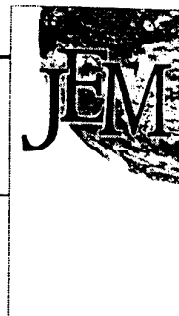


# Airborne thermal degradation products of polyurethane coatings in car repair shops



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A methodology for workplace air monitoring of aromatic and aliphatic, mono- and polyisocyanates by derivatisation with di-*n*-butylamine (DBA) is presented. Air sampling was performed using midget impinger flasks containing 10 ml of 0.01 mol l<sup>-1</sup> DBA in toluene and a glass-fibre filter in series after the impinger flask, thereby providing the possibility of collecting and derivatising isocyanates in both the gas and particle phases. Quantification was made by LC-MS, monitoring the molecular ions [MH]<sup>+</sup>. Air samples taken with this method in car repair shops showed that many different isocyanates are formed during thermal decomposition of polyurethane (PUR) coatings. In addition to isocyanates such as hexamethylene (HDI), isophorone (IPDI), toluene (TDI) and methylenediphenyl diisocyanate (MDI), monoisocyanates such as methyl (MIC), ethyl (EIC), propyl (PIC), butyl (BIC) and phenyl isocyanate (PhI) were found. In many air samples the aliphatic monoisocyanates dominated. During cutting and welding operations, the highest levels of isocyanates were observed. In a single air sample from a welding operation in a car repair shop, the highest concentrations found were: MIC, 290; EIC, 60; PIC, 20; BIC, 9; PhI, 27; HDI, 105; IPDI, 39; MDI, 4; and 2,4-TDI and 2,6-TDI 140 µg m<sup>-3</sup>. Monitoring the particle size distribution and concentration during grinding, welding and cutting operations showed that ultrafine particles (<0.1 µm) were formed at high concentrations. Isocyanates with low volatility were mainly found in the particle phase, but isocyanates with a relatively high volatility such as IDI, were found in both the particle and gas phases.

## Introduction

Polyurethane (PUR) products are used in large amounts in the car industry, as different lacquers, flexible foams, glues and electrical circuit boards, etc. Isocyanates as air pollutants constitute well known occupational hazards and exposure can result in respiratory diseases.<sup>1-5</sup> In the car industry, isocyanate-induced asthma among spray painters is a well known occupational disease.<sup>6-8</sup> In addition to the obvious exposure risk when workers are handling isocyanates in the production of PUR products, workers who are heating PUR can also be exposed to isocyanates.<sup>9,10</sup> Isocyanates can also be formed during thermal decomposition of other materials that do not contain PUR or isocyanates as such.<sup>11</sup> Thus there is a clear need for methods to assess the exposure to airborne isocyanates.

Several methods are used today for monitoring aromatic and aliphatic diisocyanates in air.<sup>12-15</sup> The authors have previously found that air sampling using impinger flasks and di-*n*-butylamine (DBA) in the sampling solution provided fast derivatisation of isocyanates. The removal of DBA in the following work-up procedure greatly facilitated the chromatography and allowed the use of DBA at high concentrations in the sampling liquid. The derivatisation procedure and the LC-MS method were found to be robust, with no influence from interfering compounds.<sup>9</sup>

The purpose of this study was to develop a method for the sampling and determination of aromatic and aliphatic, mono- and polyisocyanates in both the gas and particle phases. The method should be suitable for workplace monitoring. In this

paper, the method has been applied to the study of airborne isocyanates emitted in car repair shops.

## Experimental

### Sampling

**The impinger-filter sampling system.** For the sampling of airborne isocyanates, midget impinger flasks (30 ml, old model; Werner-Glas & Instrument AB, Stockholm, Sweden) containing 10 ml of 0.01 mol dm<sup>-3</sup> DBA in toluene were used. A 13 mm glass-fibre filter with a pore size of 0.3 µm (type AE; SKC Inc., Eighty Four, PA, USA) was placed in series after the impinger flask. Filter holders (Swinnex 13 mm polypropylene) were from Millipore (Bedford, MA, USA). After sampling the filter was immediately placed in a test tube containing 10 ml of 0.01 mol dm<sup>-3</sup> DBA in toluene. The airflow through the sampling system was 1.0 l min<sup>-1</sup>. Particles smaller than about 1.5 µm passed through the impinger and were collected on the filter.<sup>16</sup> Gas molecules were collected in the sampling liquid by diffusion and absorption.

A personal air sampling pump (AirChek 2000 universal sampler; SKC Inc.) and a charcoal vapour trap was used with the impinger-filter system. A DryCal<sup>®</sup> DC-Lite flow meter (BIOS International Corp., NJ, USA) was used for airflow measurements.

**Particle characterisation.** Particle size measurements of the workplace aerosol were made with an electrical differential mobility analyser (DMA). The DMA was combined with a

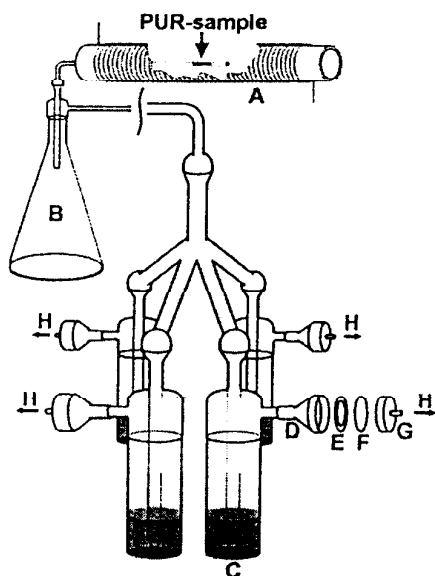


Fig. 1 The sample heating system with parallel sampling, using four impinger-filter systems. A: tube furnace; B: mixing chamber; C: all-glass midjet impinger; D: filter cassette, inlet; E: gasket; F: glass-fibre filter; G: filter cassette, outlet; H: connection to vapour trap and sampling pump.

condensation particle counter (CPC) to a Scanning Mobility Particle Sizer model 3934, consisting of an Electrostatic Classifier model 3071 and a CPC model 3022A (TSI Inc., St. Paul, MN, USA). Each measurement was made during 135 s ( $t_{up} = 90$  s,  $t_{down} = 45$  s), in the particle diameter ( $D_p$ ) range 0.014–0.7  $\mu\text{m}$ .

**Sample heating system.** A tube furnace (model ETF 30/12; Entech, Angelholm, Sweden) connected to a 2 l mixing chamber was used for testing PUR samples at different temperatures (Fig. 1). All connections were made of glass. The system was also used for evaluation of the influence of the DBA concentration on the impinger-filter sampling system. From one outlet of the mixing chamber, four parallel samples were collected ( $1.0\text{ l min}^{-1}$ ) during 10 min. The average PUR sample weighed 10 mg.

#### Analysis

**Work-up procedure.** The sampling solution from the impinger flask and the solution containing the filter were spiked with 100  $\mu\text{l}$  acetonitrile solution containing the deuterium-labelled isocyanate DBA derivatives (about 0.3  $\mu\text{g}$ ). The filter solutions were then placed in an ultrasonic bath for 5 min and the solution was transferred to a new test tube. The sample solutions were evaporated in a vacuum centrifuge (model SC210A; Savant Instruments Inc., Holbrook, NY, USA) and the residues were dissolved in 0.5 ml acetonitrile.

The purity and stability of the DBA derivatives have been studied in previous papers.<sup>9,10,11,17</sup>

**Liquid chromatography-mass spectrometry.** A mass spectrometer (Platform LCZ; Micromass, Altrincham, Cheshire, UK) was used in the electrospray mode monitoring positive ions ( $\text{ESP}^+$ ). Quantitative measurements were made by monitoring the molecular ion  $[\text{MH}]^+$ . The cone voltage was 30–50 V, the temperature of the ion source was 110°C and the desolvation temperature was 150°C. Selected ion recording (SIR) was performed by monitoring 12 ions with a dwell time of 0.2 s. Full continuous mass spectra of 100–1100 u were obtained during

4 s, which were refined by maximum entropy reconstruction. The mass spectrometer was connected to a Phoenix 40 micro-LC pump (Fisons Instruments, Carlo-Erba, Milan, Italy). Partially filled loop injections of 4  $\mu\text{l}$  in a 9.6  $\mu\text{l}$  loop volume containing 5.6  $\mu\text{l}$  of a wash liquid of 50:50% v/v acetonitrile-water solution, were made with a CMA/200 autosampler (Carnegie, Stockholm, Sweden).

The DBA-isocyanate derivatives were analysed using linear gradient elution for 30 min with a mobile phase of acetonitrile-water (from 50:50 to 95:5% v/v) and 0.05% formic acid. The flow rate was 40  $\mu\text{l min}^{-1}$ . The LC column was a Hypersil C18, 150  $\times$  1.0 mm with 5  $\mu\text{m}$  particles (Hypersil, Cheshire, UK). The influence of the cone voltage on the formation of the  $[\text{MH}]^+$  ions for the different derivatives was optimised to achieve the best response possible.

The variation of the slopes and the influence of external or internal calibration from calibration plots ( $n = 10$ ) analysed during a period of 6 months was studied.

**Preparation and characterisation of deuterium labelled internal standards and aliphatic monoisocyanate-DBA derivatives.** The deuterium-labelled internal standard derivatives of MIC-, HDI-, 2,4-TDI-, 2,6-TDI- and MDI-DBA, and the monoisocyanate derivatives, MIC-, EIC-, PIC- and BIC-DBA, have been prepared with the method described for monoisocyanates, deuterium-labelled MIC and deuterium-labelled HDI in previous papers.<sup>11,17</sup>

MIC-, EIC-, PIC- and BIC-DBA derivatives have been analysed using cold on-column GC with thermoionic detection (TSD).<sup>11</sup> Elemental analysis of 2,4-TDI-, 2,6-TDI- and 4,4'-MDI-DBA has been made previously.<sup>14</sup>

A nitrogen-specific HPLC detector (model 8060; ANTEK Instruments, Houston, TX, USA) was used for chemiluminescence detection (CLND) in the investigation of the purity and stability of the synthesised derivatives.

**Chemicals.** Toluene, isooctane and HPLC grade acetonitrile were obtained from Lab-Scan (Dublin, Ireland). Butylamine and ethylchloroformate were obtained from Janssen Chimica (Beerse, Belgium) and formic acid and butan-1-ol from Merck (Darmstadt, Germany). Methylamine was obtained from Riedel-de Haën AG (Seelze, Germany) and ethylamine was obtained from Sigma (St. Louis, MO, USA). DBA, propylamine and trideuterium-labelled methylamine were obtained from Acros Organics (NJ, USA). Dideuterium-labelled 4,4'-methylenedianiline, trideuterium-labelled 2,6- and 2,4-TDA were from Synthelec (Lund, Sweden). Tetradeuterated HDA was from MSD isotopes (Montreal, Quebec, Canada). 2,6-TDA was from TCI (Tokyo Kasei Kogyo Co. Ltd, Tokyo, Japan).

#### Characterisation of the impinger-filter sampling system

The influence of the DBA concentration on the impinger-filter system was studied by sampling thermal degradation products from PUR coating samples, heated to 400°C in the sample heating system. Four samples were collected simultaneously with impinger-filter systems and the procedure was repeated four times. The concentrations studied were 0, 0.001, 0.01 and 0.1  $\text{mol dm}^{-3}$  DBA in toluene. The filters were transferred to 10 ml of 0.01  $\text{mol dm}^{-3}$  DBA solution immediately after sampling. To the samples for which the impinger solution did not contain DBA, 50  $\mu\text{l}$  of pure DBA was added immediately after sampling.

The formation of MIC-, EIC-, PhI-, HDI-, TDI- and IPDI-DBA derivatives was studied by heating PUR coating samples from a car to 350°C. The sampling method variation for the amount of isocyanates was studied in seven pairs of samples from the same PUR coating. The influence of the time between the end of sampling and the transfer of the filter to a

reagent solution was studied. This was made by comparing filters transferred immediately and up to 60 min after the sampling to 10 ml of  $0.01 \text{ mol dm}^{-3}$  DBA. The influence of the presence of  $0.01 \text{ mol dm}^{-3}$  TDA in the sampling solution was studied. The possible transfer of isocyanates or derivatives from one impinger-filter system to another, placed in series after the first, was also studied during 10 min of sampling. Losses of MIC-DBA derivative from the filter was studied by adding  $0.5 \mu\text{g}$  MIC-DBA to a filter and thereafter sampling clean air for 15 min at  $1 \text{ l min}^{-1}$ .

#### Thermal degradation of PUR coatings

Samples ( $n=69$ ) of about 10 mg of two different PUR coatings were heated, to temperatures in the range  $100\text{--}500^\circ\text{C}$ , in the sample heating system. The emission of isocyanates was studied by air sampling.

#### Field measurement in car repair shops

Air samples were collected from two car repair shops during grinding, cutting and welding in car metal sheets. Particle size and concentration measurements were made continuously during operation. Isocyanate samples were collected in the breathing zone of the worker. Particle characterisation was made continuously at a distance of 0.3–2 m from the worker.

At the first car repair shop (A), measurements ( $n=24$ ) were made in a newly built room, seen in Fig. 2, used for prototype rebuilding at a car manufacturer. The room ( $7 \text{ m} \times 7 \text{ m}$ , 4 m high) had mechanical ventilation of displacement type with an air exchange rate of approximately  $10 \text{ h}^{-1}$ . One local ventilation exhaust ( $1000 \text{ m}^3 \text{ h}^{-1}$ ) was used during measurement.

The second car repair shop (B) was an ordinary car repair shop with six workplaces. Each workplace had a local exhaust, but was not otherwise separated from the other workplaces. The building had mechanical ventilation but the air exchange rate was unknown. Very short duplicate air samples (10–40 s) were taken during a welding operation. The local ventilation exhaust was not used during this operation. The samples were taken 0.2 m from the welding spot.

## Results

#### The impinger-filter sampling system

There was a trend of increasing total amount of MIC-, PhI- and TDI-DBA derivatives with the increase of DBA concentration in the sampling solution up to  $0.01 \text{ mol dm}^{-3}$  (Table 1). HDI-DBA and IPDI-DBA on the filter increased

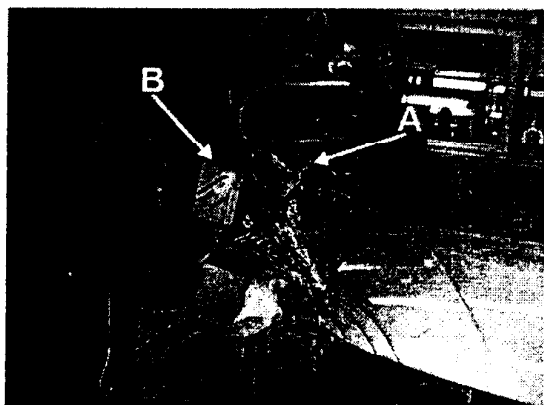


Fig. 2 Air sampling during a cutting operation in car repair shop A. A: impinger-filter sampling system; B: direct reading filter-tape instrument. Results from this instrument are not presented in this paper.

with the DBA concentration. However, the amount of aliphatic isocyanate derivatives in the impinger was equal for all DBA concentrations. No derivatives of MIC or PhI were seen on the filter for any of the DBA concentrations studied.

When comparing the sampling systems with pure toluene and  $0.01 \text{ mol dm}^{-3}$  DBA as sampling solutions, 40–80% less derivatives were seen in the impinger containing pure toluene, except for HDI and IPDI where the yield seems to be independent of the DBA concentration. On the filters at least 95% less derivatives were found for HDI, 2,6-TDI, and 2,4-TDI. For IPDI about 50% less derivatives were found on the filter in the sampling system using pure toluene.

The variation of the total amount of the sampled isocyanates, in seven pairs of parallel samples, were for MIC, EIC, PhI, HDI and TDI < 3% and for IPDI < 12%. The total amount of isocyanates varied less than 7% and the mean variation was 3%, within the pairs. The amount of isocyanates in the impinger flask varied by less than 8% and the mean variation was 3%, within the pairs. The amount of isocyanates on the filter varied less than 17% and the mean variation was 6%, within the pairs.

Within the analytical errors, the time between the end of sampling and the transfer of the filter to a reagent solution had no influence on the yield of HDI, TDI and IPDI.

Within the analytical errors, the presence of  $0.01 \text{ mol dm}^{-3}$  TDA in the sampling solution had no influence on the yield of MIC, EIC, PhI, 2,4-TDI, 2,6-TDI, HDI or IPDI.

When sampling isocyanates using two impinger-filter systems in series, no isocyanate derivatives were detected in the second sampling system. When spiking isocyanates to one impinger flask and thereafter connecting it to an impinger-filter system no isocyanate derivatives were detected in the impinger solution or on the filter.

No loss of MIC-DBA derivative was seen, when 15 l of air was drawn through a filter spiked with  $0.5 \mu\text{g}$  of MIC-DBA derivatives.

#### Thermal decomposition of PUR coatings

The amount of isocyanates released from samples of PUR coating heated to temperatures in the range  $100\text{--}500^\circ\text{C}$  is shown in Fig. 3. Of the total sample weight, up to 1% was emitted as different isocyanates. Large differences were observed for different kinds of coatings. At temperatures <  $350^\circ\text{C}$  isocyanate monomers such as TDI, HDI, and IPDI dominated, whereas at temperatures >  $350^\circ\text{C}$  monoisocyanates dominated. This was a typical pattern found for many different kinds of coatings. Isocyanates in both the gas and particle phases were observed.

#### Chromatography and mass spectrometry

Using gradient elution during 30 min (from 50:50 to 95:5% v/v acetonitrile-water and 0.05% formic acid) the resolution was sufficient for separation of the 11 standard derivatives. Formic acid was used in the mobile phase to obtain more reproducible mass spectra. The deuterium-labelled internal standards eluted a few seconds earlier than the undeuterated isocyanates. To achieve the best response as possible the cone voltage had to be individually optimised as shown in Fig. 4.

#### Quantification

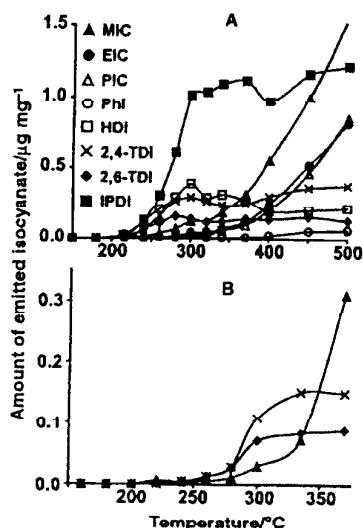
Aliquots of 10 ml toluene solutions, containing  $0.01 \text{ mol dm}^{-3}$  DBA, were spiked with, IPDI, HDI, 4,4'-MDI, 2,4-TDI, 2,6-TDI and PhI. The aliquots were also spiked with the DBA-derivatives of MIC, EIC, PIC and BIC to six concentrations in the range  $0.01\text{--}0.7 \mu\text{g}$  isocyanate in the sample. The sample work-up procedure was then performed. Using SIR and peak area ratio measurements linear calibration graphs were obtained with correlation coefficients of between 0.9970 and

**Table 1** The total amount of isocyanates in both impinger and filter when different concentrations of DBA in toluene were used as sampling solutions. The total amount of isocyanates (T), the amount of isocyanates in the impinger flask (I) and the amount of isocyanates on the filter (F) found in a sample is given as a percentage of the total amount of isocyanates found when using 0.01 mol dm<sup>-3</sup> DBA as sampling solution (average of 4 samples)

	DBA concentration in sampling solution/mol dm <sup>-3</sup>											
	0			0.001			0.01			0.1		
	I	F	T	I	F	T	I	F	T	I	F	T
MIC	19	0	19	82	0	82	100	0	100	95	0	95
PhI	70	0	70	100	0	100	100	0	100	91	0	91
HDI	74	1.2	75	75	11	86	76	24	100	71	34	105
2,4-TDI	20	2.3	22	62	32	94	56	44	100	45	53	98
2,6-TDI	51	1.1	52	76	20	96	69	31	100	55	41	96
IPDI	51	24	75	51	37	88	50	50	100	47	59	106

0.9999 ( $n=14$ ). The precision for HDI-DBA and for the two IPDI-DBA isomers was 1.2, 1.7 and 2.9% ( $1 \text{ nmol l}^{-1}$ ,  $n=8$ ). For MIC-, EIC-, PIC-, BIC- PhI-DBA it was <2% ( $1 \text{ nmol l}^{-1}$ ,  $n=8$ ). The precision for 2,4-, 2,6-TDI-DBA and MDI-DBA was 0.5, 0.9 and 1.4%, respectively ( $500 \text{ nmol l}^{-1}$ ,  $n=8$ ). The instrumental detection limit for aliphatic isocyanates was about 50 fmol. It was 2 fmol for aromatic isocyanates. For a 151 air sample this corresponds to 0.04 and  $0.002 \mu\text{g m}^{-3}$  for HDI and TDI, respectively.

During a period of 6 months, several calibration plots were made and the result from 10 representative series is presented in Table 2. With the exception of MDI, the relative standard deviations (RSDs) of the slopes of the standards having a corresponding deuterium-labelled internal standard were less than 4%, whereas it was 12% for MDI. The RSDs of the slopes were in the range 15–25%, for the isocyanates without a corresponding internal standard. The RSDs of the slopes, for external calibration, were in the range 23–40%. Within sample series, both external and internal calibration can be used. Between series, only internal calibration showed good consistency. The use of an appropriate internal standard clearly influences the correlation. The correlation coefficients for isocyanates with deuterium-labelled internal standards (MIC, HDI, 2,4-, 2,6-TDI, MDI) were much better, compared with the other standards (EIC, PIC, BIC, PhI, IPDI).



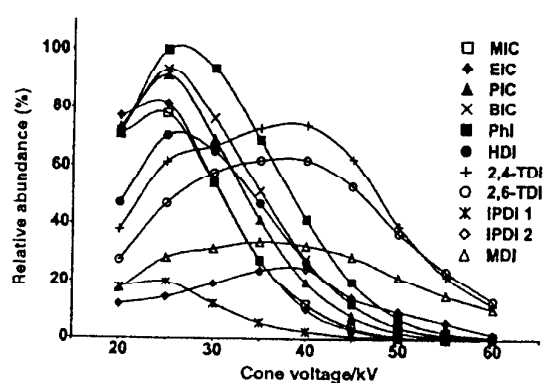
**Fig. 3** Emission of isocyanates from two different types of PUR coating ( $\mu\text{g}$  emitted isocyanates per mg PUR coating). Weighed amounts (about 10 mg) of coating removed from two different car metal sheets were thermally decomposed in a tube furnace. Samples of the generated aerosol were collected during the first 15 min of heating.

#### Airborne isocyanates in car repair shops

Air samples ( $n=24$ ) were collected during grinding, cutting and welding operations in car repair shop A. Depending on the work task, high levels of different isocyanates were observed, as seen in Fig. 5. The monoisocyanates were collected in the impinger flask (100% for MIC), whereas the isocyanates having a lower vapour pressure (IPDI and MDI), dominated on the filter (40–90% on the filter), as seen in Fig. 6.

When studying the emitted airborne particles with a diameter between 0.014 and  $0.7 \mu\text{m}$ , high concentrations of ultrafine particles ( $<0.1 \mu\text{m}$ ) were observed, even for a relatively mild treatment such as grinding (Fig. 7). During cutting operations even higher concentrations of ultrafine particles, up to  $10^7 \text{ particles cm}^{-3}$  (in this case 50 000 times the background level), were observed. The particle size distribution was found to be similar for all studied work tasks (Fig. 8). However, the size distribution changed with time, probably due to particle coagulation, from a geometric mean diameter of around  $0.05 \mu\text{m}$  to  $0.2 \mu\text{m}$ .

A welding operation was studied in car repair shop B (Fig. 9). During 8 min of welding the highest total NCO concentrations found was  $1730 \mu\text{g m}^{-3}$  (20 s sample), and the mean total NCO concentration was  $160 \mu\text{g m}^{-3}$  ( $n=18$ ). The total NCO concentration was calculated from the MIC, PhI, IPDI and IPDI concentrations, where 2,4-TDI dominated the emission with about 60% of the total NCO concentration.



**Fig. 4** The relative abundance of the  $[\text{MH}]^+$  ions, of the different isocyanate-DBA derivatives, with the variation of the cone voltage. The same volume of the same solution, containing 11 isocyanate-DBA derivatives, was repeatedly injected onto the LC-MS system. The cone voltage (20–60 kV) was varied between the injections and gradient elution was performed.

**Table 2** A comparison between external and internal calibration from calibration plots ( $n=10$ ) for isocyanate monomers, during a period of 6 months. The isocyanate-DBA derivatives were analysed using LC-ESP<sup>+</sup> monitoring selected positive molecular ions [MH]<sup>+</sup>. Each calibration plot contains single injections of seven concentrations in the range of 0–0.7  $\mu\text{g}$  isocyanate in the sample. Internal calibration was made by measuring the response ratio between the standard and the internal standard. External calibration was made by measuring the area response from the standard ( $R_1$ : correlation coefficient of all calibration plots;  $R_2$ : mean correlation coefficient of the different calibration plots; RSD: relative standard deviation of the slope)

	Internal calibration			External calibration		
	$R_1$	$R_2$	RSD (%)	$R_1$	$R_2$	RSD (%)
MIC	0.9984	0.9999	4.0	0.9251	0.9922	29
EIC	0.9748	0.9979	15	0.8762	0.9892	40
PIC	0.9395	0.9969	25	0.9139	0.9937	31
Phi	0.9785	0.9994	15	0.9221	0.9991	30
HDI	0.9994	0.9997	1.6	0.9053	0.9987	27
2,4-TDI	0.9979	0.9994	4.2	0.9177	0.9968	30
2,6-TDI	0.9990	0.9996	2.7	0.9163	0.9960	30
MDI	0.9852	0.9987	12	0.9463	0.9965	23
IPDI	0.9636	0.9994	19	0.9519	0.9976	24

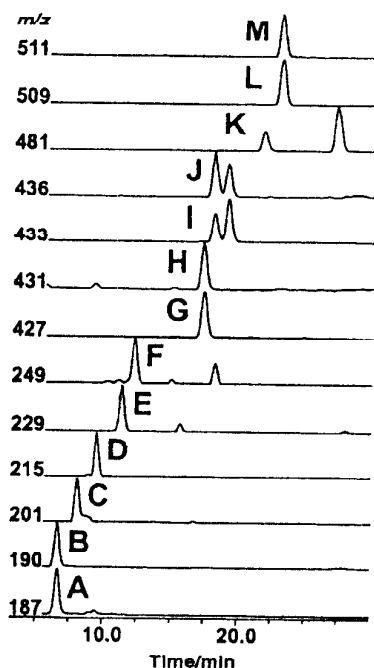
## Discussion

### The impinger-filter sampling system

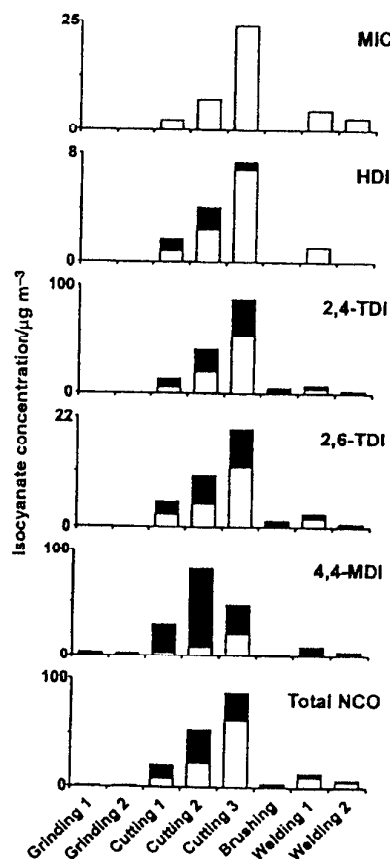
The sampling method for isocyanates in the gas and particle phases is based on the collection of the gas phase and large particles ( $> 1.5 \mu\text{m}$ ) in the midjet impinger.<sup>16</sup> When compared with a lung deposition model,<sup>18</sup> this fraction can roughly estimate particles that are mainly deposited in the nasal and tracheobronchial region. Particles collected on the filter (0.01–1.5  $\mu\text{m}$ ) may have been deposited in all parts of the respiratory tract. This comparison is very rough, but may serve as a start for the development of sampling methods that give lung

deposition relevant information needed for toxicological studies, risk assessment and the design of effective exposure preventive measures. The knowledge of health effects from exposure to sub-micrometre particles is today insufficient to formulate sampling criteria for these particles.

If the impinger sampling solution has a sufficiently high concentration of DBA, the reagent will evaporate from the solution and impregnate the filter during sampling. The DBA



**Fig. 5** Micro-LC-ESP<sup>+</sup>-SIR chromatograms of an air sample collected in an impinger flask during metal active gas (MAG) welding on a painted car, about 20 cm from the welding spot. Air concentrations are given below. The [MH]<sup>+</sup> ions are seen in chromatograms of: A, MIC-DBA (290  $\mu\text{g m}^{-3}$ ); B, (trideuterium MIC)-DBA; C, EIC-DBA (60  $\mu\text{g m}^{-3}$ ); D, PIC-DBA (20  $\mu\text{g m}^{-3}$ ); E, BIC-DBA (9  $\mu\text{g m}^{-3}$ ); F, Phi-DBA (27  $\mu\text{g m}^{-3}$ ); G, HDI-DBA (105  $\mu\text{g m}^{-3}$ ); H, (tetra-deuterium HDI)-DBA; I, TDI-DBA (140  $\mu\text{g m}^{-3}$ ); J, (trideuterium TDI)-DBA; K, IPDI-DBA (39  $\mu\text{g m}^{-3}$ ); L, MDI-DBA (4  $\mu\text{g m}^{-3}$ ); M, (dideuterium MDI)-DBA.



**Fig. 6** Isocyanate concentration in air samples, and the fractions collected in the impinger flask ( $\square$ ) and on the glass-fibre filter ( $\blacksquare$ ), taken during different operations in a car repair shop. The samples were taken with a sampling time of 5 min and collected in the breathing zone. Air concentrations of total NCO groups are calculated from the concentrations of the analysed isocyanates.

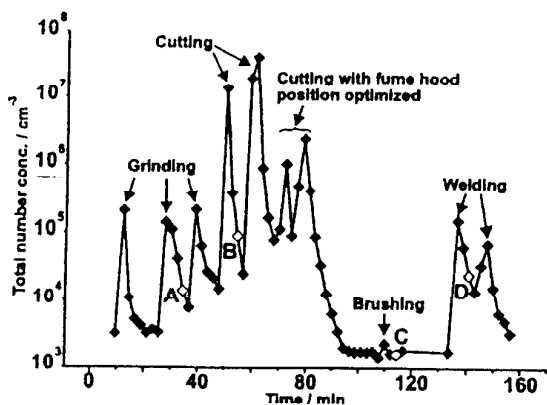


Fig. 7 The total particle number concentration ( $D_p = 0.014\text{--}0.7\ \mu\text{m}$ ) during grinding, cutting and welding on painted car metal sheet. The duration of each work task was about 5 min. The car repair shop was recently built and had a mechanical displacement type ventilation. Each data point indicates samples taken during 135 s each, about 40 cm from the working area. The size distributions for samples A–D are seen in Fig. 8. Air levels of isocyanates in the breathing zone of the worker are seen in Fig. 6.

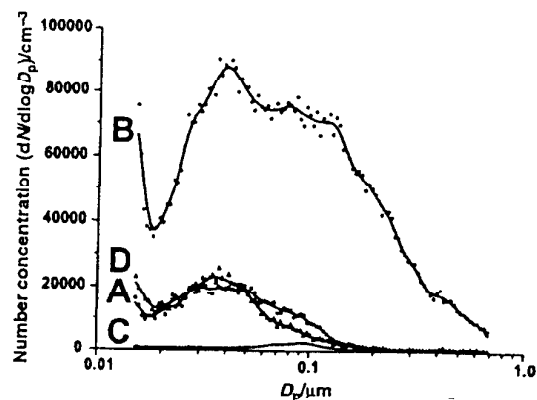


Fig. 8 Particle size distribution during grinding (A), cutting (B) and welding (D) of a painted car metal sheet and the particle size distribution of the background (C). The samples were taken during 135 s about 40 cm from the working area. The geometric mean diameter for the aerosol formed during grinding, cutting and welding was  $0.05\ \mu\text{m}$  (geometric standard deviation = 1.9). After the aerosol had aged, a mode with geometric mean diameter of  $0.2\ \mu\text{m}$  was formed. This mode was also seen in the background measurement (C).

on the filter is thereby refreshed continuously during sampling. This is indicated by the variation of the relative amount of isocyanate derivatives found on the filter when the DBA concentration in the sampling solution was varied (Table 2). If no derivatisation reagent evaporates from the impinger sampling solution and reaches the filter, there will be large losses of the isocyanates sampled on the filter. This indicates that a volatile reagent is necessary for the derivatisation process on the filter. If the filter is impregnated with a non-volatile reagent, there may be losses due to the poor diffusion rate of the reagent into the collected particles.

The result that the derivatisation of gas phase aliphatic isocyanates in the impinger flask is independent of the DBA concentration may depend on the fact that aliphatic isocyanates have slow reaction rates. They will therefore not be influenced to any greater extent by interfering compounds, even when pure toluene was used as sampling liquid, and are readily derivatised upon addition of DBA after sampling. In contrast to the impinger results, the DBA concentration had a significant impact on the amount of collected and derivatised isocyanates on the filter.

The mass flow of particles reaerosolised from the impinger solution to the filter during sampling is very low at a flow rate of  $1\ \text{l}\ \text{min}^{-1}$ . Hence, only volatile components in the impinger solution will be transferred to the filter. This is demonstrated by the absence of isocyanate–DBA derivatives on the filter after 10 l of air has flowed through the impinger–filter system, with the impinger solution containing a high concentration of derivatives. The formation of the isocyanate DBA derivatives is also sufficiently fast to prevent the evaporation of volatile isocyanates from the sampling solution. For the derivatisation and determination of isocyanates in workplace air, the DBA in a  $0.01\ \text{mol}\ \text{dm}^{-3}$  solution is in very large excess. This ensures fast reaction rates, robustness towards interfering compounds and enough reagent vapour reaching the filter to start the derivatisation process on the filter, without having an inconveniently large emission of DBA from the personal sampling pumps.

#### Thermal decomposition of PUR coatings

The isocyanates formed during thermal degradation of PUR polymers are typically mono- and diisocyanates, some of which are used in the manufacturing of lacquers. In addition, other kinds of isocyanates are formed such as the monoisocyanates seen in Fig. 5, but the mechanisms are not clearly understood at

present. The most important factors seem to be the degradation temperature and the duration of the applied heat. It is known that the urethane bonding will break at elevated temperatures and that the thermal stability depends on both the type of isocyanate and the type of polyol used in the PUR system, e.g., aliphatic or aromatic. The aromatic isocyanate–aromatic polyol urethane group is reported to have a top temperature stability of  $< 120\ ^\circ\text{C}$ .<sup>19</sup> Alkyl isocyanate–alkyl polyol has a top temperature stability of  $> 250\ ^\circ\text{C}$ .

The presence of an aerosol containing isocyanates after thermal degradation of PUR is clearly demonstrated in Fig. 6. Volatile isocyanates are collected in the impinger flask, indicating that the compounds are mainly distributed in the gas phase. Isocyanates of low volatility are mainly found on the filter indicating that these are mainly present in particles (smaller than  $1\ \mu\text{m}$ ).

In, for example, soft and rigid commercial foams, there are also urea bondings due to the addition of water during manufacturing, where the hydrolysis of isocyanates to the corresponding amines takes place. In addition to isocyanates, other related compounds such as aminoisocyanates and amines are released upon thermal degradation of PUR.<sup>9,10</sup> The formation of these compounds is more complex and will be presented in a forthcoming paper. Further, other compounds

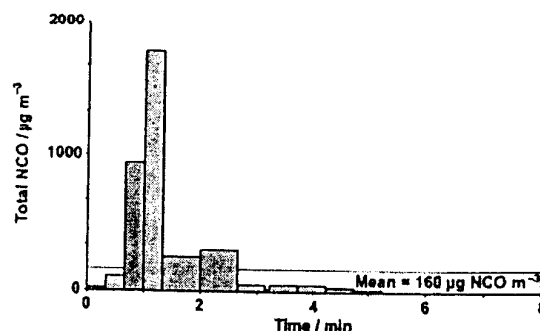


Fig. 9 Short duplicate samples (10–40 s) were taken in car repair shop B, during a welding operation that lasted for 8 min. Each bar represents a single sample. The mean total NCO concentration during the welding operation was  $160\ \mu\text{g}\ \text{m}^{-3}$  and the maximum total NCO concentration was  $1730\ \mu\text{g}\ \text{m}^{-3}$  ( $t = 20\ \text{s}$ ). The total NCO concentration was calculated from the MIC, PhI, TDI and IPDI concentrations.

in the PUR, such as fire retardants and other additives, are released when the material is heated.

#### Analysis

Thermal degradation, combustion and hydrolysis products of PUR in air results in a complex mixture of compounds occurring in both the gas and particle phases. In quantitative work, reference compounds are normally essential, but such reference compounds are missing for most of the compounds formed. Isocyanates can be analysed without derivatisation, but there are several practical limitations for the assay of work environment air samples, as the isocyanates are highly reactive and severe losses may occur. Today, essentially two methods, based on derivatisation, are used for the quantification of isocyanates.

One method is based on the selective formation of, for example, a urea derivative containing a chromophore that is expected to give a selective and equimolar response. Using a known reference isocyanate derivative, quantification of unknown isocyanate compounds can be made. Several reagents have been proposed for this purpose.<sup>20,21</sup> The determination of the total isocyanate concentration in air samples does not give any information about the types or forms of isocyanates present in the air. This information may be essential for the risk assessment of the exposure of such complex mixtures as those emitted from the thermal degradation of PUR.

The second method is based on quantification of isocyanates against known reference isocyanate derivatives that have been synthesised. Such derivatives are not readily available and they are costly to synthesise. Alternatively, the addition of known amounts of reference isocyanates to reagent or sample solutions prior to analysis can be performed. References are only available for a few isocyanates and their dilution presents a problem, as several isocyanates are difficult to dissolve in a solvent that minimises hydrolysis and other unwanted reactions.<sup>22</sup>

The use of gradient elution and selective detection was necessary for the determination of mono- and diisocyanates within the same chromatographic run. If a large fraction of the sample is injected onto the chromatographic system or the sample is diluted in a small volume, low detection limits can be obtained. Using micro-LC, the component in the mobile phase is less diluted as compared with conventional LC. On-column focusing makes it possible to inject up to 20  $\mu\text{l}$  onto the column. At least 50 times better detection limit was achieved using columns with an internal diameter of 1 mm (flow rate 40  $\mu\text{l min}^{-1}$ ), in comparison with columns having an internal diameter of 4.6 mm (flow rate 1  $\text{ml min}^{-1}$ ). The lifetime of the column is long, and at least 5000 samples can be routinely analysed in the LC-MS system before the column performance deteriorates.

When analysing different isocyanate-DBA derivatives on the MS we observe a difference between aliphatic and aromatic isocyanates (Fig. 4). The relative abundance, of the molecular ions  $[\text{MH}]^+$ , for the aliphatic isocyanates shows a maximum at a cone voltage of about 25 kV whereas the maximum for the aromatic isocyanates is about 40 kV. The optimisation of the cone voltage is dependent on the composition of the mobile phase. Optimisation can only partly be performed by monitoring fragment ions of components diluted in the same solution that is injected directly into the MS.

When identifying unknown isocyanates, the formation of typical ions such as  $[(\text{DBA})\text{H}]^+$  ( $m/z = 130$ ),  $[(\text{DBA})\text{CO}]^+$  ( $m/z = 156$ ) and the  $[\text{MH}]^+$  greatly facilitates the interpretation of the MS spectra of the isocyanate-DBA derivatives. If internal calibration is used, it is necessary to monitor both the deuterium-labelled ions and the corresponding unlabelled ions. This limits the choice to the  $[\text{MH}]^+$ ,  $[\text{MH}_2\text{O}]^+$ ,  $[\text{MNa}]^+$  and  $[\text{MH}-129]^+$  ions and possibly a few others

depending on the molecular structure. External calibration makes it possible to quantify using other typical fragments such as  $m/z = 57$ , 130, 156, which indeed are typical for the isocyanate-DBA derivatives. However, much less precise quantifications can be made using this technique.

The CLND was found to be an important tool for quantification of isocyanate-DBA derivatives in reference solutions. In principle, any nitrogen-containing compound can be quantitatively determined. This technique will be described in a forthcoming paper.

#### Airborne isocyanates in car repair shops

The concentration of isocyanates and particles in air depends largely on factors such as the type of PUR paint, the work task, the individual work procedure and the ventilation. In a car repair shop the concentration of airborne isocyanates will vary greatly with time and work task. The typical exposure is to short concentration peaks associated with heating of PUR materials, which may last only for a few seconds, as seen in Fig. 9. The isocyanate concentrations in the peaks can be very high. The thermal degradation of different lacquers shows a great variation in both the total amount and the types of isocyanates formed, as seen in Fig. 3. About 0.1–1% of the total weight is emitted as isocyanates. When monitoring isocyanates in car repair shops, it is necessary to collect samples on many different occasions or when processing all different materials used, to get representative exposure estimation.

Note that if particles larger than 1.5  $\mu\text{m}$  are present in the air, they will be collected in the impinger together with the gas phase isocyanates. Such large particles can be emitted at, for example, spray painting operations.

Particles are formed during several work tasks in car repair shops such as grinding, cutting and welding in PUR painted metal sheets (Fig. 7). PUR in cars occurs also in glue, soft and rigid foams, under-body coatings and elastomers, which may form airborne degradation products when heated. The particle size distribution seems to be similar for the different work tasks, as seen in Fig. 8. Immediately after the formation of the aerosol, the geometric mean diameter is close to 0.05  $\mu\text{m}$ . These small particles coagulate with time to larger aggregates with a geometric mean diameter of about 0.2  $\mu\text{m}$ .

According to the ICRP lung deposition model the fractional deposition of 0.2  $\mu\text{m}$  particles can be as low as 15%, whereas 0.05  $\mu\text{m}$  particles may deposit with an efficiency of around 40% (when the subject is performing light exercise). This means that the sooner the aerosol is inhaled after the emission, the higher is the probability of deposition of the particles. If emissions happen frequently during the workday and the workers are exposed to a freshly made aerosol, the lung deposition will be higher than for an aged aerosol.

It is described in the literature that the toxicity for different isocyanates varies and that different protein adducts are formed in the body.<sup>1,23–25</sup> The deposition pattern in the respiratory system depends not only on the chemical nature of the isocyanate to which a person is exposed, but also largely on the physical form. The air monitoring method and the sampling technique used are required to give more detailed information regarding both the chemical and physical form of the air contaminants. To ensure that other workers at the same work place will not be exposed to degradation products of PUR, work tasks resulting in emissions of these air contaminants need to be isolated in a ventilated workspace.

#### Conclusions

In car repair shops, complex mixtures of isocyanates can be emitted in high amounts during operations such as grinding, cutting and welding of painted metal sheets. Since both gases and particles have to be efficiently collected and derivatised,

there are high requirements for the careful design of the sampling and analysis methods in order to determine such complex mixtures of isocyanates. The analysis has to be capable of separating, identifying and quantifying a wide range of derivatives.

The air sampling method described in this paper was found to be well suited to workplace monitoring due to its capability for collecting isocyanates in both the gas and particle phases and its robustness against interfering compounds in the sample matrix. The use of LC-MS is needed for the interpretation and quantification of the collected samples.

Samples taken in car repair shops show that many types of isocyanates, for which the toxicology is mostly unknown, are emitted. The particle size information given by the described method is yet not sufficient to correctly assess the lung deposition. The use of methods, like the one presented in this paper, are necessary for workplace monitoring of isocyanate emissions. There is also a need for continual method development to be able to better assess the health risk of exposure.

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