and so the filter theory may not be the answer. The results from further inter-comparison studies will provide more data to ascertain the causes and determine effective solutions.

#### **1.3.4 Bio diesel Replicates**

EN 14530:2004 (E) stipulates that the OC determination temperature has to be in the range 500 to 850 °C. This was the range of temperatures used by the various laboratories to determine OC, and inter-laboratory studies had demonstrated that over this range of temperature the effect on the OC result was small. However, it is preferable to determine OC at a temperature above 650 °C.

These trials had all been carried out with particulate from standard diesel fuel and there had been no specific studies with bio diesel.

In an earlier project HSL had collected on the diesel test bed a number of replicate bio diesel particulate filter samples and these had been stored in a desiccators for use in the future as reference samples or for development work.

Using a number of replicate bio diesel samples an experiment was carried out to see if the OC determination temperature was more critical with bio diesel samples. The results showed that there was 41 % more EC recorded when the OC was determined at 500 °C as oppose to 800 °C.

This finding would explain the disparity between the laboratory EC results in Table 1.4c. All four laboratories with high EC results determine OC at 500 °C and all the other laboratories use 650 or 800 °C.

However, this does not explain the very low results for two of the laboratories in Table 1.3c. But what is clear is that the EC results for these two laboratories are in line with the other laboratories. The difference is the OC component of the total carbon result. Both of these laboratories have lost OC. It may be that they placed the filters into a hot environment before they did the analysis causing this difference.

### **1.4 CONCLUSIONS**

An inter-laboratory diesel particulate sampling and analysis exercise was carried out at IGF in Dortmund, Germany. Nine laboratories simultaneously collected, using their own equipment, diesel particulate samples from within a large exposure chamber. Within the scope of BS EN 14530:2004 '*Workplace atmospheres – Determination of diesel particulate matter – General requirements*', each laboratory used their own method to determine the particulate organic and

elemental carbon mass collected on their samples. All the data was then pooled and analysed statistically.

The results show there was very good agreement between all the laboratories when measuring diesel particulate generated by an old design Mercedes Benz engine running on standard low sulphur diesel. However, when a modern turbocharged VW engine was used the agreement was not so good and the laboratories appeared to be dividing into two distinct groups. There was even less agreement between laboratories when the VW engine was run on Rapeseed Methyl Ester (RME) a bio diesel fuel and the two distinct groups became more apparent with one group of four laboratories recording EC levels more than twice those of the other group of five laboratories.

A short study carried out at HSL suggests the problem lies in the OC determination temperature. A number of replicate bio diesel particulate samples were analysed for OC and EC. In one batch the OC was determined at 500 °C (the lowest OC determination temperature as stipulated in EN 14530) and the second batch the OC was determined at 850 °C, the highest stipulated temperature. The result was that there was 41% more EC recorded when the OC was determined at 500 °C as opposed to 850 °C.

All the laboratories in the high EC group use 500 °C to determine OC and it is almost certain that this is the reason for the disparity between the two groups of laboratories.

The problem is exacerbated by the fact that bio diesel produces far more OC than does standard diesel. Typically, particulate from standard diesel has an OC/EC ratio of approximately 1. However, with bio diesel the OC/EC ratio is much higher and can be 4 or 5. Any OC left behind after the first stage in the analysis, will be recorded as EC. With bio diesel particulate the amount of OC left can be a significant percentage of the total EC. These findings will be presented at the next meeting in Brussels on the 30th June 2005. HSL will continue to determine the OC at 850 °C which clearly avoids the any problems posed when analysing bio diesel.

## **2 COULOMAT CARBON ANALYSIS OF TONER POWDER**

### **2.1 INTRODUCTION**

Black toner powder used in printers, fax machines and photocopiers is an extremely fine powder ink made up from a mixture of carbon black, which is pure elemental carbon (EC) and a polymer. In use the toner is charged and the image is translated into bit mapped charges of the opposite polarity on a special drum in the printer. The toner is then transferred to the paper and "set", usually by heat acting on the polymer.

There are many different types of toner dependent on their use. For example high speed photocopiers, which require the print to set very rapidly, will use a different carbon black/polymer mix to a much slower office printer or fax machine.

Many thousands of toner cartridges are disposed of or recycled each week and there are companies who provide this service. Consequently, workers are exposed to airborne carbon black, which has an approved workplace exposure limit (WEL) of 3.5 mg/m<sup>3</sup>.

### **2.2 BACKGROUND**

An enquiry was received from an independent laboratory as to whether the elemental carbon method used for measuring occupational exposure of workers to diesel engine exhaust emissions, could also be used for measuring exposure to airborne toner powder.

The laboratory in question had carried out some work for a company that recycles and disposes of toner cartridges and they had used a gravimetric technique to measure the exposure of workers to airborne toner levels and had obtained time weighted exposure (TWA) concentrations of around 4.3 mg/m<sup>3</sup>.

The laboratory made the assumption that this was all carbon black and informed the company that the exposure levels were above the WEL for carbon black. The company pointed out that the carbon black content of the toner amounted to less than 10% of the total mass and that most of the particulate mass collected would be polymer. But what exactly are the proportions?

Increasingly, more and more toner cartridges are being used and as a consequence during disposal or recycling more people are being exposed to airborne toner powder. It is important therefore that a suitable method for determining exposure to carbon black in toner is made available. This short piece of work examines if the Coulometric method of determining organic and elemental carbon in diesel soot can be applied here to measure exposure to airborne toner powder.

### **2.3 EXPERIMENTAL**

Two types of both new and used toner powder were obtained:

Toshiba T-3500E and Toshiba T-1710E

(Note: used toner is toner that has been through a machine but was not used to form the print).

Small amounts of both new and used toner were deposited onto pre-weighed quartz filters and the mass of toner determined. Each sample was analysed for organic carbon (OC) and elemental carbon (EC) using the diesel particulate method as outlined previously (Dabill et al, 1996).

## 2.4 RESULTS

### 2.4.1 Organic and Elemental Carbon

The results are presented in Table 2.1. and show that each case the carbon black (elemental carbon) in the toner sample, was less than 8% of the sample mass. The remainder of the mass being attributed to the organic carbon polymer. With the T-3500E toner there was a non-combustible yellow brown residual left on the filter after analysis but there was no residual associated with the T-1710E toner. There was no evidence that the polymer interfered with the EC determination and more especially there was no evidence that the polymer charred to give high EC results.

**Table 2.1.** Organic and Elemental Carbon Results

Toner Type	Mass (mg)	Organic Carbon (mg)	Elemental Carbon (mg)	%OC	%EC
T-3500E (new)	0.85	0.66	0.063	77.6	7.4
T-3500E (used)	1.22	0.95	0.079	77.8	6.5
T-1710E (new)	1.42	1.163	0.081	82	5.7
T-1710E (used)	1.69	1.398	0.048	82.7	2.8

### 2.4.2 Pyrolysis Gas Chromatography/Mass Spectrometry

Small amounts of each type of toner were placed into a pyrolyser where they were heated to 700 °C under helium. The released volatiles were transferred onto a gas chromatography (GC) column for separation and mass spectrometer (MS) for chemical identification. The results show that in each case the polymer was styrene with very small amounts of butyl acrylate and butylene.

## 2.5 CONCLUSIONS

Toner powder is a homogeneous mixture of extremely fine carbon black and polymer with smaller amounts of other substances dependent on the properties required. Carbon black has a workplace exposure limit of 3.5 mg/m<sup>3</sup>. However, measuring occupational exposure to carbon black in toner using simple gravimetric techniques leads to high results due to the polymer present. Therefore, a method specific to carbon black (elemental carbon) is required. One such method is the coulometric organic carbon (OC) and elemental carbon (EC) method used for measuring exposure to diesel engine exhaust emissions. The method was used to measure the carbon black content of two types of toner.

The results show that the OC and EC method works well and the carbon black content of each toner was determined and found to be less than 8% of the total mass. There was no indication that the polymer interfered with the analytical method or that the polymer charred to form EC during the OC determination. This was a concern but if this had occurred then the carbon black result would have been much higher.

Pyrolysis GC/MS analysis of the toner showed the polymer to be styrene. There was little evidence of any other components. Other toners may use different polymers to styrene dependent on the toner properties.

What is not known from this study are the effects on workers health from breathing in extremely fine particles of styrene and possibly other polymers.

## 3 ROSIN-FREE SOLDERS

### 3.1 INTRODUCTION

Reduced and modified rosin and rosin-free solders are becoming more widely available as alternatives to traditional solders containing rosin based flux which is a known asthmagen when inhaled. These products have been produced to reduce the potential for exposure to rosin fumes during soldering, however it is possible that the colophony content of the fume may have been replaced by something for which there may be just as much concern. Consequently, in 1999, a selection of twelve reduced colophony solders was tested to identify the components present in the flux and released on heating (Pengelly, 1999). Whilst this work identified a range of acidic (and other components) in the flux/fume, subsequent tests suggested that some lower molecular aliphatic acids, in particular various dicarboxylic acids, may have been missed. This is because, when methylated, these lower molecular weight acids are not sufficiently separated from the large solvent peak to be identified by gas chromatography-mass spectrometry (GC-MS), which requires a solvent delay to avoid damaging the detector.

An alternative derivatisation procedure was therefore used to look again at the test solders examined in the 1999 investigation. The chosen procedure was to use pentafluorobenzyl bromide to convert any carboxylic acid components present to their corresponding pentafluorobenzyl (PFB) esters (Dethlefs *et al.*, 1996). These are less volatile than the equivalent methyl esters and, in the case of the lower molecular weight acids, should be sufficiently separated from the solvent to be identifiable by GC-MS. However all derivatives need to be synthesised for calibration and MS library matching purposes.

### 3.2 EXPERIMENTAL

The PFB derivatisation process is as follows:-

- Place sample solution in a 1.5 ml GC vial and evaporate to dryness under nitrogen;
- Add 200 µl of a 2% solution of PFB bromide in toluene;
- Add 10 µl of triethylamine;
- Cap vial and heat to 90°C for 1 hour;
- Make up to 1 ml with toluene.

### 3.3 RESULTS

The pentafluorobenzylated samples produced good quality symmetrical peak shapes with, as expected, longer retention times than for the equivalent methyl esters. Analysis of the thirteen solders tested in 1999 produced the following revised results:-

#### **Solder 1 (Control)**

Results unchanged from those obtained using standard methylation procedure.

#### **Solder 2**

Main component is azelaic (nonanedioic) acid, with lesser amounts of C<sub>8</sub> – C<sub>30</sub> aliphatic carboxylic acids, C<sub>4</sub> – C<sub>18</sub> aliphatic dicarboxylic acids, C<sub>1</sub> – C<sub>13</sub> aliphatic aldehydes and styrene.

Of these, many of the lower molecular weight acids, including the azelaic acid, had not been previously observed using the standard methylation procedure.

### **Solder 3**

Main component is azelaic acid, with lesser amounts of C<sub>8</sub> – C<sub>30</sub> aliphatic carboxylic acids, C<sub>4</sub> – C<sub>18</sub> aliphatic dicarboxylic acids, formaldehyde, acetaldehyde and styrene. Of these, many of the lower molecular weight acids, including the azelaic acid, had not been previously observed using the standard methylation procedure.

### **Solder 4**

Main components are palmitic (hexadecanoic) acid, glutaric (pentanedioic) acid, adipic (hexanedioic) acid and cyclopentanone, with lesser amounts of C<sub>12</sub> – C<sub>18</sub> aliphatic carboxylic acids, succinic (butanedioic) acid, cyclohexanone, formaldehyde, acetaldehyde and acetone. Of these, many of the lower molecular weight acids, including the glutaric and adipic acids, had not been previously observed using the standard methylation procedure.

### **Solder 5**

Results unchanged from those obtained using standard methylation procedure.

### **Solder 6**

Main components are adipic acid, suberic (octanedioic) acid, sebacic (decanedioic) acid, acetophenone and tolualdehyde, with lesser amounts of indene and methylstyrenes. Of these, the adipic, suberic and sebacic acids had been previously unobserved using the standard methylation procedure.

### **Solder 7**

Main components are glutaric acid, benzoic acid, aromatic carboxylic acids, benzaldehyde and acetophenone, with lesser amounts of styrenes and tetrahydrofuryl alcohol. Of these, the glutaric acid had been previously unobserved using the standard methylation procedure.

### **Solder 8**

Main components are glutaric acid/anhydride, with lesser amounts of toluene, 2(5H)-furanone, succinic acid and adipic acid. Of these, the succinic and adipic acids had been previously unobserved using the standard methylation procedure.

### **Solder 9**

Results unchanged from those obtained using standard methylation procedure.

### **Solder 10**

Results unchanged from those obtained using standard methylation procedure.

### **Solder 11**

Main components are adipic acid, suberic acid, sebacic acid, acetophenone, tolualdehyde and benzaldehyde, with lesser amounts of indene and methylstyrenes. Of these, the suberic and adipic acids had been previously unobserved using the standard methylation procedure.

### **Solder 12**

Results unchanged from those obtained using standard methylation procedure.

### **Solder 13**

Results unchanged from those obtained using standard methylation procedure.

## **3.4 CONCLUSIONS**

These tests identified a number of additional aliphatic acidic components, particularly in the rosin-free products. In many cases, these additional components were the main components present. These components are also important as some, such as glutaric acid are listed as "irritants", and others, such as adipic acid, are suspected as possible causes of asthma.

The PFB derivatisation procedure is not as simple or convenient as the methylation procedure, so it is recommended that further work is carried out to look for other alternatives. Also, in view of the hazardous nature of some of the additional acidic components identified, it is recommended that consideration be given to devising a procedure for personal monitoring of fume from rosin-free solders.

## **4 WELD-THRO' PRIMERS**

### **4.1 INTRODUCTION**

HSL is participating in an investigation into a selection of weld-thro' products with The Welding Institute (TWI), Cambridge, the Finnish Institute of Occupational Health (FIOH), Turku, Finland, FORCE Technology, Denmark and Arcelor, France/Belgium.

The objective of the work is to provide information on test methods, analytical methods and sampling procedures for determination of thermal degradation products generated during welding involving weld-thro' products and coatings. The information is, amongst other things, intended to aid completion of European Standard prCEN/ISO/TS 15011-5.

HSL testing work is being supported by HSE under Project No. JS2003898, however some initial work to optimise the test procedure for weld-thro' primers was carried out as part of this call-off contract. This work is described in detail in a separate report (Pengelly, 2005), however the findings and recommendations are shown below.

### **4.2 FINDINGS**

Samples were examined using either a GC-mounted pyrolyser (HSL method) or by heating in a glass oven tube with various indirect sampling methods (FIOH method).

A standard method of sample preparation has been developed at HSL. This allows easy preparation of samples of a consistent, standard size which, in turn, leads to good reproducibility. The sample is applied to aluminium foil in a film which, when dry, is around 50 µm thick. The dry foil-backed sample is then placed on to a quartz filter and a 1.4 mm circle punched out. The quartz filter material is used to prevent contact (and possible reaction) between the aluminium foil and the platinum pyrolyser filament.

The HSL samples were pyrolysed for 2 seconds under helium at 450°C, 650°C and 850°C; the FIOH samples were heated to 450°C in air for several minutes. In addition, the FIOH samples were much larger than those used by HSL. Despite these differences, the two techniques were found to give broadly similar results, particularly in terms of the range of components observed. The FIOH results showed significant levels of the various pyrolysis products at the test temperature of 450°C. By comparison, the amounts of material generated by the HSL method at 450°C were relatively small, possibly due to a combination of the much smaller sample and the much shorter heating period. However, by increasing the pyrolyser temperature to 650°C, the total amount of material produced by the HSL technique increased by 6 – 10 times. A further increase in pyrolyser temperature to 850°C did not significantly increase the total amount of material produced, but did result in the appearance of many more minor/trace components (including naphthalene and other aromatics).

### **4.3 CONCLUSIONS**

The optimised pyrolysis method should be used in the next stage of the main project (JS2003898). This will involve testing of five weld-thro' products by members of the project team, both in the laboratory (using pyrolysis and oven heating technique) and in actual welding

tests. Data from the various tests can then be compared with a view to providing input and recommendations on a standard method of analysis.

## 5 GLOVE PERMEATION TESTING RIG

### 5.1 INTRODUCTION

The initial aim of this work was to set up an operating system for testing gloves to BS EN 374-3, the European standard that determines the resistance of protective gloves to permeation by chemicals, initially to support a HSE project to test gloves against a number of chemical washes used in the printing industry. The HSL system would be available for future use in HSE studies and would provide a truly independent assessment of PPE performance for chemical resistance.

To summarise BS EN 374-3, a specimen taken from the palm of a glove is placed in a commercially available test cell (Figure 5.1.). A test substance (permeant) is placed in contact with the outer surface of the glove specimen, and the inside surface is then monitored for its emergence following permeation. The test needs to be performed three times at  $23\pm 1^{\circ}\text{C}$ . The test is completed when either a permeation rate of  $1\ \mu\text{g}/\text{cm}^2/\text{min}$  is reached (the breakthrough time, measured to the nearest minute) or 480 minutes have passed. A similar ASTM standard exists (method F739-99a) which measures the 'normalized' breakthrough time at  $0.1\ \mu\text{g}/\text{cm}^2/\text{min}$  and also measures any steady state permeation rate reached.

The permeation testing rig should also have the capabilities to be further developed so that it can test a wide variety of fabrics and chemicals (liquid and vapour) at different temperatures (e.g. body temperature). The need to be able to cover a wide variety of chemicals means that the system should be able to swap and change to different detectors suitable for the analytes in question. Volatile organic compounds (VOCs) can be detected using a Flame Ionisation Detector (FID). Acids and bases can be detected using a pH meter. Other substances may need more specific detectors (e.g. Infrared or Ultraviolet Spectroscopy, or gas chromatography (GC)).



Figure 5.1. Glove Permeation Test Cell

## **5.2 EXPERIMENTAL**

### **5.2.1 Equipment**

Signal 3000HM HFID heated total hydrocarbon analyser (H<sub>2</sub> fuel option) with heated sample transfer line (set to 200°C). Full range 0-10,000 ppm. Although the instrument reads to 0.001 ppm, its working limit of detection when used on the system is approximately 0.6 ppm. The time constants used were set to 0.5 s on all ranges.

Hanna Instruments HI 8915 handheld pH meter with recorder output and temperature probe.

VICI Valco Instruments valve EMT-3-SC-4-MWE: Low pressure four position valve with a common outlet flow path configuration for non-selected positions. It is suitable for operation at up to 200 psi and 200°C. It is controlled by a microelectronic actuator operating a 24 V stepper motor. The valve is positioned inside a heated valve enclosure (200°C) with the actuator positioned outside, because the actuator is suitable only up to 30-40°C.

RS 12 V brushed DC motor with 5:1 ovoid gearbox to be used to turn the (optional) test cell stirrer rod.

Grant SUB 36 water bath (63 cm x 30 cm, and 20 cm deep), range 15 to 99°C.

BioRad circulating heater / chiller, range -20 to 60°C.

PC control utilising LabVIEW software and National Instruments M series DAQ card (PCI-6221) connected to a shielded connector body. The card has 8 differentials, 2 analogue outputs, 24 digital I/O with 16 bit resolution, capable of communicating at 250 k samples/s.

Remote start switch

Home made unit containing three switches connected to the DAQ card I/O channels.

Ancillary Equipment

Existing laboratory test atmosphere equipment and ATD-GC-FID instrumentation, and newly acquired puncture testing rig.

### **5.2.2 Development**

#### **5.2.2.1 Detectors**

It was initially decided to produce a system that could use either a FID or a pH meter to detect the permeant. This was considered a reasonable first step that would cover the majority of substances under consideration. Detection of other compounds not covered would need to be considered as and when the need arose.

To reduce time and effort during testing it was decided to construct a system whereby multiple tests (three) could be performed simultaneously. In the case of monitoring using pH meters, a dedicated meter was purchased for each test cell, but because of the cost implications, a single FID was used to monitor all three of the test cells when measuring VOCs. To enable this, a valve was purchased that allowed air to be sampled from each test cell in turn at 20 s intervals, and directed to the FID. In order to avoid condensation of analyte between the cell and the FID, the valve and the transfer line to the FID were both heated to 200°C. The tubing from the cell to the valve was made from PTFE, all other tubing was made from stainless steel.

### **5.2.2.2 Temperature Control**

To temperature control the test cells it was originally conceived for them to be placed in a heating incubator, however it was not possible to identify a commercially available product which was spark proof. It maybe an option in the future to buy a custom made spark proof model. Construction by HSL of a dynamic temperature controlled cabinet was considered, controlled by an air conditioning unit, however a suitable unit capable of controlling temperatures to  $\pm 1$  °C couldn't be identified.

The test cells are designed to be capable of being immersed in a temperature controlled water bath. This approach is adequate for hydrophobic rubber type products, however a problem occurs when specimens to be tested contain a porous layer (e.g. cotton) that could act as a wick and draw water into the cell. Attempts were made to waterproof the cell by taping around the flanges of the cell, and placing rubber washers around the bolts and petroleum jelly on the nuts, but with inconsistent results. Placing the test cell in a plastic bag before immersing it in the water bath was considered, however problems were encountered with leaks, either at the seams or through minute punctures. This approach remains open to further investigation.

The final approach was to place the test cells on stainless steel platforms within the water bath, and placing an insulated PVC / polystyrene lid on top. The water in the bath heats the bath contents and the lid prevents the air being disturbed. This solution is not perfect, and at high temperatures (e.g. 35°C) there is a temporary period of cooling when the lid is removed (see below).

To complement the water bath, which controls temperature by heating alone, a circulating heater/chiller was piped into the water bath through the insulating lid so that low temperatures could be achieved.

To maintain the temperature inside the cell during operation, the test substance was maintained at the same temperature as the cell prior to charging of the cell by storing it in a stoppered conical flask placed in the bottom of the water bath. When the system was configured for use with the FID, the air flowing through the test cell to the FID was preheated (or cooled) by directing it through a 3 m coil of ¼ inch diameter copper tubing positioned at the bottom of the water bath. Two views of the completed test system are shown in figures 5.2 and 5.3.

### **5.2.3 Instrument Control**

A PC was programmed (in-house) using Labview 7.1 to control the permeation testing system. The PC is interfaced to the peripherals via its serial port and via a data acquisition (DAQ) card. It controls the switching of the valve via an RS232 cable and collects data from either the pH meters or the FID via their respective analogue outputs. Additionally the air temperature inside the water bath was monitored via the temperature probe of an additional pH meter. Three switches located next to the water bath were connected to the I/O channels to enable the program to be notified when each test cell had been charged with the test substance.



Figure 5.2. Glove testing rig, showing modified water bath and valve.



Figure 5.3. Glove testing rig, showing FID to the right.

## 5.3 VALIDATION

### 5.3.1 Method

The performance of the system hardware and software was first evaluated by performing a test on a specimen of the ASTM 0.43 mm neoprene standard reference material for permeation testing, using acetone. This test followed the ASTM 739-99a test method conditions and measured breakthrough time and permeation rate at 23°C. A second validation test was performed by reproducing one of the tests from the recent Printing Industry Chemical Study report, where a

contract laboratory challenged a commercially available glove (Marigold Tripletec+ G44R) with a chemical wash (BASF Ultraking).

The temperature control characteristics of the permeation testing rig were then investigated at 10 and 35°C, by measuring the air temperature within the test cell during a simulated test. The test cell was configured for water to be placed in the liquid challenge hemisphere, and air to be passed through the other side to the FID. The temperature was measured before and after the start of the test, when the insulating lid was removed and the test cell was charged up. The temperature was then monitored until it returned to its initial temperature.

## 5.4 RESULTS

An example of the FID output during the testing of the ASTM neoprene sample with acetone is presented in Figure 5.4. The normalised breakthrough detection times were 5.9, 6.8 and 8.5 minutes (at 0.1  $\mu\text{g}/\text{cm}^2/\text{min}$ ); the permeation rates peaked at  $\sim 270$   $\mu\text{g}/\text{cm}^2/\text{min}$  before settling at 193, 197 and 205  $\mu\text{g}/\text{cm}^2/\text{min}$ .

A permeation graph for the print cleaning chemicals test is presented in Figure 5.5. The normalised breakthrough detection times were 55, 55 and 64 minutes (at 1.0  $\mu\text{g}/\text{cm}^2/\text{min}$ ).

The changes in temperature that occurred during the positioning of the cells in the water bath and during the addition of a test substance (water) are presented in Figures 5.6 and 5.7.

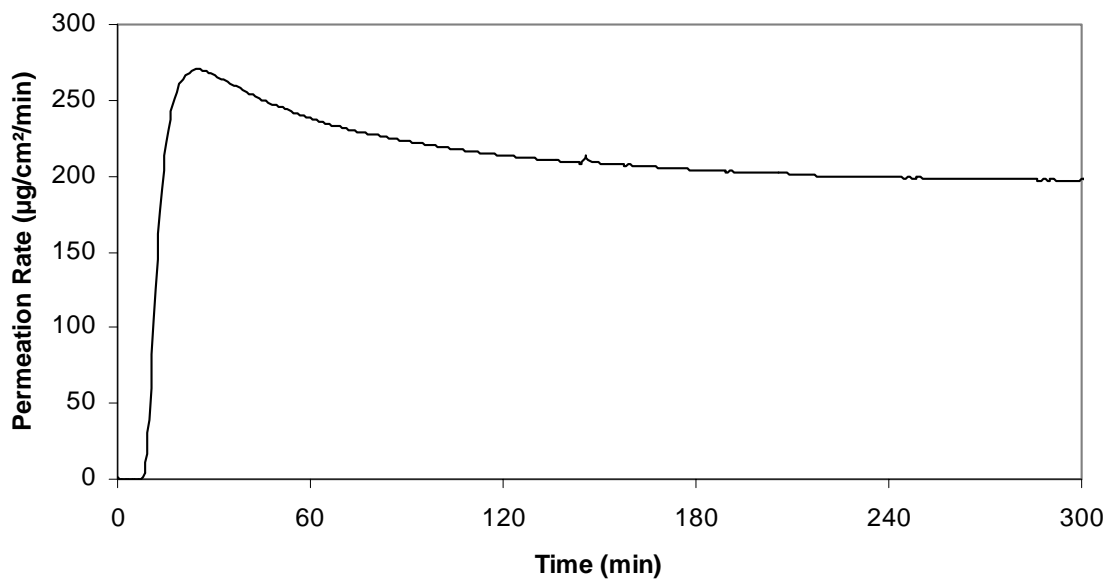


Figure 5.4. Permeation of Acetone through ASTM neoprene standard reference material

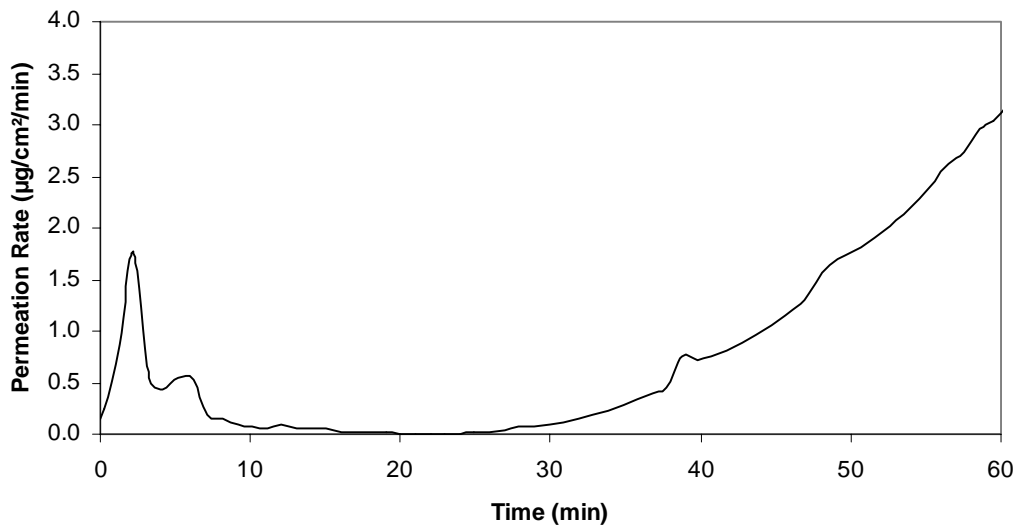


Figure 5.5. Permeation of BASF Ultraking through Marigold Tripletec+ G44R

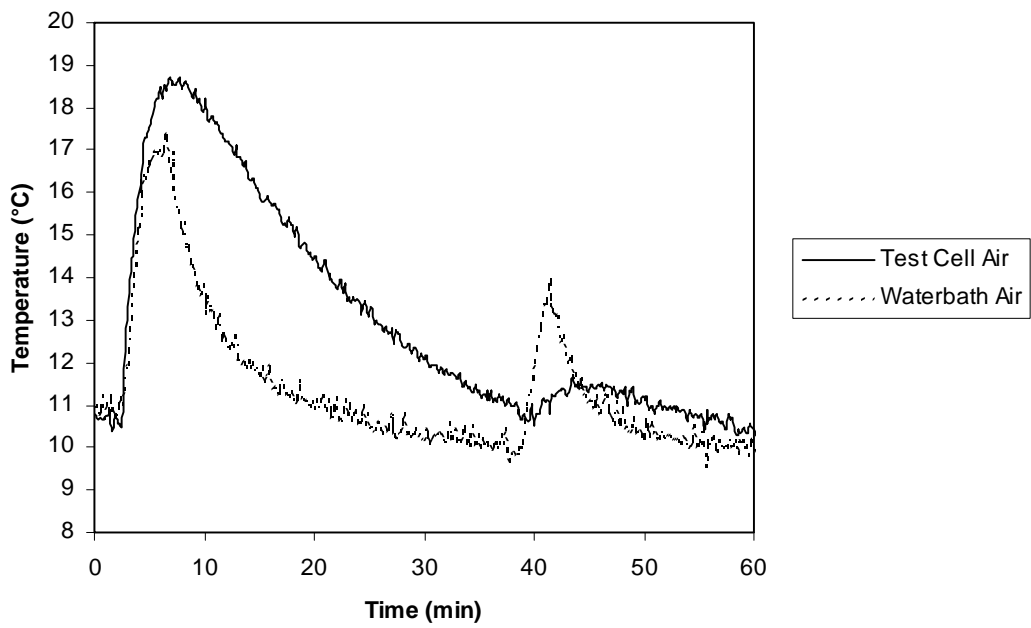


Figure 5.6. Temperature Changes During Testing at 10°C

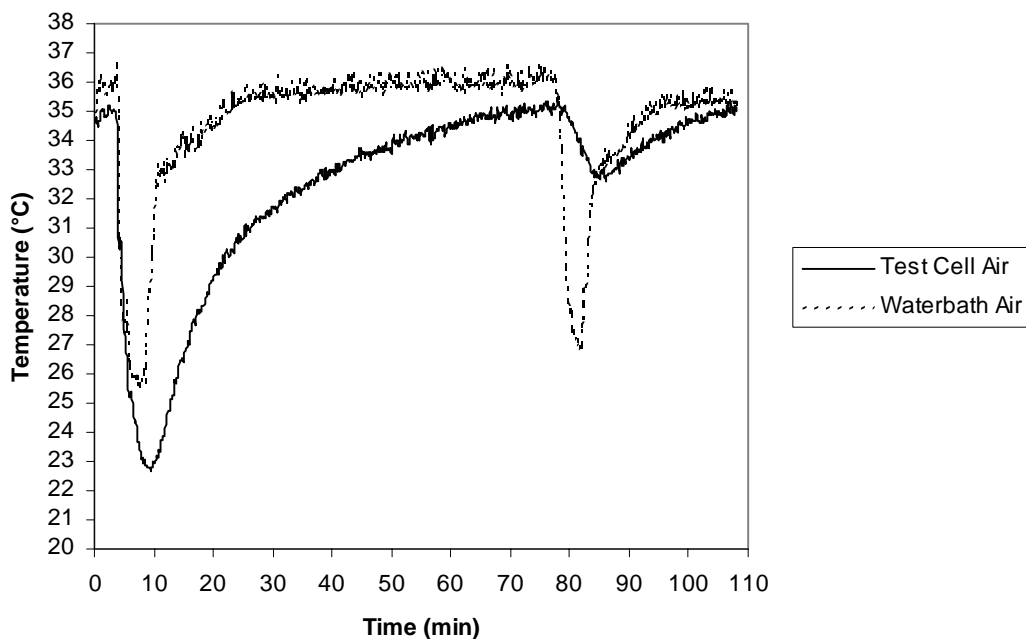


Figure 5.7. Temperature Changes During Testing at 35°C

## 5.5 DISCUSSION

The validation test using the ASTM neoprene standard reference material was done using ASTM method F739-99a 'Standard Test Method for Resistance of Protective Clothing Materials to Permeation by Liquids or Gases Under Conditions of Continuous Contact'. The main differences with BS EN 374-3 are the reduced flow rate through the cells (50-150 ml/min versus 450-550 ml/min) and the normalised breakthrough detection time (0.1  $\mu\text{g}/\text{cm}^2/\text{min}$  versus 1  $\mu\text{g}/\text{cm}^2/\text{min}$ ).

The normalized detection times of 5.9, 6.8 and 8.5 minutes recorded compare well to the 7.2 minute mean and 4.8 to 9.6 minutes ASTM acceptance limits derived from an inter-laboratory evaluation. Comparison of the permeation curve appearance with literature permeation curves (Bromwich 1998) shows that although a peak followed by a decline in the permeation rate may have been expected, it does appear more pronounced in the curve produced at HSL. Correspondence with the supplier however confirms that the results are satisfactory, and the 193, 197 and 205  $\mu\text{g}/\text{cm}^2/\text{min}$  steady state permeation rates compare well to the mean of 245  $\mu\text{g}/\text{cm}^2/\text{min}$  and range of 152 to 397  $\mu\text{g}/\text{cm}^2/\text{min}$  from the standard.

The printing industry chemical wash test results of 55, 55 and 64 minutes also compare well to the reported values of 62, 63 and 71, having similar and overlapping ranges of values. The permeation curve shows a couple of interference peaks originating from vapour present around the equipment during charging of the cells. At this time the entry for the make up air for the FID was in close proximity to the cells.

### **5.5.1 Temperature**

The European standard, 'Protective gloves against chemicals and micro-organisms' (BS EN 374-3:2003) specifies standard test conditions to be 23 +/- 1°C. Because breakthrough time is affected by temperature, it says that additional tests may be run at other temperatures (+/-1°C). The test chemical should also be at the same temperature as the test cell, prior to introduction.

It can be seen from Figures 5.6 and 5.7 that there are changes in temperature during the set up for the tests. The first deviation occurs when the test cells are placed in the water bath and plumbed into the tubing connecting them to the valve. At 10°C, it took around 40 minutes for the test cell air (and so presumably the glove specimen) to cool to the test temperature following installation, whereas at 35°C it took just over an hour. The test cells placed into the test rig were all at room temperature. Pre-warming or cooling the cells may have achieved faster equilibration.

The second smaller temperature deviation occurred on charging the cells with the test chemical. At 10°C the temperature rose 1°C and returned after 15 minutes, at 35°C it fell 2°C and returned after 25 minutes.

Although the temperature control was acceptable during these tests, generally the control offered by the current system is not as robust as would be desired. Changes in room temperature can result in changes in the water bath air temperature. One cause is its current position in a fume cupboard that makes entrance holes vulnerable to draughts. The laboratory temperature must be stable if fine-tuning of instrument temperature settings is to be avoided before tests. The time taken for equilibration of newly installed test cells at extreme temperatures could also have significant impact on the total test duration, unless installation is on the evening before the day of a test (tests may last for eight hours). The temperature control could be improved if the test cell could be immersed in the water of the water bath, however as mentioned earlier, problems arise when porous materials are present in the glove specimens. It is recommended that further work be done on temperature control of the cells.

## **5.6 CONCLUSIONS**

A computer controlled glove permeation testing rig has been constructed and validated with a standard reference material. The system has been shown to be capable of making measurements in the range 10 to 35°C. However the system at present would benefit from further development work, including temperature control and additional detectors.

## 6 ISOCYANATE SAMPLING AND ANALYSIS

### 6.1 INTRODUCTION

Isocyanates (NCO) are highly reactive species used in the motor vehicle repair, aircraft, printing, component manufacture, adhesive, polyurethane and coating industries. They are known respiratory tract and skin sensitizers and are the most common cause of occupational asthma in the UK (HSE, 2004). The Health and Safety Executive (HSE) has set workplace exposure limits (WELs), for total isocyanate exposure (i.e. all NCO species), of  $70 \mu\text{g}/\text{m}^3$  (short term, 15 minute) and  $20 \mu\text{g}/\text{m}^3$  (8 hour TWA) (HSE, 2005).

Described here is work carried out by HSL looking at a variety of NCO related uses, their potential to cause NCO exposure and developments to improve sampling and analytical methods for workplace isocyanates. The work described falls into the following sections;

- Determination of airborne NCO from hot melt glues
- Development of MDHS 25/3
- Development of a surface sampling method for NCO
- Development of improved sampling methods for airborne NCO aerosols

These sections and the reasons for the work carried out in this report will now be discussed in more detail.

#### **Determination of Airborne NCO from Hot-Melt Glues**

As part of HSE enforcement and routine monitoring activities HSL was asked to examine the potential for airborne isocyanate (NCO) emission from a number of NCO based glues from a variety of industrial uses (motor vehicle repair (MVR), aircraft and printing). Glues under study were based on the most common di-isocyanates e.g. toluene 2,6-diNCO and toluene 2,4-di-isocyanate (TDI), 1,6-(diisocyanato)hexane (HDI) and 4-4'-methylenebis(phenyl isocyanate) (MDI). Of particular interest in this work were the NCO species produced on heating i.e. were monomeric or polymeric NCO produced and the temperatures at which appreciable amounts of NCO are produced.

#### **Development of MDHS 25/3 – Analysis of Workplace NCO**

MDHS 25/3 (Methods for the Determination of Hazardous Substances #25/3, Organic NCO in Air) is the sampling and analysis method for airborne organic NCO developed over ~ 20 years by the HSL. HSL has extensively and continuously researched and modified this method in response to the following HSE requirements.

- the analysis of more complex NCO formulations (e.g. determination of oligo-NCO and low molecular weight NCO)
- the need for better analytical sensitivity (e.g. because of lower sampling volumes or to answer workplace control related questions)
- the need for more robust analytical techniques (e.g. because of HSE forensic needs, response to scientific criticism and cost considerations).

The work presented here describes some of the recent work carried out by HSL in this area.

NCO for which a reference standard exists or can be prepared may be quantified using a UV/vis detector. However, for the majority of industrially used oligo-NCO no standards exist. This can pose a problem for quantification by MS based methods if no bulk material or purified oligo-NCO derivative is available. MDHS 25/3 quantifies these compounds using the electro-chemical (EC) detector, which oxidises the –OMethyl group on the MP derivatisation reagent to give the EC signal. This group is common to all MP derivatized NCO and has been found to give the same response irrespective of which NCO it is bonded to (Warwick et al, 1981; Bagon et al, 1984; Schmidtke and Seifert, 1990; HSL, 1997b). The oligo-species may therefore be calibrated using the corresponding NCO monomer i.e. HDI monomer for oligo-HDI, MDI monomer for oligo-MDI etc. Standards of the various oligo-NCO are therefore not required. The liquid chromatographic peak (LC) for the MP derivatized NCO monomer also acts as a useful retention time marker for MP derivatized bulks and samples. Some of the work presented here investigates the validity of this EC calibration approach.

During analysis of WASP QA (Workplace Analysis Scheme for Proficiency, NCO quality assurance scheme) filters and analysis of research and enforcement samples by HSL it has been noticed that generally the EC detector is more variable than the UV/vis detector. A common method of reducing this variation is the use of an internal standard. In order to correctly model the behaviour of the analyte throughout the work-up process, the ideal internal standard is a chemical that is very similar to the analyte. Deuterated internal standards are commonly used in mass spectrometry but for the NCO under study they are either not available i.e. NCO bulk formulations, or difficult to procure and expensive. A cheaper, more readily available alternative, the reagent 1-(2-ethoxyphenyl) piperazine (EP), available from Aldrich as the hydrochloride salt was investigated as an internal standard for 1-(2-methoxyphenyl)piperazine (MP) derivatized MDI (HSL, 2004). For analysis using MDHS 25/3, EP derivatives also have the advantage that the LC retention time of the NCO-EP is increased ~ by 50% compared to that of the NCO-MP so giving good peak resolution. The work presented here gives details of work carried out by HSL evaluating the use of an internal standard for EC quantification of monomeric and oligo- NCO. Some of the work presented here has been included in a peer-reviewed paper (White, 2006).

Previous work at HSL (HSL, 2001) has looked at the stability of NCO WASP filters on storage in the laboratory, at room temperature, in the dark. This work found a recovery of ~ 85% for storage times from 0 (i.e. immediate desorption) to 22 months. This finding does not agree with all the other work carried out by HSL and others and it was suggested that this was an anomalous finding caused by an analytical, instrumental or calibration problem. Work was carried out to confirm or refute this statement and is reported here.

### **Development of a Surface Sampling Method for NCO**

Although the Organic Measurement Section (OMS) of HSL has concentrated primarily on developing methods for the monitoring of airborne exposure to NCO, during NCO project and support work it has been noted that dermal exposure because of drips, splashes etc is common, especially when mixing and pouring NCO bulk materials. Whether or not dermal exposure to NCO can cause respiratory sensitisation in a similar manner to that proven for airborne NCO is a moot point. However, HSL has been asked to sample surfaces for possible NCO contamination. The work presented in this section gives the initial details of HSL work aimed at developing a surface monitoring method for NCO.

## **Development of Improved Sampling Methods for Airborne NCO Aerosols**

Sampling and analysis of airborne NCO is a significant challenge. NCO occur in a variety of chemical forms, such as, monomers, oligomers, larger and more structurally complex polymers and often as mixtures of all these forms. NCO oligomers and polymers are commonly used in industry as they are less volatile than the monomers and so pose less of a vapour hazard. NCO occur in a variety of physical forms, for example, vapours, aerosols and liquids. A sampling method that is suitable for one physical form of NCO is not automatically suitable for another. In the workplace other substances are also present in the air, such as, water vapour, dust, amines and alcohols, depending on the product and industrial process involved and these can interfere with the LC analysis. Standards of the oligo-NCO are not available, but under UK law, these species must be quantified to give a total NCO result. Because of the reactive nature of NCO, analysis in the workplace is commonly carried out by trapping the NCO with a derivitization reagent to produce a stable derivative. Numerous samplers, derivitization methods and detectors have been proposed for NCO.

The sampling device currently recommended in MDHS 25/3 depends upon the physical form of the NCO. NCO vapours can be actively (pump) sampled onto an impregnated filter in a suitable sampling head (Institute of Medicine sampling head (IOM) or similar). The recommendation in MDHS 25/3 is that NCO aerosols are most effectively sampled by a combination of impinger containing MP solution backed up by an MP impregnated filter. This recommendation is based on a study carried out by the International NCO Institute (III) (Hext et al, 2003). This work found that impregnated filters alone were unsuitable for collecting large particle sizes ( $>10\ \mu\text{m}$ ) because of the particles sticking to the filter cassette and local depletion of sampling reagent on the filter. However, it is widely acknowledged that toluene filled impingers are difficult to use for personal monitoring and because of this, several groups are currently researching the limitations and applicability of filter only sampling methods (Sennbro et al, 2004; Ekman et al, 2002; Bello et al, 2002; Rudzinski et al, 2001; England et al, 2000). Work carried at HSL comparing alternative sampling devices for NCO aerosols is reported here. For static sampling, the problems described above for the impinger/filter sampler are less prevalent and so this sampler is still recommended for static samples.

## **6.2 EXPERIMENTAL**

### **6.2.1 Chemicals**

The solvents used (acetonitrile, methanol, isopropanol, cyclohexane, diethyl ether and toluene) were of LC grade or better (from Rathburns, Walkersburn, UK or Fisher Scientific, Loughborough, Leics, UK). The LC buffers were prepared using water purified in-house using an Elgastat UHQ II system (Millipore Ltd., High Wycombe, Bucks, U.K.). Acetic acid, sodium acetate, 1-(2-methoxyphenyl)piperazine (MP), 1-(2-ethoxyphenyl)piperazine (EP), toluene 2,6-diNCO and toluene 2,4-diNCO (TDI), naphthyl NCO (NDI), 1,6-(diisocyanato)hexane (HDI), 4-4'-methylenebis(phenyl NCO) (MDI) and oligo- HDI bulks (Desmodur N 3300) were purchased from Aldrich Chemical Co, Gillingham, Dorset, UK or from the manufacturers (Bayer AG, Leverkusen). Di-NCO and mono-NCO MP and EP derivatives were prepared at the Health and Safety Laboratory (HSL) from the relevant monomers and from samples submitted by HSE Inspectors during routine occupational hygiene monitoring and enforcement actions.

### 6.2.2 Typical LC conditions

Typical LC and EC conditions for the analysis of oligo-NCO containing formulations are given below;

mobile phase

isocratic, 60% acetonitrile, 40% sodium acetate buffer (5 g/l), pH 6, flow rate 1 ml/min.

ESA Coulochem II

guard cell +1500 mV, E1(screen) + 450 mV, E2(analytical) + 800 mV, 1  $\mu$ A scale

UV detection @ 242 nm

10  $\mu$ l injection volume

LC column

suitable C18 analytical column and guard column. .

### 6.2.3 Airborne NCO from Hot Melt Glues

#### Pyrolysis GC/MS of a TDI based glue (Bostik Mybond 3095 Part 2)

As part of an HSE enforcement activity HSL was asked to examine the potential for airborne NCO emission from a TDI based glue used to stick car door trims to the car door. HSE factory inspectors informed HSL that, for the factory under investigation, ~ 4 mixes were made per day and ~ 150 trim strips were glued in the 2 month trial period the glue was in use. HSL carried out pyrolysis gas chromatography (GC/MS) and workplace simulation experiments on the NCO containing "part 2" of the glue.

A series of pyrolysis gas chromatography (GC/MS) experiments were carried out to provide information on the "lift-off" temperature for the glue under study. The glue was diluted 100x with ethyl acetate. An aliquot of this solution (20  $\mu$ l) was spiked onto a glass fibre filter paper and heated in the pyrolysis device at the desired temperature for a few seconds. The vapour emitted on heating was then analysed by GC/MS. The pyrolysis GC/MS work was carried out on a HP 5971 GC/MS system with pyrolysis attachment and cold trap. Calibration was by pyrolysis of a known amount of pure TDI (both isomers) to give a response factor. Samples were 20  $\mu$ l of a 100 fold dilution of the part 2 in ethyl acetate, spiked onto a glass fibre filter and heated to the required temperature. This system is described in full in HSL reports OMS/2003/10 and OMS/2002/02. The results of this work are given in Figure 6.1.

#### Simulated Workplace use of the TDI based glue (Bostik Mybond 3095 Part 2)

A series of operations were simulated in a fume cupboard, namely, mixing and pouring of the glue, painting the glue onto the trim strip parts and heating the glue, to make it "tacky", before sticking the trim strip parts together. During these operations airborne monitoring for NCO (TDI vapour) was carried out as described in MDHS 25/3 (HSE, 1999).

For the mixing and pouring simulations parts 2 and 1 (NCO containing hardener and non NCO activator respectively) of the glue (100 ml) were mixed in a beaker and then stirred with a glass rod for about 1 minute. Airborne monitoring for NCO was carried out during this process. The sampling heads (IOM head containing a 1(2-methoxyphenyl)piperazine (MP) glass fibre (GF/A) filter) were placed on opposite sides of the mixing beaker, at a height of ~ 25 cm and ~ 25 cm apart. The laboratory temperature was 21.5 °C.

For the painting experiments 5 strips of glue were painted, in duplicate, onto the trim strip. The trim strip was 35 cm long. The brush used was ~ 3 cm wide and the painting process took about

2 minutes. Airborne monitoring for NCO, as described in MDHS 25/3, was carried out during this process. The sampling heads (IOM head containing a 1-(2-methoxyphenyl)piperazine (MP) filter) were placed on opposite sides of the mixing beaker, at a height of ~ 20 cm and ~ 23 cm apart. The laboratory temperature was 21.5 °C. The painting process was carried out twice. The trim strip was then left overnight to dry.

For the heating experiments, the painted trim strip was heated using a heat gun (Steinel). Test 1 heated the trim strip after the glue had been allowed to dry overnight. Test 2 heated the trim strip immediately after the glue had been painted on and was still "tacky". Airborne monitoring for NCO was carried out during these processes. The sampling heads (IOM head containing a 1-(2-methoxyphenyl)piperazine (MP) filter) were placed on opposite sides of the trim strip, at a height of ~ 18 cm and ~ 11 cm apart. The glue was heated at 300 and 500 °C and duplicate runs for each temperature were undertaken. As a control, airborne samples were taken near the painted trim strip prior to heating (laboratory temperature 21.4 °C). LC analysis was carried out as described in MDHS 25/3 (see section 6.2.2). The results of the workplace simulations are given in Table 6.1.

#### **Simulated Workplace use of a MDI based glue (Sericol SFE05)**

This glue was used in the printing industry. Samples (50 µl) of MDI based mesh catalyst were heated, to various temperatures between 25 and 100 °C, in a quartz tube. The air above the tube was sampled onto an MP impregnated GF/A filter at 2 l/min. as described in MDHS 25/3. Analysis was by LC with electro-chemical (EC) and diode array UV/vis detection (242 nm) as described in MDHS 25/3 (see section 6.2.2). The results of this work are given in Figure 6.2.

#### **Simulated Workplace Use of a HDI based 2-pack Adhesive (Herberts Hardener 507/ Adhesive 9523)**

This glue was used in the manufacture of small components in the aircraft industry. Samples (1g) of a HDI based hardener (Herberts 507) were heated, to various temperatures between 60 and 200 °C, in a glass chamber (5 l). Full details of this chamber are available elsewhere (HSL, 1997a). The air above the tube was sampled onto an MP impregnated GF/A filter at 2 l/min. as described in MDHS 25/3. Analysis was by LC with electro-chemical (EC) and diode array UV/vis detection (242 nm) as described in MDHS 25/3 (see section 6.2.2). The results of this work are given in Figure 6.3.

The glue was then mixed (5% hardener/ 95% adhesive as per the manufacturer's instructions) and allowed to cure overnight. The cured glue (~ 1 g) was then heated, in the chamber, for 1 hour at temperatures between 20 and 200 °C. Sampling and analysis was carried out as described above. The results of this work are given in Figure 6.3.

### **6.2.4 Development of MDHS 25/3 – Analysis of Workplace NCO**

#### **Effect of an Internal Standard on Analytical Variance for NCO Determination by EC detection**

The 1-(2-ethoxyphenyl)piperazine derivative of 4,4'-methylenebis (phenyl NCO), (MDI-EP) was spiked onto filters that had been prepared for the WASP QA scheme (MDI-MP spiked onto MP impregnated glass fibre filters). These filters were then worked up and analysed as described in MDHS 25/3. Similar experiments were carried out with filters spiked with oligo-HDI (HDI-

isocyanurate) using 4,4' MDI-MP as an internal standard and on workplace air samples (oligo-MDI sampled onto an impinger/filter combination) using NDI-MP as an internal standard. Analysis was by LC with electro-chemical (EC) and diode array UV/vis detection (242 nm) as described in MDHS 25/3 (see section 6.2.2). The results of this work are given in Table 6.2.

### **Response factors of NCO using EC Quantification**

NCO and reagents were sourced as described above. Isophorone di-isocyanate (IPDI) and phenyl NCO (PI) were purchased from Aldrich Chemical Co, Gillingham, Dorset, UK. MP derivatives were prepared at HSL. Instrumental conditions as described in section 6.2.2.

Solutions in acetonitrile, containing a known amount of NCO, of a variety of pure NCO-MP derivatives were prepared and analysed using the EC detector (MP derivatives prepared and purified at HSL). The response factors (counts/ng NCO on column) were calculated and compared. Analysis was by LC with electro-chemical (EC) and diode array UV/vis detection (242 nm) as described in MDHS 25/3 (see section 6.2.2). These results are reported in Table 6.3.

### **Long-Term storage of MDI spiked MP impregnated filters (WASP QA scheme filters)**

A repeat set of analyses was carried out on WASP QA scheme filters to see if this finding was confirmed. The results of this work are given in Table 6.4.

#### **6.2.5 Development of a Dermal/Surface Sampling Method for NCO**

Glass and metal surfaces were spiked with ~ 450 µg of underivatized MDI (equivalent to ~ 150 µg NCO) in acetonitrile solution. The surfaces were swabbed (Regal filmated medical swabs used dry and moistened with ~ 5 mls of toluene), immediately desorbed in 50 ml MP in toluene solution (impinger solution as described in MDHS 25/3, 50 µg/ml) and sonicated for 30 minutes. An aliquot (10 ml) of this solution was then processed and analysed as described in MDHS 25/3. The results of this work are given in Table 6.5.

#### **6.2.6 Alternative Personal Sampling Devices for Airborne NCO Aerosols**

Air samples were taken either at an MVR body-shop during spray painting or during simulated spray painting activities carried out at HSL's Buxton spray room. Sampler spiking experiments were carried out initially to check recoveries and a "worst case" scenario (experiment 2). Paints used in the MVR body-shop and at HSL were industrial 2-pack aliphatic NCO based paints. The paints used at HSL were purchased from Hallam Factors, Sheffield and were a topcoat/lacquer (primarily HDI-biuret and HDI-dimer, ~ 50% and 30% of the NCO content respectively) and a primer (primarily HDI-isocyanurate, > 90% of NCO content). They were mixed prior to spiking and spraying as instructed by the manufacturer.

The following experiments were carried out:

- Experiment 1. Spiking experiment using Mirrorcyl Top Coat
- Experiment 2. "worst case" Spiking experiment using Highfil Primer
- Experiment 3. MVR body shop –spraying and sampling time varied with job.
- Experiment 4. HSL, spray room, 2 minute spray time (Highfil Primer), 90 minute sample time. It was noted that the primer could clearly be seen on the GF/B filters prior to desorption i.e. they were heavily loaded.

- Experiment 5. HSL Spray room, 2 minute spray time (Mirrorcryn Top coat), 50 minute sampling time.
- Experiment 6. HSL Spray room, 2 minute spray time (Mirrorcryn Top coat), 60 minute sampling time. These samplers were all placed in front of the car bonnet (i.e. they were all heavily loaded).

For the spiking experiment, the mixed NCO based paint was spiked onto the filter and the samples were processed as described in MDHS 25/3. In experiment 1 the solid-state samplers (PUF sponge, GF/A and GF/B) were spiked at between 0.1 to 5 µg/sampler and then "field-desorbed" into MP solution 5 minutes after spiking. The % recoveries relative to the amounts spiked are given in Table 6.6. Experiment 2 was designed as a "worst case" experiment. Possible causes of sample loss for the solid-state samplers have been identified as;

- Local depletion of reagent on the sampler
- Clogging of the sampler – leading to pump failure
- Film formation on the sampler – leading to self-reaction and curing of the paint after sampling.

Experiment 2 was designed to investigate these effects. The paint used (Highfil Primer) had been observed to "skin over" much more rapidly than the lacquer (Mirrorcryn Topcoat). The primer formed a skin in 10 minutes and was dry to the touch after 1 hour. The primer was also more viscous than the lacquer and formed distinct "blobs" when spiked onto the sampler suggesting a strong possibility of local depletion and self-reaction effects. The samplers were left in the laboratory, at room temperature for 4 hours before "field-desorbing" into MP to allow a good possibility of self-reaction and curing. Immediate field desorption has been shown to be important for some NCO species (HSL, unpublished data; Karoly, 1998).

For the spraying experiments, the three different designs of air samplers were placed as close together as possible during spraying operations and pumps set at the following flow rates; MP filled impinger/MP coated back-up GF/A filter (MDHS 25/3) @ 1 l/min, MP coated GF/B filter ("thick filter" or "FINMP" method) @ 2 l/min using an Institute of Medicine sampling head (IOM head) and a MP impregnated polyurethane (PUF) sponge/MP coated GF/A back-up ("Rudzinski" or "PUF" method) @ 2 l/min (IOM head). The sampler trios were placed at various points around the spray room except for experiment 6 where they were all placed in front of the bonnet to see the effect of heavy loading on the samplers. In the HSL simulations, spraying was carried out for 2 minutes with > 30 minutes then allowed as a "clearance time" for the spray room. The samples were then "field-desorbed" into MP solution. For the MVR work, sampling times were dependent upon the job and varied from ~ 30 to ~ 60 minutes. The samples were then "field-desorbed" into MP solution. Analysis was as described in MDHS 25/3. The results of this work are given in Table 6.6 and Figures 6.4 and 6.5.

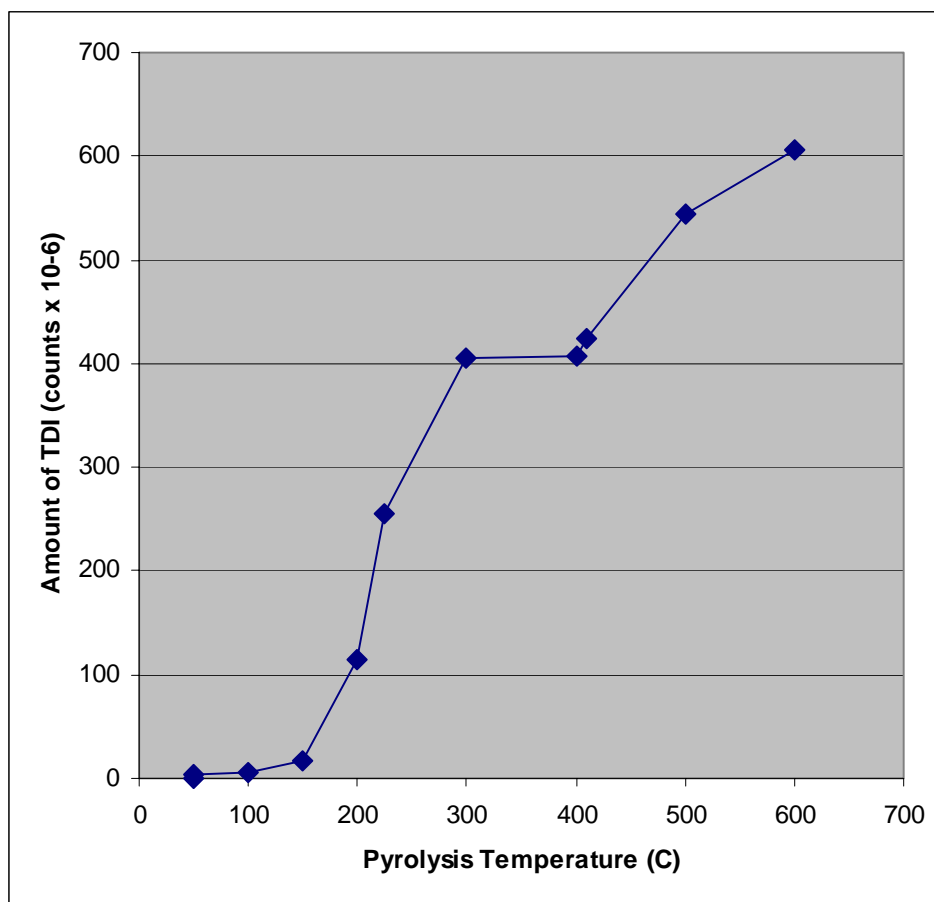
For the work at HSL, the paint was sprayed in the HSL spray room using an automatic system designed and built by HSL and is described more fully elsewhere (HSL, 2005a). Sampling and analysis was carried out as described in MDHS 25/3. Instrumental conditions were similar to those described above. Three types of sampler were investigated; MP filled impinger and MP coated back-up GF/A filter (MDHS 25/3), MP coated GF/B filter ("thick filter" "double filter" or "FINMP" method) and a MP impregnated polyurethane sponge (PUF) and MP coated GF/A back-up ("Rudzinski" method). The "FINMP" method uses a GF/B filter (or 2 x GF/A filters in some versions), which is a double thickness filter, spiked with 2 x the amount of MP used for the GF/A (400 µl instead of 200 µl ), placed in an IOM head and desorbed into 5ml of acetonitrile at

a sampling rate of 2 l/min. The "Rudzinski" sampler is a polyurethane foam sampler (PUF), spiked with 3 ml of MP reagent solution, allowed to dry and then placed in an IOM head with a back up MP impregnated GF/A. The PU foam sampler and back up were then desorbed in 10 ml of acetonitrile. The sampling rate used for this sampler was 2 l/min. MDHS 25/3 uses an impinger with ~10 ml of MP solution and an MP coated GF/A back up filter at a sampling rate of 1 ml/min. The results of this work are shown in Table 6.6 and Figures 6.4 and 6.5.

### 6.3 RESULTS AND DISCUSSION

#### 6.3.1 Airborne NCO from Hot Melt Glues

Figure 6.1. Pyrolysis GC/MS of TDI based Glue- Bostik Mybond 3095 Part 2



#### Comments

From Figure 6.1 it can be seen that, for this formulation, appreciable amounts of NCO vapour begin to be produced at ~ 175 °C i.e. "lift-off" temperature of ~ 175 °C. These experiments show that appreciable amounts of TDI vapour will be generated if the glue is heated above ~ 200 °C. This is in agreement with a literature value found for the boiling point of toluene 2,4 NCO of 251 °C at 760 mm Hg pressure.

Table 6.1. Simulated Workplace use of a TDI based glue (Bostik Mybond 3095 Part 2)

<b>Test 1</b>						
Pyrolysis GC/MS, carried out on HP 5971 GC/MS with pyrolysis attachment and cold trap. (See Figure 6.1).						
<b>Test 2</b>						
Simulation of Pouring and Mixing of Parts 1 and 2 of Bostik Mybond 3095.						
	Sample Volume (l)	T 2,4 DI $\mu\text{g NCO/m}^3$	T 2,6 DI $\mu\text{g NCO/m}^3$	Total $\mu\text{g NCO/m}^3$		
Left 1	4	N.D.	N.D.	N.D.		
Right 1	4	N.D.	N.D.	N.D.		
Left 2	4	N.D.	N.D.	N.D.		
Right 2	4	N.D.	N.D.	N.D.		
<p>Notes: N.D. = not detected, Estimated Limit of Detection <math>\sim 5 \mu\text{g NCO/m}^3</math> for a 4 l air sample. No airborne TDI was detected.</p> <p>It was noticed during the pouring that the part 2 of the glue tended to “glug” out of the containers putting small splashes on to the protective gloves that were being worn. This happened during both experiments. Dermal exposure to NCO is therefore a possibility.</p>						
<b>Test 3</b>						
Simulation of painting of mixed glue						
	Sample Volume (l)	T 2,4 DI $\mu\text{g NCO/m}^3$	T 2,6 DI $\mu\text{g NCO/m}^3$	Total $\mu\text{g NCO/m}^3$		
Left 1	4	N.D.	N.D.	N.D.		
Right 1	4	N.D.	N.D.	N.D.		
Left 2	4	N.D.	N.D.	N.D.		
Right 2	4	N.D.	N.D.	N.D.		
<p>Notes: N.D. = not detected, Est. LOD <math>\sim 5 \mu\text{g NCO/m}^3</math> for a 4 l air sample. No airborne TDI was detected.</p>						

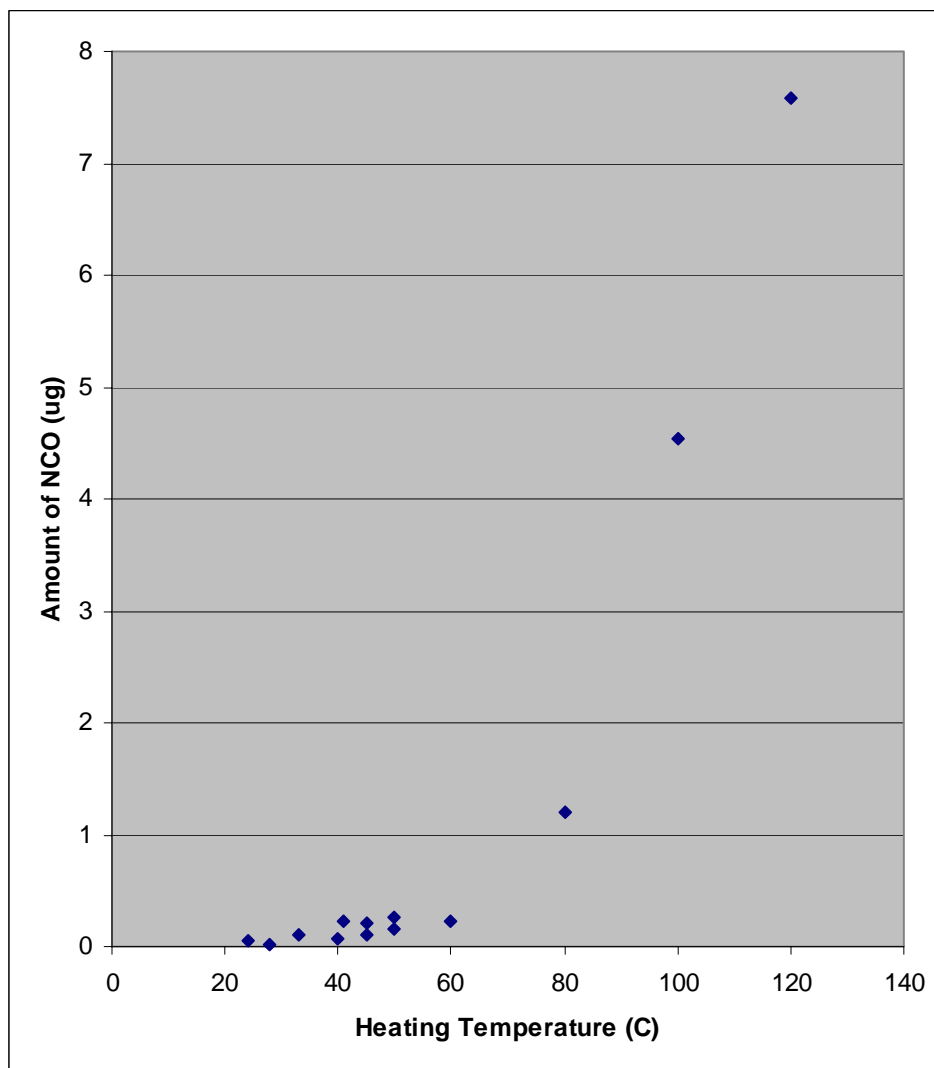
Test 4					
Simulation of heating of glue					
	Sample Volume (l)	T 2,6 DI $\mu\text{g NCO/m}^3$	T 2,4 DI $\mu\text{g NCO/m}^3$	Total $\mu\text{g NCO/m}^3$	
Run 1 - dried trim strip					
Blank 1 21 °C	20	N.D.	N.D	N.D	
Blank 2 21 °C	20	N.D	N.D	N.D	
300 °C LEFT	8	N.D.	N.D	N.D	
300 °C RIGHT	8	N.D	N.D	N.D	
500 °C LEFT (30 seconds)	1	30,486	57,710	88,196	
500°C RIGHT (30 seconds)	1	17,329	31,377	48,706	
Run 2 – “tacky” glue					
Blank 1 21°C	20	N.D.	N.D	N.D	
Blank 2 21 °C	20	N.D	N.D	N.D	
300°C LEFT	8	217	524	741	
300°C RIGHT	8	207	470	677	
500°C LEFT (30 seconds)	1	29,532	34,288	63,820	
500°C RIGHT (30 seconds)	1	20,419	33,924	54,343	
Notes: N.D. = not detected. Est. LOD ~5 $\mu\text{g NCO/m}^3$ for a 4 l air sample. Est. LOD ~20 $\mu\text{g NCO/m}^3$ for a 1 l air sample. Short Term Exposure Limit for NCO (STEL)(EH40/2005) 70 $\mu\text{g NCO/m}^3$ for a 15 l air sample.					

#### Comments

From Table 6.1 it can be seen that no airborne NCO was detected during the mixing, pouring and brush painting experiments. This is in agreement with similar work carried out at HSL (HSL, 2005b). For the heating experiments no airborne NCO was seen at room temperature. The airborne values for the 500°C experiments are hundreds of times in excess of the STEL. The 300°C “tacky” glue experiments are also in excess of the STEL. This suggests that airborne exposure during heating of the glue is a strong possibility and suitable safety measures should be taken. During the 500°C heating experiments the glue “boiled” as (presumably) any residual solvent in the glue was driven off. When the heat gun was switched off it could be seen that the glue was smoking and the impregnated filters used for the airborne NCO determination were discoloured.

These results show that MDHS 25/3 can be used to take very short-term samples (30 seconds) and still give an estimated limit of detection (Est. LOD) below than the STEL. This approach is useful if the NCO is in use for very short tasks e.g. SMART repair in the MVR industry (HSL, 2005c) as short time-period task-centred samples will enable the occupational hygienist to form a better picture of the sources of NCO exposure and their relative importance. The electrochemical detector available for NCO analysis at HSL is even more sensitive than the UV detector used here.

Figure 6.2. Simulated Workplace Use of a MDI based Glue (Sericol SFE05)

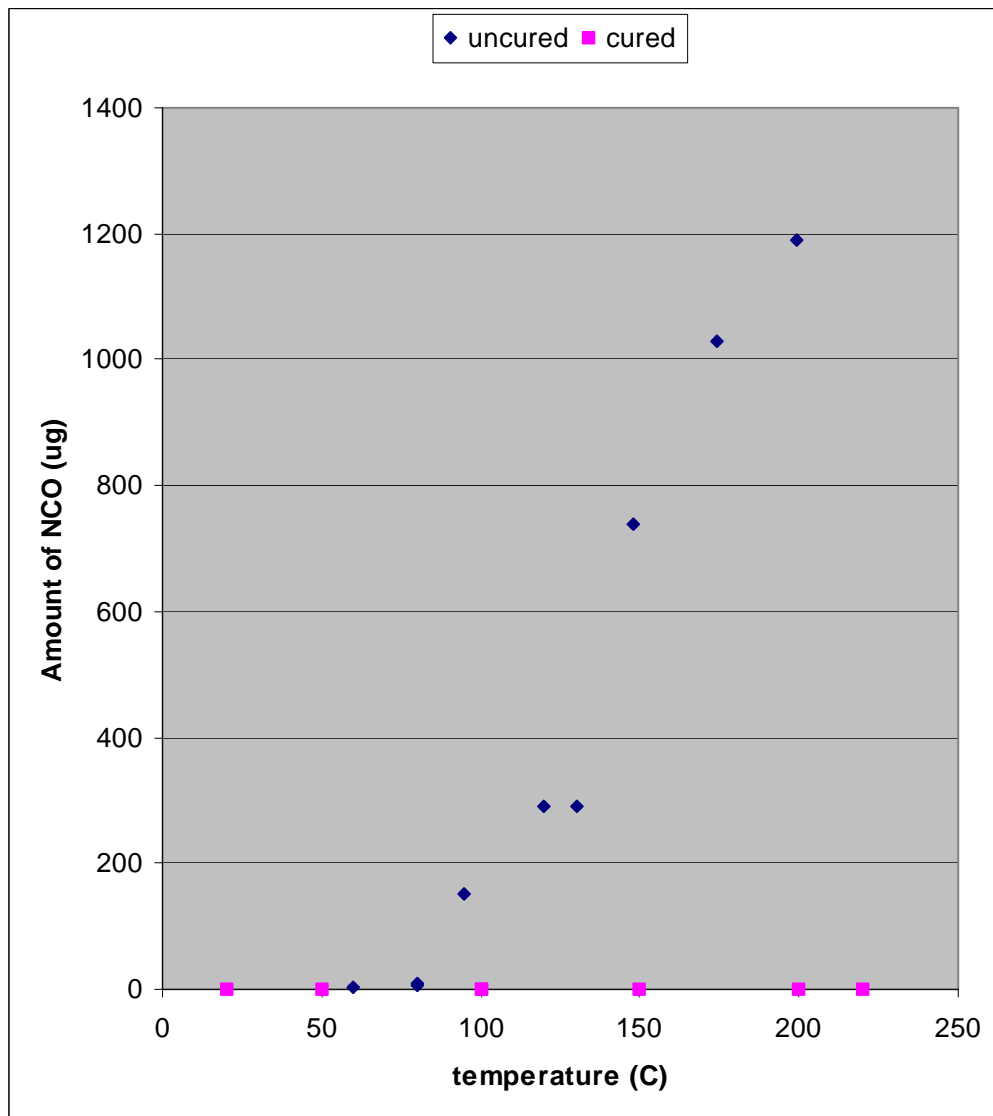


#### Comments

From Figure 6.2 it can be seen that, for this formulation, appreciable amounts of NCO vapour starts to be produced at ~ 100 °C i.e. "lift-off" temperature of ~ 100 °C. The industrial process of

interest to HSE that was using this glue was being carried out at ~ 50°C suggesting a very low risk of airborne NCO. No oligo-NCO species were detected.

Figure 6.3. Simulated Workplace Use of a HDI based 2-pack Adhesive (Herberts Hardener 507/ Adhesive 9523)



#### Comments

From Figure 6.3 it can be seen that, for the uncured hardener formulation, appreciable amounts of NCO vapour starts to be produced at ~ 100 °C i.e. "lift-off" temperature of ~ 100 °C. The industrial process of interest to HSE that was using this glue was being carried out at ~ 150°C suggesting a significant risk of airborne NCO for this product and process.

The cured glue produced no NCO vapour at any of the temperatures tested suggesting that once this product has cured it is no longer a hazard at the temperatures likely to found in the industrial process in use. No oligo-HDI species were detected.

### 6.3.2 Development of MDHS 25/3 – Analysis of Workplace NCO

#### Effect of an Internal Standard on Analytical Variance for NCO Determination by EC detector

Table 6.2. Effect of an Internal Standard on Analytical Variance for NCO Determination by EC detector.

Determination of MDI-MP on filters using MDI-EP as internal standard				
Sample	Result	X ( $\mu\text{g}$ NCO/g solvent)	%RSD	n
filter 1	EC, no ISTD	0.113	10.7	5
	EC, ISTD corrected	0.109	4.8	5
	UV (242nm)	0.093	4.2	5
filter 2	EC, no ISTD	0.191	3.7	5
	EC, ISTD corrected	0.178	2.6	5
	UV (242nm)	0.177	1.8	5
filter 3	EC, no ISTD	0.312	11.3	5
	EC, ISTD corrected	0.322	2.3	5
	UV (242nm)	0.318	2.2	5
filter 4	EC, no ISTD	0.162	9.2	5
	EC, ISTD corrected	0.141	2.6	5
	UV (242nm)	0.136	2.4	5
Determination of oligo-HDI (isocyanurate)-MP on filters using MDI-MP as internal standard				
Sample	Result	X ( $\mu\text{g}$ NCO/g solvent)	%RSD	n
filter A	EC, no ISTD	0.117	22.0	10
	EC, ISTD corrected	0.086	2.6	10
	UV (242nm)	0.089	3.6	10
Determination of oligo-MDI-MP in workplace air using NDI-MP as internal standard				
Sample	Result	X ( $\mu\text{g}$ NCO/g solvent)	%RSD	n

sample A	EC, no ISTD	0.085	22.4	20
	EC, ISTD corrected	0.086	6.1	20
	UV (242nm)	0.096	5.4	20
sample B	EC, no ISTD	0.653	2.4	20
	EC, ISTD corrected	0.622	3.1	20
	UV (242nm)	0.671	1.9	20

The results in Table 6.2 suggest that an internal standard greatly reduces the variability associated with EC detector. For EC detection with an internal standard the %RSD are comparable with those obtained for the UV detector. This effect was much more pronounced at the lower level samples. The variance of the higher level samples would not be expected to be so sensitive to detector type. Care must be taken on choosing an internal standard to make sure it does not interfere with the sample peaks, this is particularly important for oligo-NCO samples where many NCO peaks may be present e.g. NDI-MP was not suitable as an internal standard for HDI because of co-elution. The distinctive UV spectra of MDI-MP and NDI-MP are useful for identification purposes. The specific NCO-EP or NCO-MP derivative used as an internal standard for any particular NCO formulation depends on factors such as interfering/co-eluting peaks and ease of identification. Any NCO MP/EP derivative with acceptable performance may be used as internal standard.

Table 6.3. Response factors of NCO using EC Quantification

NCO-MP derivative	EC counts	Amount of NCO on column (ng)	No. of NCO groups per unreacted molecule	EC Response Factor (counts/ng NCO)
HDI-isocyanurate	8,967,324	382	3	23,475
MDI	12,507,815	604	2	20,708
T 2,4 DI	8,427,556	353	2	23,874
T 2,6 DI	17,234,257	997	2	17,286
HDI	9,197,986	444	2	20,716
NDI	13,627,938	586	2	23,256
IPDI	21,635,115	960	2	22,537
PI	5,794,066	251	1	23,084

#### Comments

From Table 6.3 it can be seen that all the NCO-MP derivatives studied gave similar response factors (average 21,901, % RSD 10.2, n=8). These results suggest that the "equivalent response" theory for NCO by EC is sound.

Table 6.4. Long-Term storage of MDI spiked MP impregnated filters (WASP QA scheme filters)

Storage time (months)	% Recovery	% RSD (n=6)
11	108	12
23	104	5
Analysis by EC detector as in MDHS 25/3 Filter 1 to 4 from WASP round 44 used (0.3 – 0.7 µg/filter)		

Comments

These results suggest that the MDI-MP spiked WASP filters are stable on storage for at least 23 months. The finding of ~ 85% recovery, over all time periods (0 to 22 months), reported in previous work (HSL, 2001) may therefore be considered anomalous. This is probably because of a calibration error or a deterioration of the MP standard solutions in use in the original work.

**6.3.3 Development of a Surface Sampling Method for NCO**

Table 6.5. Development of a Dermal/Surface Sampling Method for NCO

Swab type	% Recovery	% RSD (n=6)
dry	69	51
moistened with toluene	125	28
150 µg NCO spiked (equivalent to ~446 µg MDI)		

Comments

The moistened swab technique gives better and more reproducible recoveries than the dry swab technique. The > 100% recoveries suggest a co-eluting interference so a clean-up step or slightly modified LC method may be required. This work has shown that a swab method for surface monitoring is feasible but more work is required to develop a fully validated method. Other approaches, e.g. the use of colorimetric wipes or MP impregnated swabs should also be investigated.

### 6.3.4 Alternative Personal Sampling Devices for Airborne NCO Aerosols

Table 6.6. A Comparison of Alternative Personal Sampling Devices for Airborne NCO

Sampler	MDHS 25/3	"Rudzinski"	"FINMP"
	Impinger + GF/A filter	PU foam + GF/A filter	GF/B filter
Experiment 1. Spiking, topcoat			
µg NCO/sampler (% recovery)			
1	4.52 (90.4)	4.81 (96.2)	5.15 (103.0)
2	2.60 (104.0)	3.13 (125.2)	2.63 (105.2)
3	2.31 (92.4)	3.70 (148.0)	2.55 (102.0)
4	0.45 (90.0)	0.64 (128.0)	0.49 (98.0)
5	0.09 (90.0)	0.10 (100.0)	0.08 (80.0)
6	0.94 (94.0)	0.83 (83.0)	0.88 (88.0)
Average % recovery	93 ± 5.4	113 ± 24.3	96 ± 9.9
% RSD	5.8	21.5	10.3
Experiment 2. "worst case" spiking, primer			
µg NCO/sampler (% recovery)			
1	251 (100.4)	224 (89.6)	312 (124.8)
2	263 (105.2)	260 (104.0)	298 (119.2)
3	1186 (94.9)	1385 (110.8)	1203 (96.2)
4	1114 (89.1)	1328 (106.2)	1275 (102.0)
5	584 (116.8)	652 (130.4)	546 (109.2)
6	446 (89.2)	562 (112.4)	604 (120.8)
Average % recovery	99 ± 10.7	109 ± 13.3	112 ± 11.4
% RSD	10.7	12.2	10.2
Experiment 3. MVR body-shop			
µg NCO/ m <sup>3</sup>			
1	FAIL	524	679
2	1591	850	2096
3	3247	1082	2707
4	2720	1602	2225
5	1371	959	1336
6	1520	1112	1313
Experiment 4. HSL spray room simulation, primer			
µg NCO/ m <sup>3</sup>			
1	527	734	479
2	234	672	230
3	98	728	141
4	618	878	743
5	468	915	314
6	336	1032	353

Experiment 5. HSL spray room simulation, topcoat/lacquer			
µg NCO/ m <sup>3</sup>			
1	78	75	106
2	114	117	153
3	93	90	78
4	90	98	112
5	44	37	45
6	23	29	31
Experiment 6. HSL spray room simulation, topcoat/lacquer – "heavy loading"			
µg NCO/ m <sup>3</sup>			
1	174	163	168
2	179	198	175
3	254	284	199
4	291	270	255
5	556	588	518
6	572	589	609
Notes. FAIL = pump failure during sample – sample lost			

#### Comments

Spiking experiment 1 showed that all three methods gave acceptable recovery for this HDI formulation over the range spiked (0.1 to 5 µg NCO). Spiking experiment 2 was expected to show lower recoveries for the "solid state" samplers (PUF, GF/A and GF/B) because of local depletion of the MP reagent on the filter (because of the high amount of NCO spiked) and self-reaction and other side reactions (because of the delay before the samples were "field desorbed" and the observed "blobbing" of the spike) but in fact the results for these samplers were slightly higher than the standard MDHS 25/3 method. These results suggest that for this HDI formulation losses because of these processes are not significant over a typical sampling time frame (~ 4 hours). This is probably because of the extremely rapid nature of the derivatizing reaction (MP + NCO) in comparison with the curing reactions e.g. with water and alcohols. The following relative rates of reaction are given as an indicator;

Table 6.7. Relative rates of reaction of Phenyl NCO with active Hydrogen compounds in toluene @ 25 °C

Compound	Relative Rate
MP	> 10, 000,000
water	1
1- butanol	5 - 10

Adapted from data in Saunders and Frisch, 1978, p 208 and Wu et al. 1991

It should be noted that NCO formulations as used in industry will have catalysts or may be heated to increase curing speed and that the MP reagent for the "solid state" methods is not in solution until the field-desorption stage. These factors will affect the relative reaction rate but the

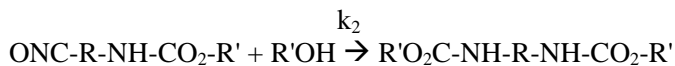
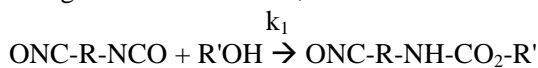
likelihood is still that the rate of reaction with the MP derivatizing agent will be orders of magnitude faster than the curing reactions. This probably explains why, for HDI based NCO, the patterns of NCO species seen in airborne samples are very similar to those obtained from derivatized bulks. The situation for the faster reacting aromatic NCO may be different. As a guide the relative rates of reaction for various NCO with alcohols are given in Table 6.8.

Table 6.8. Relative rates ( $k_1$  and  $k_2$ ) for the reaction of the first and second NCO groups of Common Di-isocyanates with Alcohols

Isocyanate	$k_1$	$k_2$
TDI	400	33
MDI	320	110
HDI	1	0.5
HMDI	0.6	0.4
IPDI	0.6	0.2

Adapted from data in Saunders and Frisch, 1978, p 170 and Bayer, 1978 – see HSL, 2003.

The general reactions are;



The results of experiments 1 and 2 and the data given in tables 6.7 and 6.8 suggested that the "solid state" samplers maybe of use for sampling airborne HDI based NCO as used in MVR spraying and this speculation was tested in experiments 3 to 6 (Table 6.6).

The results for the airborne monitoring of HDI based NCO (experiments 3 to 6) using the new samplers (PUF+GF/A and GF/B) were plotted against those for the standard impinger/filter method (MDHS 25/3, see Figures 6.4 and 6.5).

Investigation of the results for the PUF+GF/A combination sampler (Figure 6.4) shows that for the MVR body-shop samples this sampler is under-reporting relative to MDHS 25/3, whereas for the HSL simulation using the primer this sampler is over-reporting. This is probably because of the different NCO formulations in use. The results for the lacquer experiments appear to compare well with those obtained by MDHS 25/3. Figure 6.4 and accompanying linear regression statistics show a moderate correlation between the results obtained by the "Rudzinski" sampler and MDHS 25/3. The slope of the graph and examination of the plot clearly suggest that the "Rudzinski" method under-reports at high NCO loadings relative to MDHS 25/3. These findings suggest that the PUF+GF/A combination is a possible alternative to the impinger/filter combination used in MDHS 25/3 but that more work would be required to fully validate this approach.

The results given in Figure 6.5 and accompanying linear regression statistics for the comparison of MDHS 25/3 and the "FINMP" method (GF/B sampler) show an acceptable correlation. The results for the "FINMP" method give a better match to the reference method (MDHS 25/3) than those for the "Rudzinski" method and the MP impregnated GF/B filters are easier to prepare, store and use than the MP coated PUF samplers (from discussions with HSL sampling officers and personal experience). In particular the slope of the plot of MDHS 25/3 against FINMP

(figure 6.5, slope 0.8700) is nearer to 1 (i.e. perfect correlation) than that for MDHS 25/3 against PUF (Figure 6.4, slope 0.3877). Inspection of the plot for MDHS 25/3 against FINMP (figure 6.5) showed that the slope of this plot is strongly affected by the two highest points plotted, these were from the MVR body-shop, experiment 3. Removal of these two points gave a line with the following regression statistics;

linear regression of y (= FINMP) on x (= MDHS 25/3) without the 2 highest points

(FINMP) = -19.2492 + 1.0680(MDHS 25/3)

intercept	-19.2492	standard error	39.4146
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slope	1.0680	standard error	0.0613
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correlation coefficient	0.9700
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$r^2$	94.10 %
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P value	< 0.0001
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This finding suggests that either these two results are in error or that the "FINMP" method under-samples slightly at these high NCO (~ 3000  $\mu\text{g}/\text{m}^3$  loadings).

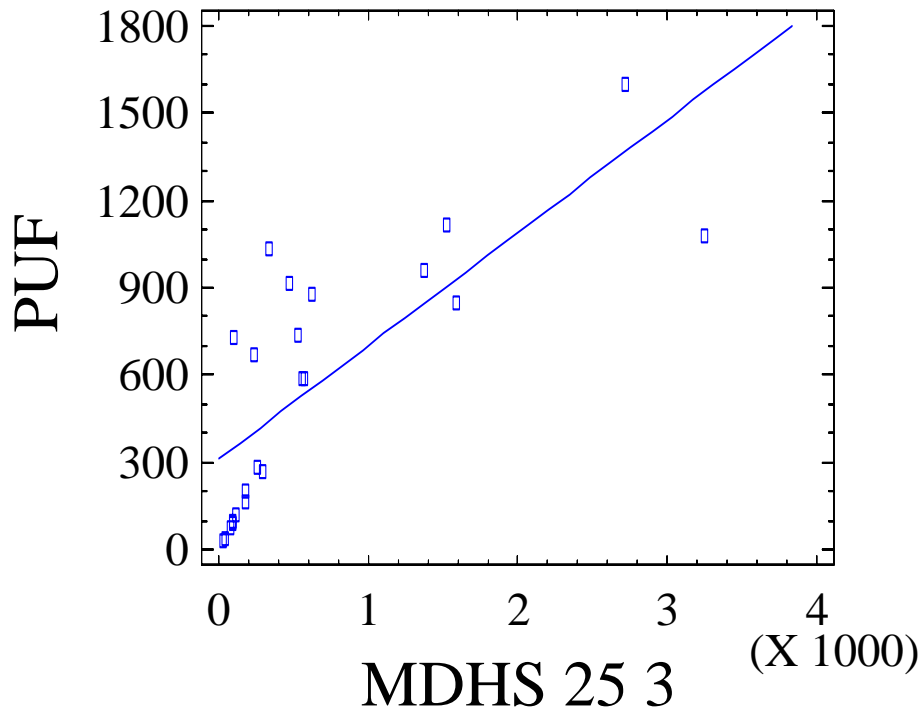


Figure 6.4. Comparison of Sampler types for NCO Aerosol Analysis; MDHS 25/3 (impinger and filter) vs "Rudzinski" (PUF+ GF/A)

Notes

Units are  $\mu\text{g NCO}/\text{m}^3$

linear regression of y (= PUF) on x (= MDHS 25/3)

(PUF) = 313.493 + 0.3877(MDHS 25/3)

intercept      313.493 standard error    77.5432

slope            0.3877                                  standard error    0.0721

correlation coefficient    0.7611

$r^2$     57.92%

P value    < 0.0001

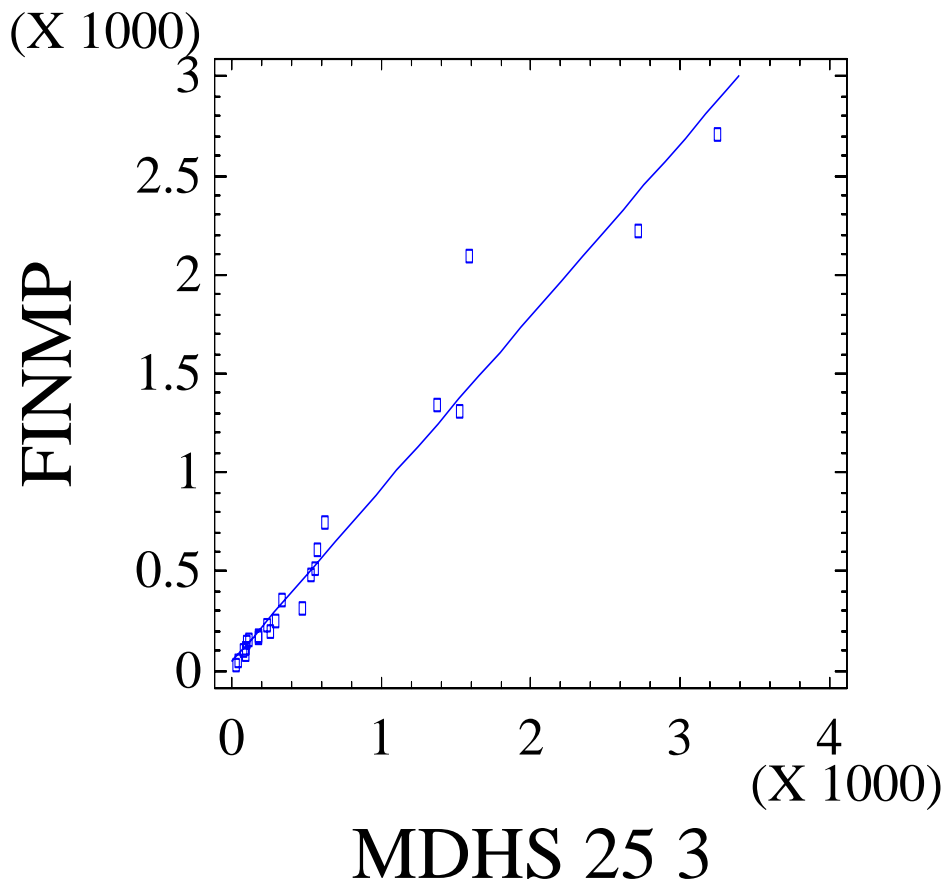


Figure 6.5. Comparison of Sampler types for NCO Aerosol Analysis; MDHS 25/3 (impinger and filter) vs "FINMP" (GF/B)

Notes

Units are  $\mu\text{g NCO}/\text{m}^3$

linear regression of y (= FINMP) on x (= MDHS 25/3)

(FINMP) = 50.5639 + 0.8701(MDHS 25/3)

intercept 50.5639 standard error 43.9743

slope 0.8701 standard error 0.0409

correlation coefficient 0.9776

$r^2$  95.57%

P value < 0.0001

## **6.4 CONCLUSIONS**

### **Hot Melt Glue Work**

For the glues tested (HDI, MDI and TDI based) all were shown to be able to liberate appreciable NCO vapour at temperatures above 100 °C. Pyrolysis GC/MS was found to be a useful technique for determining the NCO given off during heating of hot melt glues. No NCO was detected in the air during brushing, mixing and pouring operations. MDHS 25/3 has the required sensitivity to detect airborne NCO from very short-term tasks (~ 30 seconds or less).

### **Development of MDHS 25/3 (Analytical method)**

The use of a suitable internal standard greatly improves the reproducibility of the EC detector. MP derivatized MDI on WASP filters has been found to be stable for ~ 2 years. This work corrects an anomalous earlier finding. Work on the EC response of mono, di- and tri- NCO MP derivatives has shown that the "equivalent response" assumption for the EC quantification of NCO is valid.

### **Development of MDHS 25/3 (Surface Sampling method)**

The feasibility of a surface sampling method based on the chemistry employed in MDHS 25/3 has been demonstrated.

### **Development of MDHS 25/3 (Air Sampling method)**

Two alternative "solid state" sampling methods ("FINMP" and "Rudzinski") have been investigated and found to give acceptable correlation to the reference method MDHS 25/3 (impinger and filter back-up sampler) for the sampling of HDI based NCO aerosols. The "FINMP" method was judged to give the best correlation with MDHS 25/3. These results suggest that for the sampling of aerosols produced during the spraying of slow curing HDI based paints e.g. during MVR work, sampling using the "FINMP" method is an acceptable alternative to the impinger/filter method described in MDHS 25/3. The use of an MP impregnated "thick" filter (GF/B) or two MP impregnated GF/A filters in an IOM head is a significantly more user friendly personal sampling device than the impinger/filter method.

Future work at HSL will concentrate on the "FINMP" method and further work should be carried out to evaluate the GF/B sampler e.g. extending sampling times, consideration of breakthrough and sampling of aromatic (more reactive) NCO aerosols.

A limited number of experiments have been carried out at HSL using two MP coated GF/A filters back to back (instead of a single GF/A filter) in an IOM head to sample NCO given off when heating polyurethane foams and paints. It was noted that the first filter was heavily discoloured after sampling but the back-up (second) filter was not. The GF/A filters were then desorbed separately to see if any breakthrough from the first filter had occurred. No breakthrough was noted (HSL, 2005d).

## **7 INVESTIGATION OF ON-GUN EXTRACTION IN MVR**

### **7.1 INTRODUCTION**

HSE has recently completed four pilot Safety Health and Awareness Days (SHADs) targeted at the Motor Vehicle Repair (MVR) industry. Feedback from the events and an evaluation study has demonstrated that the events were very successful in communicating HSE key messages to the MVR industry. However, feedback did highlighted that one of the sessions needed some visual improvements in order to strengthen HSE's message. HSE decided this would be best achieved by incorporating video footage into an existing HSE presentation and asked HSL to carry out the work.

### **7.2 EXPERIMENTS**

HSL organised and undertook, with the assistance of an external contractor, a sanding operation of a painted body panel with and without on-tool extraction. Both stills and video footage was recorded. To enable the viewer to see the full extent of the dust cloud a larger area around the worker was 'Tyndall' illuminated.

### **7.3 DISCUSSION AND CONCLUSIONS**

Both stills and video, which were taken during the tests, were edited for inclusion in to a PowerPoint presentation. When sanding was carried out the photographic material clearly showed the full extent of the dust cloud when the on-tool extraction was switched off. With the on-tool extraction on the lack of airborne dust clearly demonstrated the high efficiency of the extraction device. In addition to this, the absence of Tyndall lighting showed that the dust cloud was not visible under normal lighting conditions.

## **8 SMART REPAIRS**

### **8.1 INTRODUCTION**

Within the Motor Vehicle Repair (MVR) industry SMART (Small to Medium Area Repair Techniques) repairs are becoming increasingly common as a cheaper alternative to a full body shop repair. These SMART repairs are primarily performed to improve the cosmetic appearance of vehicles prior to being sold, these repairs are routinely carried out on garage forecourts. SMART repairs are ill defined, however they should not require replacement or respray of a complete panel, the repair area be no more than around 7000cm<sup>2</sup> and the amount of paint used is unlikely to exceed 25 ml per coat.

HSE has had concerns about exposure to NCO for workers in the SMART repair industry and also the risk of secondary exposure for others in close proximity to the repair operation. Considerable difficulties have been met when trying to find suitable collaborators to assess the potential for NCO exposure. General research into the nature and prevalence of SMART repairs has been funded under this contract. It has been found that the appropriate respiratory protective equipment (RPE) is often not used, HSE guidance requires the use of air-fed RPE when spraying NCO paints. It appears the fact that the added air dilution offered by the open-air environment is considered adequate protection by some SMART repairers. Data on NCO exposure during SMART repairs was required to fully validate the guidance.

### **8.2 EXPERIMENTAL**

Given the problems encountered finding SMART repairer to assist the research, it was decided that for exposure assessments measurements could be taken here at HSL by employing, on a contract basis, a SMART repairer to carry out repairs or spraying experiments to mimic repairs. Such work would require approval by the Ethics Committee, preparation of relevant documentation and submission to the committee has been carried out under this call-off contract.

Under this call-off contract two sampling visits to SMART repairers have been conducted to evaluate likely NCO exposures. The more recent visit, which sampled more than 40 separate spraying tasks, is key to deciding the nature of future work into SMART repair NCO exposures. Four different repair scenarios were monitored;

- Spraying outside – no canopy
- Spraying outside – under canopy
- Spraying inside industrial unit – extraction system on
- Spraying inside industrial unit – extraction system off

Sampling for airborne NCO was carried out using MDHS 25/3, six replicates were performed in all cases. The results obtained are shown in table 8.1.

To assess the effectiveness of controls biological monitoring was carried out on the sprayer.

### **8.3 RESULTS AND DISCUSSION**

The results show that SMART repairing does generate short term peak exposures above the workplace exposure limit (WEL), and given the hazardous nature of NCO it is not considered reasonable to allow time weighted averaging to be applied.

For each the four given experimental scenarios, the time spent spraying was broadly the same, with an average spray time of 16.8s. Additionally, the time elapsed between each replicate was only around 2-3 minutes and yet the highest and lowest results for a particular scenario varied by as much as factor of ten. Clearly atmospheric conditions have a considerable effect on the potential NCO exposure during SMART repair and that air-fed RPE is essential for ensuring adequate protection from airborne NCO.

A separate report on the findings (OMS/2005/12) has been produced.

It is envisaged that further work will be carried out on SMART repairs as a separate support job, with consideration given to the potential for secondary exposure for those working near to the repair operation.

Table 8.1. Short-term NCO exposures from simulated SMART repairs

Laboratory sample No.	Sample Type	[NCO] µg/ sample	[NCO] µg/m <sup>3</sup>	Air Volume (l)	Sample duration Mins:secs	Comments
Outside spraying						
05278/05	Impinger + filter	0.075	11.3	6.666	3:20	Sample 1 - spraying for 20s
05279/05	Impinger + filter	N.D.	N.D.	3.333	1:40	Sample 2 - spraying for 16s
05280/05	Impinger + filter	0.092	46	2	1:00	Sample 3 - spraying for 20s
05281/05	Impinger + filter	0.299	149.5	2	1:00	Sample 4 - spraying for 15s
05282/05	Impinger + filter	0.715	327.5	2	1:00	Sample 5 - spraying for 15s
05283/05	Impinger + filter	0.125	62.4	2	1:00	Sample 6 - spraying for 18s
05284/05	Impinger + filter	N.D.	N.D.	10.333	5:10	Sample 7 - 6 x sprays
Outside spraying under canopy						
05285/05	Impinger + filter	0.035	13.1	2.666	1:20	Sample 1 - spraying for 19s
05286/05	Impinger + filter	0.058	24.9	2.333	1:10	Sample 2 - spraying for 20s
05287/05	Impinger + filter	0.143	53.6	2.666	1:20	Sample 3 - spraying for 18s
05288/05	Impinger + filter	0.05	20	2.5	1:15	Sample 4 - spraying for 20s
05289/05	Impinger + filter	0.09	45	2	1:00	Sample 5 - spraying for 17s
05290/05	Impinger + filter	N.D.	N.D.	2.333	1:10	Sample 6 - spraying for 19s
05291/05	Impinger + filter	0.524	32.8	16	8:00	Sample 7 - 6x sprays
Spraying inside extraction on						
05292/05	Impinger + filter	0.089	53.4	1.666	0:50	Sample 1 - spraying for 15s

Table 8.1. Short-term NCO exposures from simulated SMART repairs

Laboratory sample No.	Sample Type	[NCO] $\mu\text{g}/\text{sample}$	[NCO] $\mu\text{g}/\text{m}^3$	Air Volume (l)	Sample duration Mins:secs	Comments
05293/05	Impinger + filter	0.816	233.1	3.5	1:45	Sample 2 - spraying for 14s
05294/05	Impinger + filter	0.047	20.1	2.333	1:10	Sample 3 - spraying for 20s
05295/05	Impinger + filter	0.479	205.3	2.333	1:10	Sample 4 - spraying for 16s
05296/05	Impinger + filter	0.252	107.8	2.333	1:10	Sample 5 - spraying for 16s
05297/05	Impinger + filter	0.193	82.9	2.333	1:10	Sample 6 - spraying for 13s
05298/05	Impinger + filter	N.D.	N.D.	21.666	10:50	Sample 7 - 6 x sprays
Spraying inside extraction off						
05299/05	Impinger + filter	0.342	171	2	1:00	Sample 1 - spraying for 15s
05300/05	Impinger + filter	0.161	64.4	2.5	1:15	Sample 2 - spraying for 14s
05301/05	Impinger + filter	0.947	437.1	2.166	1:05	Sample 3 - spraying for 20s
05302/05	Impinger + filter	0.693	346.5	2	1:00	Sample 4 - spraying for 16s
05303/05	Impinger + filter	0.268	100.5	2.666	1:20	Sample 5 - spraying for 16s
05304/05	Impinger + filter	0.176	75.4	2.333	1:10	Sample 6 - spraying for 13s
05305/05	Impinger + filter	0.451	19	23.666	11:50	Sample 7 - 6 x sprays

Note: sprayer was using air-fed RPE throughout the spray tasks.  
 ND= not detected (below LOD)

## **8.4 CONCLUSIONS**

SMART repairs have the potential to generate airborne NCO concentrations much greater than the WEL. It is essential that air-fed respiratory protective equipment be used when spraying NCO paints during SMART repairs.

Considerable variation was observed in the replicate samples, most likely to the prevailing atmospheric conditions.

Further work has since been carried out under JS20.04642, see report OMS/2006/04.

HSE, together with other interested parties, is currently preparing a “Good practice for SMART repairs” guidance document.

## 9 VALIDATION OF CYANOACRYLATE SAMPLERS

### 9.1 INTRODUCTION

Ethyl-2-cyanoacrylate (ECA) and methyl-2-cyanoacrylate (MCA) are commonly used adhesives due to a fast cure time and high bond strength. Many different industries use cyanoacrylate adhesives including window manufacturers, electronic component and loudspeaker assembly, shoemaking, lampshade production and police forensic laboratories.

Work was carried out to assist with the method validation of two newly developed sampling tubes for the measure of ECA and MCA. Both tubes are based on a commercially available Tenax sampling tube (SKC part number 226-35-03), one was treated with phosphoric acid ( $H_3PO_4$ ) and the other substitutes a glass wool plug at the sampling end of the tube for a steel mesh which is held in place by a polypropylene o-ring. Development of the alternative sampling tubes was originally funded under JS20.02400 (see report OMS/2003/23). It was decided validation of the new tubes should be carried out according to British Standard EN 482, which makes an assessment performance over a range of concentrations, temperatures and humidities.

### 9.2 EXPERIMENTAL

A dynamic standard atmosphere was set up. The system was capable of generating a range of cyanoacrylate concentrations over differing temperature and humidity; see tables 9.1 and 9.2.

Six tube samples were taken per experiment. The sample flow rate was 200 ml/min over a 15-minute reference time. Samples were then desorbed into 2 ml acetonitrile with 0.2% phosphoric acid added. Six impinger samples containing 10 ml acetonitrile with 0.2 % phosphoric acid were taken at the same time for use as a reference method. Flow rate for the impingers was 500 ml/min and samples were made back up to 10 ml prior to analysis.

Analysis was carried out by HPLC with UV detection. The HPLC-UV equipment comprised; Waters 600 controller, Waters 996 Diode Array Detector (DAD) and Waters 717plus autosampler. HPLC column was a Waters spherisorb 5 $\mu$ m ODS2 4.6 x 250 mm, the column was kept at a constant 0°C by a Jones 7955 heater/chiller system. Injection volume was 50  $\mu$ l. Column flow was 1 ml/minute using a 70/30 0.2 % aqueous phosphoric acid/acetonitrile mobile phase. Using this instrument set-up, the retention times were; MCA 9.1 minutes and ECA 15.5 minutes. The processing wavelength used was 212.5 nm

#### *Short-term storage trials*

As samples are often sent to analytical laboratories by post it can often be a number of days after sampling before the Tenax sorbent beds can be solvent desorbed prior to analysis; it was decided that an assessment of any potential losses incurred during transit should be made.

A series of tubes were loaded up at levels slightly above the work place exposure limit, some were analysed immediately and others were left in sealed bags at room temperature for 5 days.

### 9.3 RESULTS

Tables 9.1 and 9.2 indicates the performance (pass/fail) of the samplers under the various conditions.

Satisfactory performance of the analytical method, is based on the relative overall uncertainty;

$$\text{Relative overall uncertainty, } A = \frac{B - C + 2S}{C} \times 100 \%$$

Where:

B = mean value of results from repeated measurements using the test method (must be at least 6)

C = true or accepted reference value of concentration (i.e. the mean of the impingers results)

S = standard deviation of measurements taken by the test method

BS EN 482 requires that, for the purposes of measuring for comparison with limit values, the overall uncertainty is  $\leq 30 \%$  at  $0.5 - 2 \times \text{WEL}$  and  $\leq 50 \%$  at  $0.1 - 0.5 \times \text{WEL}$ .

Table 9.1. Validation data for phosphoric acid treated tube.

<b>EXPERIMENT</b>	<b>Concentration (15-min TWA WEL)</b>	<b>Temperature (°C)</b>	<b>Relative Humidity (%)</b>	<b>Validation – Pass/Fail</b>
<b>Ethyl cyanoacrylate (ECA)</b>				
1	0.1	10	10	PASS
2	0.1	10	60	PASS
3	0.1	30	40	PASS
4	0.1	30	10	PASS
5	2	10	10	PASS
6	2	30	10	PASS
7	2	30	60	FAIL
8	2	10	60	PASS
9	1	20	10	PASS
<b>Methyl cyanoacrylate (MCA)</b>				
10	0.5	30	60	FAIL
11	0.5	10	10	PASS
12	1 x	20	35	PASS
13	2 x	20	35	PASS
14	2 x	10	20	FAIL
15	2 x	30	75	FAIL

Table 9.2. Validation data for steel mesh/polypropylene o-ring Tenax tube.

<b>EXPERIMENT</b>	Concentration (15-min TWA WEL)	Temperature (°C)	Relative Humidity (%)	Validation – Pass/Fail
<b>Ethyl cyanoacrylate (ECA)</b>				
16	0.1	10	10	PASS
17	0.1	10	60	PASS
18	0.1	30	50	PASS
19	0.1	30	10	PASS
20	2	10	10	PASS
21	2	30	10	PASS
22	2	30	60	PASS
23	2	10	60	PASS
24	1	20	10	PASS
<b>Methyl cyanoacrylate (MCA)</b>				
25	0.5	30	65	PASS
26	0.5	10	10	PASS
27	1	20	35	PASS
28	2	20	35	PASS
29	2	10	20	PASS
30	2	30	70	FAIL

Table 9.3. Validation of short-term storage of cyanoacrylates.			
Tube type	Concentration – desorbed immediately	Concentration – desorbed 5 days later	Percentage lost over short term storage
ECA			
H <sub>3</sub> PO <sub>4</sub> treated	0.4520 ppm	0.4334 ppm	4 %
Steel mesh/o-ring	0.7311 ppm	0.6719 ppm	8 %
MCA			
H <sub>3</sub> PO <sub>4</sub> treated	0.7274 ppm	0.6830 ppm	6 %
Steel mesh/o-ring	0.8113 ppm	0.7266 ppm	10 %

#### 9.4 DISCUSSION AND CONCLUSIONS

The steel mesh tube performed very well in the validation, failing just the one experiment (MCA atmosphere at 2 x WEL, high temperature and high humidity). The conditions under which the validation failed are unlikely to be experienced in the workplace environment. Additionally the use of MCA is far less common than ECA.

The phosphoric acid tube did not perform quite as well, with four failures. However, all but one of these was at high temperature and humidity.

There are some small losses over a 5-day storage period; thus it is recommended that tubes be desorbed immediately after sampling.

The tube of choice for use in field work is the steel mesh with polypropylene o-ring.

## **10           ACRYLAMIDE IN COOKING FUME (JS2003162)**

Work was carried out in completion of an existing project (JS2003162, report number OMS/2004/10) on the investigation of acrylamide in cooking fume. Analytical method development and analysis of food samples for acrylamide were investigated.

## 11 PUBLICATIONS AND PRESENTATIONS

### 11.1 PUBLICATIONS

A draft paper entitled “An occupational hygiene survey of exposure to polycyclic aromatic hydrocarbons, has been accepted by The Annals of Occupational Hygiene for publication. The paper summarises the activity carried out by HSL for HSE over the past 15 years or so on exposure to polycyclic aromatic hydrocarbons. The main theme of the paper is concerned with an occupational hygiene survey carried out between 1998 and 2000 on 25 sites. The findings of the survey have subsequently informed HSE’s on the risks of exposure to coal tar pitch volatiles and polycyclic aromatic hydrocarbons in the workplace and has led to the introduction of a Biological Monitoring Guidance value (BMGV) in 2004 which is now being used to assess exposure from all routes (inhalation or skin absorption) in the workplace.

The published paper is available online (Unwin et al., 2006).

The draft abstract is given below

#### **Abstract**

A cross-industry occupational hygiene survey was commissioned by the Health and Safety Executive (HSE) to determine what levels of PAH exposure are found in UK industry and to determine if one or more target analytes were suitable as a marker for assessing total exposure to PAHs. There were no broadly applicable UK exposure standards for assessing total exposure to PAHs. Until 1993 a guidance value for assessing exposure in coke ovens only, where PAH exposure is known to be the highest, was based on gravimetric analysis of cyclohexane-soluble material. Biological monitoring based on urinary 1-hydroxypyrene (1-OHP) is widely reported to be an effective indicator of exposure to both dermal and inhalation routes but there was no UK guidance value. The survey involved an occupational hygiene study on 25 sites using both airborne monitoring of a total of 17 individual PAHs and biological monitoring. The results showed 8-h TWA levels of total PAH in air ranged from 0.4 to 1912.6  $\mu\text{g}/\text{m}^3$  with a GM of 15.8  $\mu\text{g}/\text{m}^3$ . The profile of PAHs was dominated by naphthalene, the most volatile 2-ring PAH. Airborne benzo(a) pyrene (BaP) correlated well ( $r^2 = 0.971$ ) with levels of carcinogenic 4 – 6 ring PAHs and was an effective marker of exposure for all industries where significant particle bound PAH levels were found and in particular for CTPV exposure. The 8-h TWA levels of BaP ranged from <0.01 to 6.21  $\mu\text{g}/\text{m}^3$  with a GM of 0.036  $\mu\text{g}/\text{m}^3$ , 90% were less than 0.75  $\mu\text{g}/\text{m}^3$  and 95% were less than 2.0  $\mu\text{g}/\text{m}^3$ . Two hundred and eighteen urine samples collected from different workers at the end of shift and 213 samples collected pre-shift next day were analysed for 1-OHP. Levels of 1-OHP in end of shift samples were generally higher than those in pre-shift next day samples and showed a good correlation ( $r^2 = 0.768$ ) to airborne BaP levels if samples from workers using respiratory protection or with significant dermal exposure were excluded. Urinary 1-OHP in end of shift samples ranged from the limit of detection (0.5  $\mu\text{mol}/\text{mol}$  creatinine) to 60  $\mu\text{mol}/\text{mol}$  creatinine with a mean of 2.49  $\mu\text{mol}/\text{mol}$  and a 90% value of 6.7  $\mu\text{mol}/\text{mol}$  creatinine. The highest 1-OHP levels were found in samples from workers impregnating timber with creosote where exposure was dominated by naphthalene. If the 11 samples from these workers were excluded from the data set the 90% value for end of shift urine samples was 4  $\mu\text{mol}/\text{mol}$  creatinine ( $n = 207$ ) and this value has since been adopted by HSE as a biological monitoring benchmark value.

A publication on some of the NCO work presented in Section 6 has been published in the Annals of Occupational Hygiene (White, 2006).

The abstract is given below;

### **Abstract**

Isocyanates are potent sensitizers and the largest cause of occupational asthma in the UK. Probably the method most commonly used worldwide for the determination of organic isocyanates in air is MDHS 25/3. This method uses an electrochemical detector (EC) to quantify oligo-isocyanates (oligo-NCO) using derivatized NCO monomers as calibrants. This paper gives the results of a validation exercise using this method to quantify industrially used monomeric and oligo-isocyanate formulations. An expanded uncertainty of ~ 56% was found for 7 formulations spiked onto 2 sampler types at four spiking levels. No differences were found between the analytical results obtained from spiked filters or spiked impinger/filter samplers. Also presented is work on the validation of the EC/UV ratio approach used in MDHS 25/3 to identify isocyanate-derived peaks. A total of 58 industrially used non-monomeric NCO formulations were studied. These formulations gave 138 peaks that were identified using MDHS 25/3 as oligo-NCO MP derivatives. One of these peaks had an EC/UV ratio outside the range given in MDHS 25/3. Work describing the use of an internal standard to improve the variability of the EC detector is reported. Finally solutions to practical problems encountered during long-term sampling using an impinger are given.

## **11.2 ORAL PRESENTATIONS**

As part of a HSE session on NCO, HSL was asked to make a 20 minute presentation on measuring personal exposure to airborne NCO at the BOHS 2004 annual conference, held in Stratford. For this a slide show was prepared, using PowerPoint, plus an accompanying talk which was subsequently presented at the conference. The presentation was well received by the audience. The PowerPoint slide show has since been re-used by one of HSE's specialist occupational hygiene inspectors as part of a similar presentation and is available from Chris Keen. Similar presentations were also made to local BOHS meetings i.e. London, Newcastle and Cardiff.

## 12 QUALITY

HSL consider the quality of all analyses to be of utmost importance. The quality of the results (generated using our standard procedures) is assured through the use of internal quality controls (QC) and participation in external quality assurance (QA) schemes and inter-comparison studies where available. The category 1 performance achieved in the Workplace Analysis Scheme for Proficiency (WASP) for NCO and formaldehyde analysis carried out during the lifetime of this project demonstrates our commitment to the generation of high quality data. The performance data is detailed in table 12.1.

Table 12.1 QA intercomparison study (WASP) details for NCO and formaldehyde.				
Round	STUDY	NUMBER OF PARTICIPANTS	HSL RANKING	ANALYST
58	MDI	16	2	J White
59	MDI	18	3	J White
60	MDI	15	3	J White
62	MDI	14	9	J White
63	MDI	14	9	G McConnachie
64	MDI	14	8	G McConnachie
65	MDI	16	6	G McConnachie
66	MDI	11	2	G McConnachie
58	formaldehyde	31	7	J Cuthbert
59	Formaldehyde	33	9	J Cuthbert
60	Formaldehyde	33	10	J Cuthbert
62	Formaldehyde	31	5	J Cuthbert
63	Formaldehyde	34	1	G McConachie
64	Formaldehyde	30	1	G McConachie
65	formaldehyde	38	3	G McConachie

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