Final Performance Report

# New Sampling and Analysis Method for Isocyanates

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# List of Abbreviations

in alphabetical order

| | |
|---|---|
| AFB | Air Force base |
| CZE | Capillary zone electrophoresis |
| Desmodur N-100 | Oligomer of hexamethylene diisocyanate |
| DMSO | dimethylsulfoxide |
| HDI | hexamethylene diisocyanate |
| HPLC | High performance liquid chromatography |
| IOM | personal inhalable sampler |
| LOD | limit of detection |
| MAP | 1-(methylanthracenyl) piperazine |
| MDI | methylenediphenyl diisocyanate |
| MI | midget impinger |
| MOP | 1-(2-methoxyphenyl) piperazine |
| NIOSH | National Institute for Occupational Safety and Health |
| NR | natural rubber |
| p | significance level |
| PTFE | Teflon |
| PUF | polyurethane foam |
| R2 | square of correlation coefficient |
| SBR | styrene-butadiene rubber |
| TDI | toluene diisocyanate |
| TLV | threshold limit value |
| VITON | Dupont fluoroelastomer |
| XAD-2 | Amberlite nonionic polymeric adsorbent |

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## Significant Findings

(1) Cassette samplers which feature a polyurethane foam (PUF) plug positioned on top of a fiberglass filter may be used for the analysis of hexamethylene diisocyanate (HDI) monomer and oligomer generated during spray-painting operations. The cassette sampler does not spill and therefore is more convenient than an impinger for use in the field. These devices may be used for personal sampling and they provide a more accurate and convenient means of testing ambient air than either a midget impinger which can spill and does not efficiently collect condensation aerosol particles less than 2.0 μm in diameter or a filter cassette which can give low results for HDI oligomer because of competing reactions which can occur on the fiberglass filter.

(2) The derivatizing reagent, tryptamine, may be used instead of 1-(2-methoxyphenyl) piperazine (MOP) for the analysis of HDI-based isocyanates generated during spray-painting operations. The use of tryptamine as a derivatizing reagent in DMSO eliminates the need to remove toluene and reconstitute the sample in methanol. Further, the fluorescence variability of tryptamine ureas is about 15% for a variety of diisocyanates and therefore tryptamine is most promising as a derivatizing reagent for the quantitation of diisocyanates when the diisocyanate is unkown or when a standard is not available.

(3) An improved derivatizing reagent , 1-(methylanthracenyl) piperazine (MAP), which has a sensitivity about five times greater than MOP by uv detection and a more uniform response toward all isocyanates ( ± 3.5 % standard deviation) may be used instead of MOP. MAP reacts quickly with the isocyanate and provides results for HDI-based isocyanate which do not differ significantly from those obtained when using MOP. When two impingers containing MAP and a third containing MOP are positioned in a side-by-side-by-side arrangement, there is no significant differance ($p < 0.05$) in the concentration of HDI oligomer.

(4) A new analytical method, capillary zone electrophoresis (CZE), offers better selectivity and sensitivity for the analysis of HDI monomer when compared with high performance liquid chromatography (HPLC).

## Usefulness of Findings

(1) Cassette samplers which feature a polyurethane foam plug positioned on top of a fiberglass filter may be used for the analysis of HDI monomer and oligomer generated during spray-painting operations. These samplers do not spill and therefore are more convenient for use in the field than impingers. These devices may be used for personal sampling and they provide a more accurate and convenient means of testing ambient air than either a midget impinger which can spill or a filter cassette which can give low results for HDI oligomer.

(2) The derivatizing reagent , tryptamine, may be used instead of MOP for the analysis of HDI-based isocyanates generated during spray-painting operations. Tryptamine is a fluorophore that is insensitive toward the nature of the isocyanate and therefore will give a relatively uniform response toward all isocyanates. This property is useful for the analysis of isocyanates when it is not clear which isocyanate is present in a sample.

(3) An improved derivatizing reagent , 1-(methylanthracenyl) piperazine (MAP), provides results for HDI-based isocyanate which do not differ significantly from those obtained using MOP. When two impingers containing MAP and a third containing MOP are positioned in a side-by-side-by-side arrangement, the results show no significant differance. MAP has an ultraviolet molar absorptivity six times greater and a limit of detection (LOD) three times lower than that of MOP. The lower LOD is useful for the analysis of HDI monomer in the spray-painting environment because its concentration is low and often below the LOD of the method which uses MOP as the derivatizing reagent.

(4) A new analytical method, capillary zone electrophoresis (CZE) offers better selectivity and sensitivity for the analysis of HDI monomer when compared with HPLC. The CZE method completely isolates HDI monomer from excess solvent, derivatizing reagent and pigment and because the method is based on a completely different separation principle than HPLC, it can be used for the confirmation of the presence of HDI monomer when there are interferences present in the HPLC chromatogram.

## Abstract

The hazards of isocyanate in the workplace have been well documented. Workers who are 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. The vapor can irritate the nose, throat and lungs, and eventually lead to pulmonary dysfunction and bronchial pneumonia. Chronic exposure can lead to sensitization in 5-10% of the population. Isocyanate aerosol can irritate the eyes, and contact with the skin can cause severe blistering and swelling.

The primary goal of this research was to develop a convenient, accurate, and sensitive sampling and analysis procedure for hexamethylene diisocyanate (HDI) monomer and HDI oligomer in the spray-painting environment.

This goal was achieved through a multi-faceted research effort:

(1) New cassette samplers were developed which feature a polyurethane foam (PUF) plug positioned on top of a fiberglass filter. These samplers do not spill and therefore are more convenient for use in the field. In a series of side-by-side sampling events, an impinger filled with MOP in toluene was compared directly with a cassette sampler containing a PUF sponge impregnated with MOP or MAP in dimethylsulfoxide (DMSO). For the analysis of HDI oligomer there is no significant difference ($p < 0.05$, $n = 7$) in the air concentration when using either sampler

(2) The derivatizing reagent , tryptamine, which has a more uniform response toward all isocyanates, was evaluated during spray-painting operations. The analytical results indicate that there is no significant differance ($p < 0.05$, $n = 5$) when comparing the air concentration of biuret obtained while sampling with an impinger filled with either MOP or tryptamine.

(3) An improved derivatizing reagent , 1-(methylanthracenyl) piperazine (MAP), which has a fluorescence sensitivity thirty times greater than tryptamine was evaluated in field studies. The analytical results indicate that there is no significant differance ($p < 0.05$, $n = 6$) in the concentration of polyisocyanate as determined by two impingers containing MAP and a third containing MOP when positioned in a side-by-side-by-side arrangement.

(4) A new analytical method , capillary zone electrophoresis (CZE), was compared with high performance liquid chromatography (HPLC). CZE offers better selectivity and sensitivity for the analysis of HDI monomer when compared with HPLC.

# Body of Report

## Background

Isocyanates are a significant hazard in the workplace(1-9). Workers who are involved in the production of polyurethane foams, elastomers and fibers as well as in the application of polyurethane paints and coatings can be exposed to diisocyanate and polyisocyanates. These are found either in the form of a vapor or an aerosol. The vapor irritates the nose, throat and lungs, and may eventually lead to bronchial pneumonia. The aerosol irritates the eyes, and causes severe blistering and swelling after contact with the skin.

Workers are exposed to a variety of isocyanates. Those who use polyurethane in upholstery, packaging, shoe soles or insulating materials are exposed to toluene diisocyanate (TDI), a potential occupational carcinogen. Auto workers are exposed to 4,4'-diphenylmethane diisocyanate (MDI). Spray painters are exposed to 1,6- hexamethylene diisocyanate (HDI) and its oligomers. Potential sources of exposure include: reactive monomer offgassing from production lines, products of decomposition, and the spray application of polyurethane foams and paints.

Sampling and analytical methods have already been developed for HDI, TDI and MDI in the vapor form (10-12). They are easily collected on a filter (13) or in an impinger (14,15), then analyzed using high performance liquid chromatography (13-15) or capillary zone electrophoresis (16). These methods are straightforward, and have a limit of detection (LOD) which is well below the threshold limit value (TLV). In a few instances there is a need for a lower detection limit (e.g. the detection of MDI from casts for people who are sensitized to isocyanate), but in most instances the available methods are adequate for the analysis of diisocyanate monomers in the vapor form.

MDI and HDI-based polyisocyanates are more difficult to analyze because they are in the aerosol form. The aerosol can be collected on a filter, but the filter does not promote adequate mixing between the aerosol and derivatizing reagent. If the filter is not extracted soon after sampling, the results may be low. The aerosol may also be collected with an impinger, but an impinger is not as efficient at collecting particles with a diameter less than 2 µm (12). Impingers also spill and expose the industrial hygienist to solvent . An alternative sampling method was needed to collect both isocyanate vapor and aerosol.

The presently accepted sampling methods for HDI, TDI or MDI monomer and oligomer use an impinger filled with either 1-(2-methoxyphenyl) piperazine (MOP) in toluene(14), or tryptamine in dimethylsulfoxide(15).

Lesage et. al. have developed a dual filter cassette which though solvent-free appears to have excellent collection efficiency. The cassette consists of a 5µm PTFE filter backed up by a glass fiber filter impregnated with 9-(methylaminomethyl) anthracene (17). The latter method has been approved for use in Quebec since 1987. The method works well because the sampling protocol involves the immediate immersion of the PTFE filter in a solution of derivatizing reagent. The key to complete recovery lies in solvating the collected aerosol.

In an effort to improve on the dual filter cassette, we have developed a sampler which contains a moistened, microporous polyurethane foam (PUF), backed up by a glass fiber filter .

A new derivatizing reagent, 1-(methylanthracenyl)piperazine (MAP), has recently been synthesized by Dr. Robert Streicher of NIOSH (18). This reagent, when compared to MOP, offers a six-fold increase in uv sensitivity, a fluorescent signal which enhances both the selectivity and sensitivity, and a uv response which is independent of the nature of the isocyanate We evaluated this derivatizing reagent impregnated within a backup filter or PUF during actual field studies.

## Specific Aims

The specific aims of the NIOSH grant (R01-OHO-3295-01) were:

1. To evaluate 1-(methylanthracenyl) piperazine in an impinger during spray painting operations.
2. To develop and compare capillary zone electrophoresis (CZE) methods with high performance liquid chromatography (HPLC) methods for the analysis of isocyanate.
3. To develop a new sampling device which is more convenient than an impinger, but still able to quantitatively capture both isocyanate aerosol and vapor.
4. To determine the amount of isocyanate generated during spray-painting with the amount originally in the paint formulation.

We have achieved each of our aims within the grant period of April, 1995 to Dec. 31, 1997.

## Results and Discussion

### Aim 1. Assessment of 1-(Methylanthracenyl) Piperazine as a Derivatizing Reagent

We have synthesized and purified 1-(methylanthracenyl) piperazine (MAP), reacted this reagent with a number of diisocyanate and polyisocyanate derivatives, and tested a high performance liquid chromatography (HPLC) procedure for HDI-based isocyanates generated during actual spray-painting operations. Though hexamethylene diisocyanate (HDI) could not be determined under the original operating conditions proposed for MAP (18), HDI-based polyisocyanate concentrations were easily obtained, and the results compared with those obtained using 1-(2-methoxyphenyl) piperazine (MOP) as the derivatizing reagent. All calibration curves based on polyisocyanate ureas were linear within the working range, 1- 20 µg/ mL, with an $R^2 > 0.997$ and an estimated detection limit of 0.5 µg/ mL. The polyisocyanate MAP urea had a sensitivity about six times as great as polyisocyanate MOP urea. Statistical analyses of the data verify there is no significant difference in the concentration of polyisocyanate during spray-painting operations when two impingers containing MAP and a third containing MOP are positioned in a side-by-side-by-side arrangement. The complete details of these experiments are presented in Rudzinski et al. (1996)

### Aim 2. Comparison of Capillary Zone Electrophoresis (CZE) with High Performance Liquid Chromatography (HPLC) for the Analysis of Isocyanates

MOP derivatives of HDI and HDI-biuret as well as MAP derivatives of HDI, TDI, and MDI were prepared and analyzed using CZE (19). Calibration curves based on MAP derivatives of HDI or HDI-biuret were linear within the working range, 0.5- 25 µg/ mL, with an $R^2 > 0.999$ (20). All calibration curves based on MOP derivatives of HDI or HDI-biuret were also linear with an $R^2 > 0.996$. Figure 1 shows that CZE is about five times as sensitive as HPLC for the analysis of HDI-MOP and about 9 times as sensitive for the analysis of HDI-biuret-MOP. The LOD is about (0.08 ppm, 1 µM NCO for each method. The linear range extends to 80 µM NCO for HDI-MOP and 120 µM NCO for the HDI-biuret-MOP .

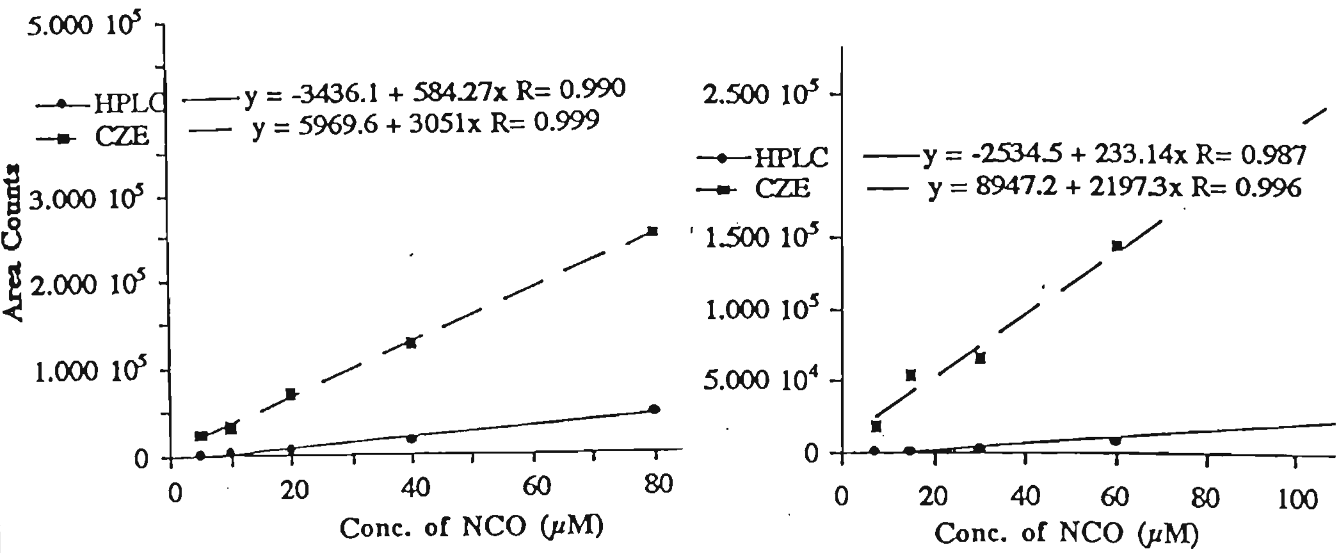

Figure 1. Comparison of calibration curves for (a) HDI-MOP and (b) HDI-biuret MOP when using HPLC and CZE. CZE conditions: Running buffer: 40% acetonitrile/60% phosphate buffer adjusted to a pH of 3.0. Effective capillary length = 40 cm. Operating voltage: 20 kV. Detector wavelength = 185 nm. HPLC conditions: Mobile phase: 35% acetonitrile/65% methanolic phosphate buffer adjusted to a pH of 6.0. Column: Prodigy (100 X 4.6 mm) 5 μm C-8 PEEK. Detector wavelength = 254 nm.

Initially the CZE analysis was run using an 0.010 M phosphate buffer adjusted to a pH of 3.0. Under these conditions, our analysis yields reasonable results for HDI, but HDI-polyisocyanate peaks are broad and the area counts are low. With the addition of acetonitrile to the running buffer, the polyisocyanate peaks become sharper and the area count increases. At about 40% acetonitrile/ 60% phosphate buffer (pH = 3.0), an electropherogram with maximum sensitivity is attained (see Figure 2).

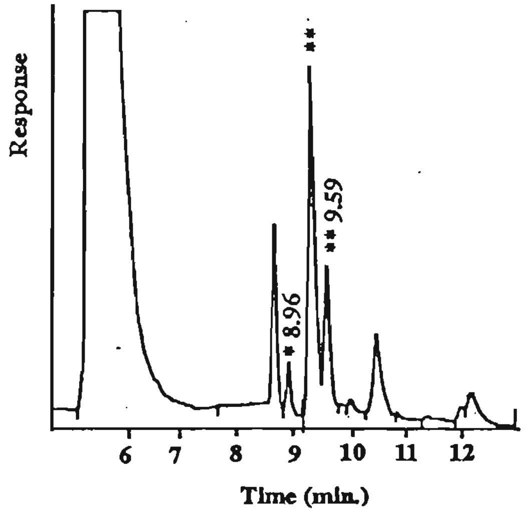

Figure 2. Capillary Zone Electropherogram of a sample, #432MOP(sponge). Running buffer: 40% acetonitrile/60% phosphate buffer adjusted to a pH of 3.0. Effective capillary length = 50 cm. Operating voltage: 20 kV. * denotes HDI and ** denotes HDI-polyisocyanates respectively.

**Table 1. Isocyanates in the Spray-paint Environment at Robins AFB (mg/m3): Comparison of HPLC and CZE analysis of Isocyanates Captured in a Sponge Cassette.**

| Sample<br># time(volume) | HDI-based poly<br>HPLC analysis | HDI-based poly<br>CZE analysis | HDI monomer<br>CZE analysis |
|---|---|---|---|
| #1801-15 m(15L) | 1.44 | 6.28 (3.49) | <LOQ |
| #1813-24h(15L) | 0.61 | 3.08 (1.69) | <LOQ |
| #1902-15 m(21L) | 1.12 | 5.76 (3.20) | <LOQ |
| #1914-24h(20L) | 1.42 | 7.16 (3.97) | <LOQ |
| #2003-15 m(13L) | 0.07 | <LOQ | ND |
| #2015-24h(12L) | 0.18 | 1.63 (0.90) | ND |
| #2104-15 m(16L) | 0.53 | 2.86 (1.59) | 0.036 |
| #2116-24h(15L) | 0.08 | 0.90 (0.50) | ND |
| #2205-15 m(31L) | 0.31 | 1.76 (0.98) | 0.074 |
| #2217-24h(31L) | 0.24 | 1.60 (0.89) | 0.102 |
| #2306-15 m(16L) | 0.26 | 1.96 (1.09) | ND |
| #2318-24h(15L) | 0.64 | 3.21 (1.77) | 0.17 |

Sample: #-time(volume) refer to the lab sample number, followed by the time until quenching by the derivatizing reagent, followed by the volume of air sampled. ND = not detected. <LOQ = below limit of quantitation. Under the heading, CZE analysis, the value in parentheses is the HDI polyisocyanate adjusted for a difference in the relative response of N-100/HDI

Table 1 compares the HPLC and CZE results obtained for HDI-based isocyanates captured in a sponge at Robins AFB. Two cassette samplers were positioned about 4 inches apart and placed on a mannequin. The samplers were 3-4 ft above the floor, and about 4-6 feet downdraft from the equipment being painted. The air sampling rate for the samplers was 1 L/min. One of the sponge samplers was placed in 10 mL of 50 ppm MOP in acetonitrile (within 15 minutes), while the other was extracted after 24 hours. The HPLC and CZE analysis conditions were as reported for Figure 1.

CZE analysis exhibits HDI monomer concentrations in the range, 0.036 to 0.17 mg/m$^3$, for four of twelve samples. HDI monomer concentrations determined from HPLC are not reported; they were consistently below the LOD for the method, or the chromatographic peak was buried in excess MOP or the DMSO solvent peak.

The concentration of HDI polyisocyanates as determined by CZE is 4 -7 times higher than that determined from HPLC. The reason lies in a different HDI polyisocyanate/HDI-MOP response ratio for CZE and HPLC. If the CZE data are adjusted by multiplying by a relative response factor of 40/72 (the response ratio of N-100-MOP/HDI-MOP from HPLC divided by the response ratio of N-100-MOP/HDI-MOP from CZE), the CZE results can be normalized for a direct comparison with the HPLC results. The recalculated concentrations of HDI polyisocyanate are presented (within parentheses) in the third column of Table 1. In all but two cases, these values are still 2.4 to 4.2 times higher than that determined from HPLC. Although these adjusted values approach the values obtained for HPLC, they are still too high. The most likely explanation is that N-100 is not a good standard to use for the determination of the N-100-MOP/HDI-MOP relative response factor. A better approach would be to calculate the relative response factor based on the bulk catalyst used in the spray painting operation.

Comparing HPLC analysis and CZE analysis, the CZE method offers better sensitivity both for HDI monomer and oligomer, a shorter analysis time, lower buffer consumption and smaller sample requirements. However, there are a few problems in the CZE method. First, the capillary used in CZE analysis is very easily ruined by some compounds (e.g. MOP) in samples so that the capillary has to be replaced every few weeks. Second, the migration time and the resolution of isocyanate peaks is very sensitive to the pH of the buffer so that it is very difficult to get reproducible migration times during routine analysis. This necessitates the use of the method of standard additions in order to be certain of the identity of HDI-MOP. These two disadvantages, however, are mitigated by the ability of CZE to determine both HDI monomer and HDI oligomer under the same optimal run conditions even in the presence of a huge excess of derivatizing reagent.

### 3. Fabrication and Assessment of New Samplers

In a side-by-side sampling study, a tryptamine-coated XAD-2 resin was compared with an impinger filled with tryptamine in DMSO. The results indicate, that on average, the relative collection efficiency of the tryptamine-coated resin was 60% of the value obtained using an impinger filled with tryptamine in DMSO. The complete experimental results are presented in Rudzinski et al. (1997)

Four VITON membranes were evaluated for their solvent resistivity when used as backup membranes in a cassette sampler. Sorption and diffusion coefficients were obtained ranging from $3 \times 10^{-9}$ cm$^2$/s for toluene up to $9 \times 10^{-8}$ cm$^2$/s for dioxane. Though the membranes were resistive to toluene, DMSO, and dioxane, we could not prepare membranes sufficiently thin to allow air penetration at a rate of 1 liter/minute. The experimental details are presented in Rudzinski, Harlapur and Aminabhavi (1996)

. Fifty latex membranes were prepared based on natural rubber (NR), styrene-butadiene rubber (SBR) and natural rubber/styrene butadiene rubber blends. Of the fifty membranes installed in cassettes and tested for air-penetration, sixteen allowed sufficient air flow so that the pump would not turn off. Though we believe the air-flow is *primarily around and not through* the membrane, we did observe a correlation between film thickness and measured flow rate (see Rudzinski et al (1997)

Samplers were prepared by installing a polyurethane foam (PUF) produced by Supelco (Bellefonte, PA) on top of a glass fiber filter in a 25 mm cassette sampler (Nucleopore). Both the PUF and glass fiber filter had been soaked previously in a 1000 ppm solution of MOP in DMSO. The PUF was squeezed until just moist, while the glass fiber filter was air dried.

Recoveries were determined for HDI and HDI-biuret at several concentrations. HDI and HDI-biuret were added to the sampler then extracted after 15 minutes with 30 mL of 50 ppm MOP derivatizing reagent in acetonitrile. Between 8 µg and 112 µg of HDI added to the sponge yielded an average recovery of 112 ± 34% (n = 6), while adding between 50 µg and 200 µg of HDI-biuret to the sponge yielded an average recovery of 97 ± 22% (n = 8). All samples were run using HPLC analysis as specified in NIOSH Method 5521(14).

In order to assess the stability of the collected sample in the PUF sponge cassette, a field study was conducted at Robins Air Force Base (AFB). Two cassette samplers were positioned about 4 inches apart and placed on a mannequin. The samplers were 3-4 ft above the floor, and about 2-5 feet downdraft from the equipment being painted. The air sampling rate was 1 L/min. One of the sponge samplers was extracted immediately after the spray painting operation (within 15 minutes), while the other was extracted after 24 hours . The HPLC and CZE analysis conditions were as reported for Figure 1.

Table 1 shows that for three sampling events, if the sample is removed and the sponge extracted after 15 minutes, the concentration of polyisocyanate is higher, while for the remainder, the concentration of polyisocyanate is lower. Though the data set is too small to draw firm conclusions (i.e., the 95% confidence level), the results are promising. Apparently waiting 24 h to extract the sponge does not necessarily result in a lower analytical concentration. If samples do not have to be extracted immediately into a sampling container in the field, this would provide a significant improvement over the dual filter cassette sampling method.

PUF cassette samplers were compared with MOP-filled impingers during field studies at Randolph Air Force Base. The MOP filled impingers contained 15 mL of a solution containing 43 mg of MOP per liter of toluene. The PUF cassette samplers contained 1 mL of 1000 ppm MOP in DMSO and fitted with a backup membrane which had been soaked in 50 ppm MOP in acetonitrile. Both samplers were positioned in the breathing zone of a spray painter. The air sampling rate was 1L/min. After sampling, the PUF cassette samplers were immediately immersed in 10 mL of a 50 ppm MOP solution in acetonitrile. All samples were run using HPLC analysis as specified in NIOSH Method 5521(14).

Table 2 reports the air concentration of HDI and HDI-based polyisocyanate obtained during seven sampling events conducted during three different spray-paint operations at Randolph Air Force Base. If sampling event, 3R(6-25-10-personal-50L), is treated as an anomaly and not included in the statistical analysis, the Paired t-test indicates no significant difference ($p<0.05$) when sampling for HDI-polyisocyanate with either an impinger or with a DMSO moistened PUF sponge (21).

**Table 2. Isocyanates in the Spray-paint Environment (Randolph AFB): Comparison of PUF Sponge Cassette and Midget Impinger Methods.**

| Sampling Event | Sample | Monomer | Oligomer |
|---|---|---|---|
| op (mo-day-time-type-sampling volume) | # reagent(sampler) | (mg/m3 of isocyanate) | |
| 1R(12-4-11-personal-50L) | #100MOP(sponge) | ND | 0.12 |
| | #101MOP(MI) | 0.007 | 0.11 |
| 2R(12-12-10-area-50L) | #807MAP(sponge) | ND | 0.17 |
| | #814MOP(MI) | 0.082 | 0.16 |
| 2R(12-12-12-area-118L) | #808MAP(sponge) | ND | 0.11 |
| | #815MOP(MI) | 0.045 | 0.13 |
| 2R(12-12-10-personal-60L) | #809MOP(sponge) | 0.012 | 0.15 |
| | #811MOP(MI) | 0.03 | 0.22 |
| 2R(12-12-12-personal-120L) | #810MOP(sponge) | 0.008 | 0.09 |
| | #812MOP(MI) | 0.04 | 0.11 |
| 3R(6-25-10-personal-48L) | #432MOP(sponge) | ND | 0.33 |
| | #431MOP(MI) | ND | 0.30 |
| 3R(6-25-10-personal-50L) | #434MOP(sponge) | ND | 0.26 |
| | #433MOP(MI) | ND | 0.05 |

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. # reagent (sampler) refer to the lab sample number followed by the acronym for the derivatizing reagent followed by the type of sampler. ND = below LOD

Sponge cassette samplers (Nucleopore) were also compared with personal IOM samplers (SKC) at Hill Air Force Base. These were both fitted with a PUF sponge which had been immersed in 1000 ppm MOP in DMSO and fitted with a backup membrane which had been soaked in 50 ppm MOP in acetonitrile. The two cassette samplers were positioned about 4 inches apart and placed on a mannequin. The samplers were 3-4 ft above the floor and about 2-6 feet downdraft from the equipment being painted. The air sampling rate was 1 L/min. Both of the sponge samplers were placed in 10 mL of 50 ppm MOP in acetonitrile within 15 minutes after the termination of spray painting. The HPLC and CZE analysis conditions were as reported for Figure 1.

Table 3 presents data obtained from 5 of 6 sampling events. The results for HDI-polyisocyanate when obtained with an IOM sampler (IOM) are generally higher than those obtained with a cassette sampler (CAS; 21). The disparity may be attributed to the loss of mechanical rigidity which can occur when the PUF sponge is immersed in DMSO. One of the disadvantages to using DMSO as the solvent is that if the PUF sponge is too wet, it loses some of its sponge volume, i.e., fluffiness. In a cassette sampler if the PUF doesn't line up against the walls, sample may be lost; whereas, in an IOM sampler the PUF is secured and only a small aperture (15 mm) is exposed to the air flow. For these reasons, the cassette sampler may miss some of the aerosol particles and provide lower concentrations.

**Table 3. Isocyanates in the Spray-paint Environment (Hill AFB): Comparison of Cassette and IOM Samplers**

| | mg/m3 of isocyanate based on HDI | | |
|---|---|---|---|
| Sample<br># sampler(volume) | HDI-based poly<br>HPLC analysis | HDI-based poly<br>CZE analysis | HDI monomer<br>CZE analysis |
| #41021-CAS(32L) | 1.55 | 1.86 (1.03) | 0.026 |
| #41101-IOM(30L) | 1.07 | 1.50 (0.84) | 0.013 |
| #42022-CAS(14L) | <LOQ | <LOQ | 1.84 |
| #42102-IOM(14L) | 1.96 | 0.05 | 0.029 |
| #43023-CAS(23L) | 0.46 | 1.87 (1.04) | 0.031 |
| #43103-IOM(24L) | 2.3 | 3.19 (1.79) | 0.012 |
| #44024-CAS(61L) | 0.41 | 0.67 (0.37) | 0.021 |
| #44104-IOM(61L) | 0.82 | 1.8 (1.00) | 0.007 |
| #45025-CAS(62L) | 0.74 | 1.26 (0.71) | 0.033 |
| #45105-IOM(62L) | 0.83 | 1.28 (0.72) | 0.003 |
| #46026-CAS(31L) | 0.04 | 0.53 (0.30) | 0.023 |
| #46106-IOM(31L) | 1.49 | 0.69 (0.39) | 0.005 |

# reagent (volume) refer to the lab sample number followed by the acronym for the sampler (CAS = cassette, IOM = personal sampler) followed by the volume of air sampled. MOP is the derivatizing reagent. <LOQ = below limit of quantitation. Under the heading, CZE analysis, the value in parentheses is the HDI polyisocyanate adjusted for a difference in the relative response of N-100/HDI

Table 3 also compares the results obtained from both HPLC and CZE analysis. HDI monomer peaks were not detected using HPLC, but HDI monomer was detected using CZE at 185 nm with a concentration in the range, 0.003 to 0.033 mg/m$^3$. For HDI-based polyisocyanates, the concentrations obtained using CZE are usually higher than those obtained from HPLC. If the HDI-based polyisocyanate CZE values are adjusted by multiplying by the relative response factor of 40/72 (the response ratio of N-100-MOP/HDI-MOP from HPLC divided by the response ratio of N-100-MOP/HDI-MOP from CZE), the CZE results can be normalized for a direct comparison with the HPLC results. If the paired t-test is then used to compare HDI-based oligomer concentrations obtained using CZE and HPLC (compare the value in column 2 with that in parentheses in column 3) the difference between means is not significant at the 0.05 level. The results indicate that either HPLC or CZE may be used for the determination of HDI oligomer in the spray-painting environment so long as the relative response ratio for HDI-based polyisocyanate/ HDI is accurate and has been determined for the sample to beanalyzed.

4. Tracer Methods.

Although we had intended to perform tracer studies, a consultation with Jacque Lesage indicated that he and his coworkers had already assessed the fate of HDI and MDI monomer and oligomer after nebulization in an aerosol generation chamber. For MDI and HDI formulations, the chamber provided 80% aerosol in the 1.5 - 3.5 µm size range. Given a formulation containing 1% HDI monomer and 95% HDI oligomer, collection of the aerosol using a dual filter cassette (a 5 µm PTFE filter followed by a MAMA impregnated glass fiber filter) indicates that the percent HDI monomer collected on the sampler increases from 1% to 5% of the total mass, while the HDI-oligomer decreases from 95% to 90% of the total mass. The results for MDI show that a 50% monomer, 50% oligomer formulation exhibits no change in the mass percent after collection. These results seem to indicate that for MDI which is an isocyanate almost entirely in the aerosol form, there does not appear to be any discrimination between the efficiency of collection for the monomer and the oligomer. However, for a sample containing both vapor and aerosol (e.g. HDI), the sampler either is more efficient at collecting HDI in the vapor form, HDI-based polyisocyanate depolymerizes during spray-painting or on the filter, or HDI-based polyisocyanate reacts with interferences.

Much of our research progress during the R01-OHO-3295-01 funding period has been detailed in the papers listed below

1. W.E. Rudzinski, S. Norman, B. Dahlquist, K. Greebon, A. Richardson, K. Locke and T. Thomas, "Evaluation of 1-(9-anthracenylmethyl) piperazine for the Analysis of Isocyanates in Spray-Painting Operations", Am. Ind. Hyg. Ass. J. 57: 914-917 (1996) .
2. W.E. Rudzinski, R. Sutcliffe, B. Dahlquist and R. Key-Schwartz, Evaluation of Tryptamine in an Impinger and on XAD-2 for the Determination of Hexamethylene-based Isocyanates in Spray-painting Operations, Analyst 122: 605-608 (1997).
3. W.E. Rudzinski, S.F. Harlapur and T.M. Aminabhavi, "Evaluation of Solvent Resistivity of Fluoropolymers For Use as Backup Membranes in Isocyanate Samplers", J. Appl. Polym. Sci. 62:1587-1595 (1996).
4. W.E. Rudzinski, T.M. Aminabhavi, S.C. George and S. Thomas. " Preparation and Evaluation of Polyurethane Foam/Rubber Membrane-Based Samplers for Use in Isocyanate Sampling", Polymer Plastics Technology and Engineering 37(1), 103-113 (1997).

We do not have any "Project-Generated Resources" nor any "Inventions and Patents".

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## List of Publications

1. Rudzinski WE, Norman S, Dahlquist B, Greebon K, Richardson A, Locke K and Thomas T: Evaluation of 1-(9-anthracenylmethyl) piperazine for the Analysis of Isocyanates in Spray-Painting Operations. Am. Ind. Hyg. Ass. J. 57: 914-917, 1996.
2. Rudzinski WE, Sutcliffe R, Dahlquist B and Key-Schwartz R: Evaluation of Tryptamine in an Impinger and on XAD-2 for the Determination of Hexamethylene-based Isocyanates in Spray-painting Operations. Analyst 122: 605-608, 1997.
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4. Rudzinski WE, Yin J, Anderson T, Norman S, Unnikrishnan G, Varkey JT, George SC, Thomas S, and Aminabhavi TM, "Preparation and Evaluation of Polyurethane Foam/Rubber Membrane-Based Samplers for Use in Isocyanate Sampling. Polymer Plastics Technology and Engineering 37(1): 103-113, 1998.
5. Rudzinski WE, Yin J, Norman S, Glaska J: Determination of Hexamethylene-based Isocyanates in Spray-painting Operations. Part 1 Evaluation of a Polyurethane Foam Sponge Sampler. Analyst : submitted.
6. Norman S: Evaluation of a New Derivatizing Reagent, 1-(9-anthracenylmethyl) piperazine (MAP), for the Analysis of Isocyanates in Spray-Painting Operations. Masters Thesis, Southwest Texas State University, San Marcos TX ,1997.