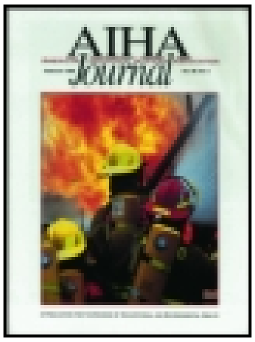

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A Comparison of Solid Sampler Methods for the Determination of Hexamethylene-Based Isocyanates in Spray-Painting Operations

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A polyurethane foam sponge impregnated with 1-(2-methoxyphenyl) piperazine in dimethylsulfoxide was mounted in both cassette and inhalable organic monitor samplers and these were then compared with a dual-filter cassette. The samplers were used for the collection of hexamethylene diisocyanate (HDI) monomer and oligomers during actual spray-painting operations. The dual filter cassettes were positioned on a mannequin. The polyurethane foam cassette (PUF CAS) and polyurethane foam inhalable organic monitor (PUF IOM) samplers were positioned on a cart in the same maximum overspray area. Data from this pilot study suggest that there is no significant difference ($P < 0.05$, $n = 6$) in the amount of HDI monomer obtained with the PUF IOM sampler when compared with the amount obtained from the dual filter cassette. The data also suggest that the PUF IOM sampler yields a higher amount of HDI oligomer than either the dual filter cassette or the PUF CAS sampler, neither of which exhibited a significant difference ($P < 0.05$, $n = 6$) from each other.

Keywords: dual cassette sampler, isocyanates, 1-(2-methoxyphenyl) piperazine, PUF cassette sampler, PUF IOM sampler, spray painting

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Isocyanates are a significant hazard in the workplace.(1–7) Workers involved in the production of polyurethane foams, elastomers, and fibers, as well as 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) and a number of reviews have appeared recently documenting the status of the sampling and analysis techniques.(11–14) National Institute for Occupational Safety and Health (NIOSH) Method 5521 is often used for the sampling and analysis of monomeric isocyanates in the United States.(15) This method is an adaptation of MDHS 25, Method for Total Isocyanate in Air, developed for use in the United Kingdom.(16) These methods use an impinger filled with 1-(2-methoxyphenyl) piperazine (MOP) in toluene for sample collection. NIOSH Method 5522, which uses tryptamine (TRYP) in dimethylsulfoxide in an impinger, also has been promulgated for the determination of total isocyanates.(17) A third method, NIOSH Draft Method 5525, involves the use of 1-(9-anthracenylmethyl) piperazine (MAP) in an impinger. MAP is a fluorescent derivatizing reagent that offers better sensitivity for the analysis of total isocyanates.(18,19) A fourth method, developed by Skarping and co-workers in Sweden, is based on the use of dibutylamine in an impinger followed by liquid chromatography/mass spectrometry.(20) MDHS 25, NIOSH Draft Method 5525, and the Skarping method have been recommended for the sampling and analysis of isocyanates by a working group of ASTM.(21)

Alternative collection methods rely on the use of filters. The United States Occupational Safety and Health Administration (OSHA) developed OSHA Method 42, which is based on the collection of isocyanate monomer on an impregnated glass fiber filter.(22) In Quebec and Ontario provinces in Canada a dual filter cassette is used. The first filter is made of Teflon®, and the second is a glass fiber filter impregnated with 9-(N-methyl aminomethyl) anthracene (MAMA).(23) The dual filter cassette is marketed commercially as ISOCHEK® and also has been recommended for use by ASTM. The total aerosol mass method (TAMM), also known as NIOSH Method 0500, can be used to estimate the upper bound of the oligomer concentration during spray-painting operations.(24)

A recent study compared NIOSH Method 5521, NIOSH Method 5522, NIOSH Method 5525, OSHA Method 42, ISOCHEK, and TAMM.(25) For hexamethylene diisocyanate (HDI) monomer sampling there were no significant differences. For HDI polyisocyanates, there were no significant differences between NIOSH Method 5521, NIOSH Method 5525, and ISOCHEK. All of these approaches, however, produced results that were lower than those calculated from TAMM.

In an effort to improve on the available filter sampling methods, the authors have explored the efficacy of using polyurethane foam (PUF) impregnated with MOP in dimethylsulfoxide (DMSO) as a medium for the collection of both monomeric and polymeric hexamethylene-based isocyanates. They constructed two novel samplers based on an impregnated PUF filter mounted inside either a cassette or an IOM sampler. This approach has not been attempted, but offers sampling advantages over both filters and impingers. Filters collect particulate effectively, but suffer from the disadvantage of not having a solubilizing solvent and a derivatizing reagent available for immediate reaction and accessibility for large particles. Impingers, though offering an immediate solubilizing and derivatizing environment, suffer from the inability to capture particles much smaller than 2 μm(13) and from losses due to paint deposition in the impinger orifice and jet.(25) Impregnated polyurethane foam offers some of the solubilizing advantages of an impinger while collecting a wider particle size distribution like a filter.

In two previous studies the authors evaluated a polyurethane foam cassette (PUF CAS) sampler(26) and a capillary zone electrophoresis approach for the analysis of total HDI-based isocyanates.(27) This article extends the previous effort by comparing the results obtained for HDI-based isocyanates collected during an actual spray-painting operation in which the PUF CAS, the polyurethane foam inhalable organic monitor (PUF IOM), and the dual filter cassette (ISOCHEK) were positioned next to each other in the area of maximum overspray.

EXPERIMENTAL

Reagents

1-(2-methoxyphenyl) piperazine (MOP) was obtained from Fluka (Milwaukee, Wis.), and HDI monomer (HDI) from Eastman Kodak (Rochester, N.Y.). 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.),(28) dimethylsulfoxide from Aldrich (Milwaukee, Wis.), acetonitrile (HPLC grade) and methanol from EM Science (Gibbstown, N.J.), and toluene from Fisher (Fairlawn, N.J.).

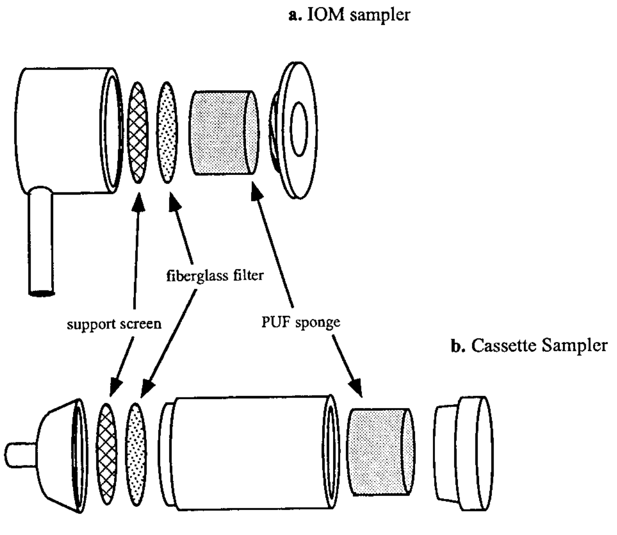

FIGURE 1. Exploded view of the polyurethane foam sampling devices: (a) PUF IOM sampler (SKC); (b) PUF CAS sampler (Nucleopore)

Standards

Isocyanate-MOP standards were prepared by directly reacting HDI-based isocyanates (which contain the NCO moiety) with MOP (which contains an accessible amine group) to form ureas (containing the -NCON- moiety) as described in NIOSH Method 5521.(15) The hexamethylene diisocyanate MOP (HDI-MOP) and N-100-MOP standards were prepared as previously described(27) and used for the analysis of the extracts obtained from the PUF CAS and PUF IOM samplers. The analysis of the extract from the dual-filter cassette (ISOCHEK) was as described previously.(23)

Samplers

Precleaned PUF sponges (60 × 76 mm; Supelco, Bellefonte, Pa.) were cut to the correct thickness using a razor blade. Sponges for use in the IOM sampler (SKC, Eighty Four, Pa.) were 15 mm thick, whereas those for use in the CAS sampler (Nucleopore, Pleasanton, Calif.) were 17.5 mm thick. The sponges for both types of samplers were then punched from the slice using a no. 15 cork borer (23 mm, i.d.). The sponges were soaked in DMSO for at least 2 hours before extracting three times with 10 mL portions of acetonitrile, then air drying. Glass-fiber filters (25 mm; Omega, Chelmsford, Mass.) were impregnated with 50 mg/L MOP in acetonitrile, then air dried.

The PUF CAS samplers were assembled by placing an aluminum mesh screen (2.5 cm in diameter) in the bottom of the cassette sampler, followed by the impregnated glass-fiber filter, then the clean sponge on top. The PUF IOM samplers were assembled by placing the impregnated glass-fiber filter in the bottom, then positioning the sponge on top, before screwing the cap back on. Figure 1 presents an exploded view of the PUF CAS and PUF IOM samplers.

To each type of sampler, 2 mL of 1000 mg/L MOP in dimethylsulfoxide were added, and the excess solution removed by pumping on the sampler at a flow rate of 1.0 L/min. The Dupont (Wilmington, Del.) Alpha 1 constant-flow air-sampling pump used to remove the excess solvent is capable of drawing up to 2.0 L/min of air and also was used to obtain air samples during spray-painting operations. Because the polyurethane foam was fitted

TABLE I. Comparison of HDI Monomer and Oligomer Concentrations in Air During Spray-Painting Operations at Hill AFB

Operation No. (Volume)[A]	Monomer Concentrations (mg/m^3) Samplers			Oligomer Concentrations (mg/m^3) Samplers		
	ISOCHEK	PUF IOM[B,D]	PUF CAS[C,D]	ISOCHEK	PUF IOM	PUF CAS
41 (31 L)	0.004	0.013	0.026	0.366	1.07	1.55
Duplicate	0.004			1.54		
42 (13 L)	0.006	0.029	—	0.678	1.96	ND
Duplicate	0.006			0.382		
43 (23 L)	0.011	0.012	0.031	0.123	2.3	0.46
Duplicate	0.013			0.079		
44 (62 L)	0.040	0.007	0.021	0.115	0.82	0.41
Duplicate	0.013			0.259		
45 (62 L)	0.007	0.003	0.033	0.608	0.83	0.74
Duplicate	0.007			0.827		
46 (31 L)	0.003	0.005	0.023	0.244	1.49	0.004
Duplicate	0.002			0.277		

Note: ND = not detected.
[A] Volume of air sampled.
[B] PUF IOM = IOM sampler containing a PUF sponge impregnated with MOP in DMSO.
[C] PUF CAS = cassette sampler containing a PUF sponge impregnated with MOP in DMSO.
[D] These results were obtained using capillary zone electrophoresis. The other concentrations were obtained using standard HPLC methods.

snugly into the cassette or IOM samplers, no channeling was observed.

ISOCHEK dual filter cassettes were obtained from Omega. An exploded view is available in Lesage et al.(23)

Description of Spray-Painting Operations

Six different spray-painting operations (36 sampling events) were evaluated at Hill Air Force Base. Operations 41 and 42 involved painting the lower fuselage of an F-16 fighter aircraft. Operations 43 and 44 involved painting aircraft parts and under the wing of a C-130 cargo aircraft, respectively. Operation 45 involved fully painting an F-16 fighter aircraft. Operation 46 involved painting the landing gear and door area of the airplane.

All spray guns were high-volume, low pressure (HVLP). In all operations, the painters used cloth coveralls and gloves, and an air supplied respirator with hood.

In Operations 41, 42, 44, and 45 a gray polyurethane paint formulation (Deft, Irvine, Calif.) was used containing a 3:1 (polyenamel:hardener) ratio. In Operations 43 and 46, sea foam green and white gloss polyurethane paint formulations (Deft) were used containing a 1:1 (polyenamel:hardener) ratio, respectively.

Sampling Strategy

For all operations, sampling was performed by positioning a PUF CAS sampler and a PUF IOM sampler about 2.5 cm apart on a cart at approximately breathing zone height (c. 1.20 m). The ISOCHEK sampler was positioned on the lapel of a mannequin. For Operations 41, 42, and 45 the cart and mannequin were positioned about 1.8 m behind the fuselage. For Operation 43 the cart and mannequin were 0.6 m behind the parts. For Operation 44 the cart and mannequin were positioned under the aircraft wing. For Operation 46 the cart and mannequin were positioned 1.2 m to the right of the parts being painted. All cart and mannequin positions were in the maximum overspray area.

The ISOCHEK and PUF CAS samplers were operated at an airflow rate of 1.0 L/min, whereas the PUF IOM was operated at an airflow rate of 2.0 L/min. Sampling times ranged from 13 to 62 min.

After collection, the sponge and backup filter in each sampler were immediately removed from the PUF CAS and PUF IOM samplers and placed in a sampling bottle containing 10 mL of 50 mg/L MOP in acetonitrile. The Teflon filter from the ISOCHEK sampler was placed in an ointment jar with a PTFE lid containing 5 mL of MOP derivatization reagent (0.1 mg/mL of MOP in toluene). The MAMA impregnated glass-fiber filter and the pad support were left in the ISOCHEK housing. All samples were shipped to the analytical laboratories within 2 days of sampling.

Sample Analysis

The polyurethane foam and backup filters from the PUF CAS and PUF IOM samplers were analyzed in the Department of Chemistry, Southwest Texas State University, San Marcos, Texas, as previously described.(27) The limit of quantitation (LOQ) for the method is 0.17 μg.

The ISOCHEK samplers were analyzed at the Institut de recherche en sante et en securite du travail, Montreal, Quebec, Canada, using the protocol as described.(23) The LOQ for the method is 0.062 μg.

RESULTS

Table I illustrates the results for the analysis of HDI monomer during spray-painting operations when using the PUF IOM, PUF CAS, and ISOCHEK samplers. The Wilcoxon signed rank test, which is a nonparametric test, was used to evaluate the data, as in a previous report,(19) whereas the two-tailed, paired t-test was used to confirm the conclusions. The Wilcoxon signed rank test was used to compare the monomer concentrations when using the ISOCHEK and PUF IOM samplers (see data pairs in Columns 2 and 3), and the data suggest no significant differences at the 0.05 level for n = 6.(29) The concentrations of HDI monomer obtained when using the PUF CAS sampler were generally higher than those obtained from the PUF IOM sampler. The Wilcoxon signed rank test has been used to compare the concentrations obtained when using the PUF IOM and PUF CAS samplers (see data pairs in Columns 3 and 4), and there was a significant difference at the 0.05 level for n = 5.(29) The results suggest that the ISOCHEK and PUF IOM samplers have similar collection efficiencies for the volatile HDI monomer, whereas the PUF CAS sampler gives higher results than the PUF IOM sampler.

Table I also provides the results for the analysis of HDI oligomer during spray-painting operations. A cursory inspection of the amount of HDI oligomer obtained when using the ISOCHEK sampler suggests that the amount obtained is usually less than or equal to the amount obtained when using the PUF IOM sampler. If the Wilcoxon signed rank test is used to compare the concentrations, when using these two samplers (see data pairs in Columns 5 and 6), there is a significant difference at the 0.05 level for n = 6.(29) A comparison of the results obtained for HDI oligomer when using the ISOCHEK and PUF CAS samplers (see Table I, Columns 5 and 7) suggests no significant difference at the 0.05 level for n = 5. The PUF IOM sampler has a higher face velocity than the ISOCHEK sampler, which may account for a higher fraction of aerosol impinging on the surface, thus providing for the higher results.(13,30) Alternatively, since the ISOCHEK sampler was used in a closed face mode on the mannequin, the inhalable fraction might be underestimated.(31)

CONCLUSIONS

The preliminary results suggest that the ISOCHEK and PUF IOM samplers are equally efficient at collecting and quantifying HDI monomer, whereas the PUF IOM may be more efficient at collecting HDI oligomer. Further work is needed to evaluate whether the PUF IOM sampler is practical for the analysis of HDI monomer and oligomer.

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