

Determination of hexamethylene-based isocyanates in spray-painting operations

Part 1. Evaluation of a polyurethane foam sponge sampler

Walter E. Rudzinski,^{*a} Jian Yin,^a Samuel H. Norman^a and Deborah A. Glaska^b

^a Department of Chemistry, Southwest Texas State University, San Marcos, TX 78666, USA

^b 12AMDS/SGPB, 221 3rd St. W., Randolph AFB, TX 78150-4801, USA

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A polyurethane foam (PUF) sponge was mounted in a cassette sampler and evaluated as a sorbent for the collection of hexamethylene diisocyanate (HDI) monomer and HDI-based oligomers. Recovery studies indicated $112 \pm 34\%$ average recovery of HDI monomer and $92 \pm 9\%$ and $97 \pm 25\%$ average recovery of HDI-based oligomers when using impregnated PUF sponges. The PUF sponge was also evaluated during actual spray-painting operations. In a series of side-by-side sampling events, an impinger filled with 1-(2-methoxyphenyl)piperazine (MOP) in toluene was compared directly with a cassette sampler containing a PUF sponge impregnated with MOP or 1-(9-anthracenylmethyl)piperazine (MAP) in dimethyl sulfoxide (DMSO). For the analysis of HDI-based oligomer, there is no significant difference ($p < 0.05$, $n = 7$) in the air concentration when sampling with either the PUF sponge cassette or the impinger. The results are significant because they indicate that a PUF sponge, which is more convenient than an impinger, may be used for the collection of HDI-based oligomer generated during spray-painting operations.

Introduction

Isocyanates are a significant hazard in the workplace.¹⁻⁷ Workers who are involved in the production of polyurethane foams, elastomers and fibers and in the application of polyurethane paints and coatings are all exposed to diisocyanate and polyisocyanates. These compounds irritate the nose, throat and lungs and may eventually lead to the development of bronchial asthma.²⁻⁶

A number of methods have been developed for the determination of atmospheric organic isocyanates.⁸⁻¹⁰ The Occupational Safety and Health Administration (OSHA) prescribes sample collection on a filter coated with 1-(2-pyridyl)piperazine followed by HPLC analysis.¹¹ The National Institute for Occupational Safety and Health (NIOSH) promulgates Method 5521¹² for the determination of diisocyanates in the USA. This method is an adaptation of MDHS 25, Method for Total Isocyanate in Air, developed for use in the UK.¹³ The latter two methods use a midjet impinger which is efficient both for the collection of vapor and aerosol particles with an aerodynamic particle diameter (d_p) greater than $2 \mu\text{m}$.¹⁴ For condensation aerosol particles smaller than $2 \mu\text{m}$ a filter is most efficient. Unfortunately, isocyanates are reactive and after collection on a filter they must be derivatized immediately or they will undergo reactions with polyol additives in the paint or atmospheric moisture.¹⁵

In order to take advantage of both the reaction-promoting characteristics of a solution in an impinger and the ease of use of a solid filter, we have developed a novel sampler based on a polyurethane foam (PUF) sponge impregnated with 1-(2-methoxyphenyl)piperazine (MOP) or 1-(9-anthracenyl methyl)piperazine (MAP) in dimethyl sulfoxide backed up by a fiber-glass filter impregnated with either MOP or MAP. Since the sponge-filter combination is moist and provides a tortuous path for air flow, the combination has the same minimal collection efficiency as a filter while providing some of the dissolution capability of an impinger. Since the sponge is impregnated with a derivatizing reagent in a non-volatile solvent, the isocyanate

reacts quickly with an excess of derivatizing reagent in a solution environment. The impregnated PUF cassette sampler has been evaluated for the first time during actual spray-painting operations.

Experimental

Reagents

1-(2-Methoxyphenyl)piperazine (MOP) was obtained from Fluka (Milwaukee, WI, USA). 1-(9-Anthracenylmethyl)piperazine (MAP) was synthesized and purified according to the procedure described by Streicher *et al.*¹⁶ HDI monomer (HDI), 98% pure, was obtained from Eastman Kodak (Rochester, NY, USA). Desmodur N-100 (N-100), which contains 99.3% polyisocyanate (predominately in the form of the biuret trimer of HDI), was obtained from Bayer Chemical (Pittsburgh, PA, USA).¹⁷ Polyester-based polyurethane foam (4CE) was obtained from Polyplastics (Austin, TX, USA) and polyether-based polyurethane foam (2405) from Supelco (Bellefonte, PA, USA). Glass fiber filters (25 mm) were obtained from Omega (Chelmsford, MA, USA). Dimethyl sulfoxide (DMSO) was supplied by Aldrich (Milwaukee, WI, USA). Acetonitrile (HPLC grade) and methanol were obtained from EM Science (Gibbstown, NJ, USA), acetic anhydride, glacial acetic acid and toluene from Fisher (Fairlawn, NJ, USA), phosphoric acid and sodium phosphate from Baker (Phillipsburg, NJ, USA) and sodium acetate trihydrate from Mallinckrodt (Paris, KY, USA).

Isocyanate recovery study

Preparation of standards. A 1.60 g l^{-1} HDI stock standard solution was prepared by dissolving 0.0400 g of HDI in 25.0 ml of acetonitrile. Various aliquots of this were added to 1.50 ml of 1.40 g l^{-1} MOP in DMSO. After 2 h, $10 \mu\text{l}$ of acetic anhydride

were added and the solution was diluted to a total volume of 5.00 ml with acetonitrile.

A 10.00 g l⁻¹ N-100 stock standard solution was prepared by dissolving 0.1000 g of Desmodur N-100 in 10.00 ml of toluene. Various aliquots of this solution were then added to a solution containing 1.50 ml of either 120–500 mg l⁻¹ MOP in acetonitrile or 1000 mg l⁻¹ MOP in DMSO. After 1 h, 10 ml of acetonitrile were added to the N-100 solution and the mixture was allowed to react for 12 h before heating to dryness under a gentle stream of nitrogen. A 30 µl aliquot of acetic anhydride was added to the dry residue, which was reconstituted up to 10.00 ml of methanol while agitating the solution in an ultrasonic water-bath for 15 min.

The preparation of methoxyphenylpiperazine derivatives and standards should be done in a fume hood in order to avoid exposure to isocyanate and solvent vapors. Isocyanates are known respiratory irritants.

Isocyanate recovery from a polyester-based PUF sponge.

The polyester-based PUF sponge (4CE) was soaked overnight and then washed with acetonitrile (HPLC grade) to remove impurities. Various aliquots of the polyisocyanate stock standard solution were added to the sponge, which was impregnated with a solution containing 1.50 ml of 120–500 mg l⁻¹ MOP in acetonitrile. After 30 min, 23.5 ml of a 500 mg l⁻¹ MOP in acetonitrile quenching solution were added to the sponge, the sponge was massaged repeatedly with a stirring rod and an aliquot then removed. Acetic anhydride (25–60 µl) was added and the solution filtered through a 0.45 µm nylon filter (Phenomenex, Torrance, CA, USA).

Isocyanate recovery from a polyether-based PUF sponge.

The polyether-based PUF sponge (2405) was cleaned by soaking in DMSO solution for at least 2 h before extracting with acetonitrile, then drying the sponge. A 1.5 ml portion of 1000 mg l⁻¹ MOP in DMSO was added to the sponge, which was squeezed until just moist. Next, an appropriate volume of concentrated isocyanate (1.600–10.00 g l⁻¹) was carefully distributed over the top of the sponge. After 1 h, the sponge was immersed in 10 ml of acetonitrile, allowed to sit overnight, then extracted twice more with 10 ml aliquots of acetonitrile. A 20 µl volume of acetic anhydride was added, the extracts were combined, then the solution was evaporated to dryness under a gentle stream of nitrogen. The precipitate was then reconstituted to a total volume of 5 ml with methanol.

Randolph field study

Preparation of the PUF cassette sampler. The open-celled, porous PUF sponges were cut into cylinders (2.5 cm in diameter and 2.5 cm in height) using a sharp-edged carbon-tipped die (1½ in, Hole-saw, Fort Worth, IN, USA). The polyether-based PUF sponge (2405) was soaked in DMSO for at least 2 h before extracting with acetonitrile, then air drying. Glass fiber filters were impregnated with 50 mg l⁻¹ MOP in acetonitrile then air dried. The impregnated glass fiber filter was fitted into the bottom of the cassette sampler on top of an aluminum mesh screen (2.5 cm in diameter), and the PUF sponge fitted on top of the filter. A 2 ml volume of 1000 mg l⁻¹ MOP in DMSO was added to the sponge and the excess solution removed by pumping on the sampler at a flow rate of 1 l min⁻¹. The DuPont (Wilmington, DE, USA) Alpha 1 constant-flow air-sampling pump used to remove the excess solvent is capable of drawing up to 2.0 l min⁻¹ of air and was also used to obtain air samples during field operations.

Impingers were prepared by adding 15 ml of a 50 mg l⁻¹ solution of MOP in toluene to the impinger.

Description of spray-painting operations. Three different spray-painting operations (seven sampling events) were evaluated at Randolph AFB. Operation 1 involved spray-painting a cabinet with blue paint, a stand with a green primer and two elbows with white and gray paints. The spray-painting of the small parts was performed in a dry filter vent booth over a period of 3 h. Operation 2 involved the spray-painting of small parts; one was painted with two coats of a light blue paint and the other was painted first with a gray primer, then with a light blue paint. The spray-painting was done in a hanger (H48). Operation 3 involved spray-painting a T38 aircraft trainer with a white base coat, in a small hanger with no air recirculation. For operations 1 and 2, the painters wore a Tyvek suit and used a supplied air respirator. For operation 3, the painters wore full body respirators.

High volume, low pressure (HVLP) spray guns were used in all the operations. All spray-painting operations were batch, performed by different painters who used a DuPont polyurethane paint formulation with a 1:1 polyenamel:hardener ratio.

Sampling strategy. Sampling was performed by positioning a cassette sampler containing a sponge impregnated with 1.5 ml of a 1000 mg l⁻¹ solution of either MOP or MAP in DMSO next to a midjet impinger which contained 15 ml of 50 mg l⁻¹ MOP in toluene. For all operations, area samplers were positioned 1.2–1.4 m above the floor and about 1.5–1.8 m downdraft from the equipment being painted. Personal samplers were positioned about 2.5 cm apart in the breathing zone of the painter. The isocyanate samples were collected at an air flow rate of 1.0 l min⁻¹. Sampling times ranged from 48 to 120 min.

After collection, the sponges in the cassette samplers were immediately removed and placed in a sampling bottle containing 10 ml of 50 mg l⁻¹ MOP or MAP in acetonitrile. The nature of the derivatizing reagent (either MOP or MAP) in the sampling bottle was always the same as that in the sponge. The midjet impinger solutions containing isocyanate were transferred to a screw-capped vial. All samplers were transported from the spray-painting location to the analytical laboratory within 6 h.

Preparation of spray-painting samples. As soon as the samples arrived in the analytical laboratory they were prepared for analysis. The toluene solution in the midjet impingers was evaporated under a gentle stream of nitrogen, then reconstituted in 3 ml of methanol. The solution was agitated in an ultrasonic water-bath for 15 min in order to ensure complete dissolution as described in NIOSH Method 5521.¹² The sponges and glass fiber filters from the sampling bottles were extracted three times with 10 ml of acetonitrile, the extracts were combined, then evaporated under a gentle stream of nitrogen to a known fixed volume (2–5 ml), and 30 µl of acetic anhydride were added to the sample.

Sponge samplers and midjet impingers which were not used for the collection of isocyanate were also treated in the same way as the actual samplers and served as method blanks.

Preparation of HDI standards and bulk catalyst. HDI–MOP urea was prepared as described in NIOSH Method 5521.¹² HDI–MAP urea was prepared as described by Streicher *et al.*¹⁶ At least six working standards for each were prepared. HDI–MOP urea standards contained 20 µl of acetic anhydride, 100 mg l⁻¹ MOP and 0.25–16 mg l⁻¹ of HDI–MOP urea in methanol. HDI–MAP urea standards contained 20 µl of acetic anhydride, 100 mg l⁻¹ MAP and 0.25–4 mg l⁻¹ of HDI–MAP urea in methanol.

A 50 µl portion of the hardener (bulk catalyst) used in the spray-painting operation was diluted in 10 ml of toluene and 50 µl of this solution were then diluted to 10 ml with 1000 mg l⁻¹

MOP in toluene. The solution was allowed to react for 12 h before heating to dryness under a gentle stream of nitrogen. A 30 μ l aliquot of acetic anhydride was added to the dry residue, which was reconstituted in 10 ml of methanol while agitating the solution in an ultrasonic water-bath for 15 min.

Analysis

Instrumentation. The field samples were analyzed at Brooks AFB (San Antonio, TX, USA). The HPLC system consisted of a Hewlett-Packard (Avondale, PA, USA) Model 1090 chromatograph equipped with a photodiode array (PDA) detector (MOP and MAP derivatives were quantified at 242 and 254 nm, respectively) followed by a Hewlett-Packard Model 1049A electrochemical detector (ECD) operated in the oxidative mode (+0.8 V *versus* Ag/AgCl). The column used was a Hewlett-Packard Lichrosorb (200 \times 4.6 mm id) RP-18 (10 μ m). Hewlett-Packard Model 3396 Series II integrators were used to determine the area under all the chromatographic peaks.

The sponges spiked with HDI and N-100 were analyzed using an HPLC system consisting of a Beckman (Fullerton, CA, USA) Model 110 B pump, Altex Model 270A sample injector, and Beckman Model 160 UV detector set at 254 nm and connected to a Hitachi Model D-2500 integrator. A BAS electrochemical cell operated in the oxidative mode (+0.8 V *versus* Ag/AgCl) followed the UV detector. The cell was controlled by a BAS (West Lafayette, IN, USA) Model LC4B amperometric detector, and the output was delivered to a Varian (Palo Alto, CA, USA) Model 4400 integrator. The column used was a Phenomenex (Torrance, CA, USA) Prodigy (100 \times 4.60 mm id) C₈ PEEK column (5 μ m with 150 Å pores).

The mobile phase used for analyzing the MOP derivatives varied between 30 + 70 and 45 + 55 acetonitrile–methanolic acetate buffer (0.6% sodium acetate in 50 + 50 methanol–water adjusted to pH 6.0 with glacial acetic acid). The mobile phase was optimized for each column type such that HDI and oligomeric MOP derivatives could be identified and quantified. The mobile phase used for analyzing the MAP derivatives was 58 + 42 acetonitrile–phosphate buffer (0.04 mol l^{−1} NaPO₄ adjusted to pH 2.50–2.85 with concentrated phosphoric acid).

The mobile phase flow rate was set at 1.0 ml min^{−1}. The injection volume was 20 μ l.

Identification and quantification. For HPLC analysis, the peak produced by derivatized HDI monomer was identified by matching its chromatographic retention time with that of the HDI–MOP urea or HDI–MAP urea standards. The N-100 oligomer peaks were also identified by matching their chromatographic retention times with that of the N-100 standards. The HDI-based oligomer peaks in field samples were identified by using the derivatized bulk catalyst used in the spray-painting operation. In addition, oligomeric isocyanate peaks were further confirmed by comparing their ECD/UV response ratio with that

of the respective HDI–MOP urea or HDI–MAP urea standards.

The percentage recovery of isocyanate after spiking the PUF sponge was determined by dividing the integrated area of the HDI peak or the N-100 peaks obtained from the extracted sponge by the integrated area expected for the amount of HDI monomer or N-100 added to the sponge. All integrated areas were based on the average of at least two runs. The average percentage recovery for HDI monomer and N-100 was determined by summing the respective percentage recoveries and dividing by the total number of sponge samples. The pooled standard deviation for the recovery of HDI monomer and N-100 was determined by taking the square root of the following: the sum of the squares of the deviations from the mean of a sponge set defined by a given amount of spiked sample divided by (total number of samples minus the number of sponge sets).

HDI monomer and HDI-based oligomer concentrations for field samples were determined by comparing the area of the HDI monomer and oligomer peaks with those of a series of HDI–MOP or HDI–MAP standards.

Results and discussion

A typical HPLC calibration curve for HDI–MOP or HDI–MAP shows an excellent correlation between detector response and concentration ($r > 0.997$). The detection limits for the HDI–MOP and HDI–MAP ureas were 0.08 and 0.03 mg l^{−1}, respectively.

An evaluation of the recovery of HDI monomer from the polyether–polyurethane sponge (2405) impregnated with 1000 mg l^{−3} MOP in DMSO yielded the following recoveries for each of the following amounts of HDI: 6% at 8 μ g, 79% at 16 μ g, 135% at 48 μ g, 121% at 80 μ g, 155% at 96 μ g and 121% at 112 μ g for an average recovery of $112 \pm 34\%$ for six sponges which had been spiked with 8–112 μ g of HDI. The results are high except at the lowest two concentrations. Because of the high concentration of MOP employed for efficient derivatization, excess MOP may interfere in the analysis of the monomer.

Table 1 illustrates recovery data for the oligomer N-100 obtained for several PUF sponge–solvent systems. The polyester–polyurethane sponge (4CE) impregnated with MOP in acetonitrile yields an average recovery of $92 \pm 9\%$ for 12 sponges which had been spiked with 50–700 μ g of N-100. The polyether–polyurethane sponge (2405) impregnated with MOP in DMSO yields an average recovery of $97 \pm 25\%$ for eight sponges which had been spiked with 100–400 μ g of N-100. The recovery for sponge 2405 varies between 73 and 133%. If two sponges with recoveries of 133 and 121% are eliminated from the computation of the average, then the recovery varies between 73 and 108% with an average of $87 \pm 15\%$. PUF sponge 2405 was chosen for use in the field because it produces fewer artifacts in the HPLC analysis. Also, because DMSO is

Table 1 Recovery data for N-100: determination of polyisocyanate recoveries when using a PUF sponge impregnated with MOP

Sponge	Solvent moistening sponge	MOP in solvent (ppm)	MOP in CH ₃ CN ^a (ppm)	N-100 spike/ μ g	Recovery (%)	No. of samples
4CE	CH ₃ CN	500	500	500	102 ± 11	3
		500	500	700	82 ± 11	3
		120	500	50	100	1
		120	500	100	85 ± 1	2
		120	500	200	90 ± 14	2
		120	500	400	98	1
2405	DMSO	1000	0	100	119 ± 15	3
		1000	0	200	80 ± 5	3
		1000	0	400	90 ± 25	2

^a Acetonitrile solution added 30–60 min after N-100 spike of PUF.

relatively non-volatile, the sponge will not dry out while sampling in the field.

Fig. 1 shows a comparison of typical HPLC traces obtained from samples acquired during spray-painting operations at Randolph AFB. The chromatograms were obtained from (a) a diluted solution of derivatized bulk catalyst, (b) the reconstituted solution obtained from a midjet impinger (MI) and (c) the acetonitrile extract from a PUF sponge cassette. As can be observed, both the midjet impinger and sponge samplers [see Fig. 1(b) and (c)] yield chromatograms which have the same isocyanate peaks and in the same relative ratio as the bulk catalyst [see Figure 1(a)] used in the spray-painting operation.

Table 2 compares the HDI monomer and oligomer concentrations (see columns 3 and 4) for samples obtained with an MI and a PUF sampler (sponge). The samples were obtained during seven sampling events at Randolph AFB. The LOD for HDI-MOP was 0.005 mg m^{-3} for a 50 l air sample. The HDI monomer concentration in air during spray-painting operations as determined using an MI ranged from 0.007 to 0.082 mg m^{-3} . Three values are above the NIOSH recommended exposure limit (REL) value of 0.035 mg m^{-3} of HDI in air. The PUF sampler (sponge) detected HDI in only two samples, and the concentration was significantly smaller than that obtained using an MI. For the analysis of HDI with MAP as the derivatizing reagent, under the conditions used in this study, the HDI could not be detected because the chromatographic peak corresponding to excess MAP obscures the peak which corresponds to HDI-MAP in the sample.

The polyisocyanate concentration in air as determined using an MI ranged from 0.05 to 0.30 mg m^{-3} . The PUF sampler yielded polyisocyanate concentrations which ranged from 0.09 to 0.33 mg m^{-3} . The manufacturer (Bayer Chemical) specifies a 1 mg m^{-3} short-term exposure limit (STEL).¹⁷ The spray-painting operations did not exceed the STEL of 1 mg m^{-3} for polyisocyanates using either method.

If the paired *t*-test is used to compare the concentration of HDI-based oligomer when sampled using an MI and a PUF

Table 2 Isocyanates in the spray-paint environment (Randolph AFB): comparison of sponge and impinger

Sampling event: op (mo-day-time-type-sampling volume) ^a	Sample: # reagent (sampler) ^b	Isocyanate/ mg m^{-3}	
		Monomer	Oligomer
1R (12-4-11-personal-50 l)	#100MOP (sponge)	ND ^c	0.12
	#101MOP (MI)	0.007	0.11
2R (12-12-10-area-50 l)	#807MAP (sponge)	ND	0.17
	#814MOP (MI)	0.082	0.16
2R (12-12-12-area-118 l)	#808MAP (sponge)	ND	0.11
	#815MOP (MI)	0.045	0.13
2R (12-12-10-personal-60 l)	#809MOP (sponge)	0.012	0.15
	#811MOP (MI)	0.03	0.22
2R (12-12-12-personal-120 l)	#810MOP (sponge)	0.008	0.09
	#812MOP (MI)	0.04	0.11
3R (6-25-10-personal-48 l)	#432MOP (sponge)	ND	0.33
	#431MOP (MI)	ND	0.30
3R (6-25-10-personal-50 l)	#434MOP (sponge)	ND	0.26
	#433MOP (MI)	ND	0.05

^a op refers to the operation; mo-day-time-type-sampling volume refer to the month, day and time at which the sample was acquired, the location of the sampler and the volume of air sampled. ^b # reagent (sampler) refer to the laboratory sample number followed by the acronym for the derivatizing reagent followed by the type of sampler. ^c ND = below LOD (0.005 mg m^{-3} for MOP and 0.01 mg m^{-3} for MAP).

sampler (sponge) containing MOP or MAP in DMSO (see data pairs in column 4 headed Oligomer) ($n = 7$), the difference between means is not significant at the 0.05 level. Two of the PUF samplers contained MAP, and if these are excluded from the data set ($n = 5$), there is still no significant difference in the concentration of HDI-based oligomer at the 0.05 level. The results indicate that a PUF sampler may be used for the efficient collection of polyisocyanates in the spray-painting environment.

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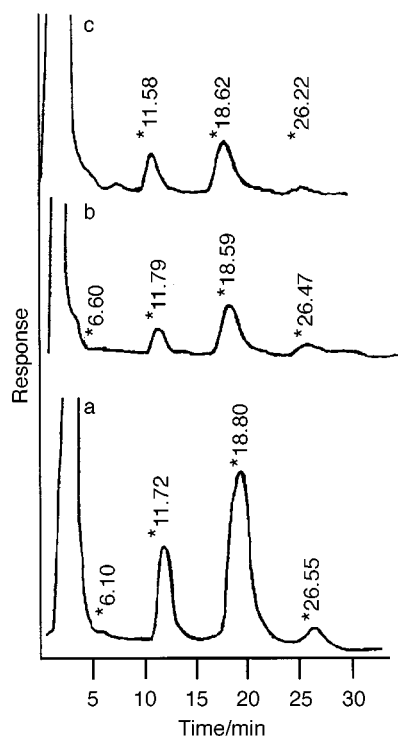


Fig. 1 Comparison of chromatograms: (a) sample 425 MOP catalyst; (b) sample 431 MOP (MI), (c) 432 MOP (sponge). Asterisks indicate HDI oligomer. Column, Phenomenex ($100 \times 4.60 \text{ mm id}$) C_{18} PEEK ($5 \mu\text{m}$); mobile phase, $30 + 70$ acetonitrile-methanolic acetate buffer (pH 6.0); flow rate, 1.0 ml min^{-1} ; UV detector set at 254 nm .

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