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WHIRLPOOL CORP.
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SUMMARY

In January 1994, the National Institute for Occupational Safety and Health (NIOSH) received a confidential employee request for a health hazard evaluation at Whirlpool Corporation, Evansville, Indiana. The request asked NIOSH to evaluate potential chemical exposures in several areas of the facility, including the polyurethane foam injection area. Additionally, exposure to environmental tobacco smoke throughout the facility was a concern. The request stated that health effects among some employees, including eye and throat irritation, asthma, emphysema, cancer, heart disease, resulted from exposure to workplace chemicals and environmental tobacco smoke. In response to the request, NIOSH investigators conducted site-visits on February 24-25, 1994, and June 21-22, 1994.

Area air sampling was conducted for monomeric and oligomeric 4,4'-diphenylmethane diisocyanate (MDI) at six locations where polyurethane foam was being injected into refrigerator doors and cabinets. At each location, six experimental sampling trains were used to differentiate between MDI vapor and condensation aerosol. These sampling trains consisted of either an impinger, fritted bubbler, or two fritted bubblers in series followed by a treated glass fiber filter (two types used). Monomeric MDI concentrations ranged from non-detected to 6 micrograms per cubic meter air ($\mu\text{g}/\text{m}^3$), less than the NIOSH Recommended Exposure Limit (REL) of $50 \mu\text{g}/\text{m}^3$, expressed as a 10-hour time-weighted average (TWA). Total isocyanate reactive group concentrations were calculated (range: 2-13 $\mu\text{g}/\text{m}^3$); these concentrations were less than the 8-hour TWA United Kingdom Common Control Limit of $20 \mu\text{g}/\text{m}^3$. The highest concentration ($13 \mu\text{g}/\text{m}^3$) was found at the foam-in-place injection area. No REL or Occupational Safety and Health Administration (OSHA) standard has been established for total reactive isocyanate group. Considering the possible low recovery for oligomeric MDI, the concentrations of oligomer and total isocyanate reactive group may be underestimated. However, if a worst-case 60% recovery is assumed, only the sample collected at the foam-in-place location could be near the Common Control Limit. No MDI was found on the treated filters or back-up bubblers (except one bubbler), suggesting little or no condensation aerosol was present.

Four personal breathing zone (PBZ) and two area air samples for 1,1-dichloro-1-fluoroethane (HCFC-141b) were collected in the foam injection areas. The PBZ

concentrations ranged from 2 to 9 parts per million (ppm), which were below the American Industrial Hygiene Association (AIHA) Workplace Environmental Exposure Level (WEEL) guide of 500 ppm, expressed as an 8-hour TWA. No REL or OSHA criteria has been established for HCFC-141b. Area air sampling with thermal desorption tubes suggested that little or no thermal breakdown products of HCFC-141b were being formed.

A health hazard from over-exposure to MDI or HCFC-141b was not found during the NIOSH evaluation. However, MDI exposure below existing criteria may cause health effects in some employees. Recommendations regarding fork-lift truck operation and environmental tobacco smoke can be found in the Recommendations section of this report.

KEYWORDS: SIC 3632 (Refrigerator cabinets, household) 4,4'-diphenylmethane diisocyanate [MDI], blowing agents, 1,1-dichloro-1-fluoroethane [HCFC-141b], fluorotrichloromethane [CFC-11], condensation aerosol.

INTRODUCTION

In January 1994, the National Institute for Occupational Safety and Health (NIOSH) received a confidential employee request for a health hazard evaluation at Whirlpool Corporation, Evansville, Indiana. The request asked NIOSH to evaluate potential chemical exposures in the foam insulation injection area, refrigerator door painting area, perchloroethylene degreaser area, the Bonderite® metal cleaning operation, the plastic molding extrusion area, and the thermal forming area. Additionally, exposure to environmental tobacco smoke inside the facility was a concern expressed by the requesters. The request stated that several health effects among some employees, including eye and throat irritation, asthma, emphysema, cancer, and heart disease, resulted from exposure to workplace chemicals and environmental tobacco smoke. In response to the request, NIOSH investigators conducted site-visits on February 24-25, 1994 (walk-through visit) and June 21-22, 1994 (air sampling conducted in the foam injection areas). Interim letters were sent to Whirlpool, the union, and the requestors in March and August 1994.

BACKGROUND

Facility Description

The Whirlpool facility in Evansville manufactures components and assembles several models of household refrigerators. The plant manufactures over 5000 refrigerators per day with a workforce of about 5000 hourly employees. During the NIOSH visits, the facility was operating three shifts per day. The foam injection areas have about 200 employees over three shifts.

Process Description

The refrigerator doors and cabinets are filled with a reacting polyurethane foam which polymerizes to a rigid form. The foam provides thermal insulation and some structural integrity for the refrigerator. Foam is injected into the refrigerator cabinet wall in the 12-station and 27-station foamers, the Old Cab Carousel, and the new Foam-In-Place process. The injection machines are automated, but are monitored by employees. Two refrigerator door foamers are also in operation. Since the interior of the refrigerator doors are open on the side where the foam is applied, a laminator (consisting of a belt of heavy tarp) is used to cover the opening to ensure even expansion of foam inside the door. Workers trim excess foam as the doors exit the laminator.

The polyurethane foam is produced from a two-part system. One component (XUS 15146.00L Developmental Isocyanate, Dow Chemical) consists of 4,4'-diphenylmethane diisocyanate (MDI), which is present in both the monomeric and oligomeric (short chain) forms. The other component (XUR 1556-48800-10 Experimental Polyol Formulation, Dow Chemical) contains a mixture of polyol blend, silicone surfactant, amine catalysts, diethylene glycol, and a blowing agent. 1,1-dichloro-1-fluoroethane (HCFC-141b) is a blowing agent currently being used as a replacement for fluorotrichloromethane (CFC-11) in insulating foams. Several foam injection units were recently converted from CFC-11 to HCFC-141b. Some foam injection machines at Whirlpool still use CFC-11, but these machines are scheduled for conversion to HCFC-141b by the end of 1994.

The MDI and polyol components are separately piped from a bulk chemical storage area to foam injection machines, and the two components are mixed at the injection nozzle just before injection into the door panel or cabinet. The MDI and polyol components are preheated to 90°F and 70°F, respectively. After injection, the exothermic polymerization reaction results in formation of a solid polyurethane foam. During polymerization the interior foam temperature reaches 320-340°F. All foam injection machines at Whirlpool have exhaust ventilation.

Previous Air Sampling Results

Whirlpool's previous air sampling results were reviewed. Personal breathing zone and area sampling had been conducted for solvent vapors in the painting area (xylene, toluene, total hydrocarbons) and blowing agents in the polyurethane foam injection areas. A consultant for Whirlpool had sampled for HCFC-141b with an infrared analyzer (Miran®), while other substances were measured using standard NIOSH methods with sorbent tubes. Continuous MDI monitoring with MDA paper-tape monitors is conducted at several foam injection units. Whirlpool representatives indicated the paper-tape monitors have never indicated the presence of MDI. Whirlpool's air monitoring results showed no overexposures to solvents or blowing agents.

EVALUATION PROCEDURES

The NIOSH evaluation consisted of the following elements:

- (1) A visual inspection was conducted to review employee work areas, work practices, administrative procedures, and engineering controls. Confidential interviews were conducted with seven employees.

- (2) A literature search was conducted to review the health effects associated with exposure to MDI and CFC-141b, to determine appropriate sampling methodologies, and to review the results of other industrial hygiene investigations involving the assessment of exposure to MDI and HCFC-141b.
- (3) Environmental monitoring was conducted to assess airborne levels of MDI and HCFC-141b. As discussed below, a complex sampling protocol was utilized to collect area air samples of monomeric and oligomeric MDI, as well as MDI condensation aerosol. Personal breathing zone (PBZ) and area air sampling was conducted for HCFC-141b.

MDI and Isocyanate Group

Background

Based on the equilibrium vapor pressure of monomeric MDI, airborne MDI is predicted to exist as both a particle and vapor at concentrations near the NIOSH Recommended Exposure Limit ($50 \mu\text{g}/\text{m}^3$).¹ Although MDI has a low vapor pressure at room temperature (5×10^{-6} mm Hg), significant vapor concentrations can be generated if MDI is preheated. Heat is also generated during the exothermic polymerization reaction. As the vapor returns to air temperature, some MDI vapor may condense into a particulate aerosol. The size range for this condensation aerosol is from 0.01 to 1 μm in diameter.²

The MDI component used at Whirlpool also contains a significant percentage (about 50%) of oligomer. Airborne MDI oligomer has a lower vapor pressure than the monomer and is likely to exist predominantly as an aerosol or particle.¹

An important problem associated with sampling for isocyanates is that they are very reactive and, therefore, unstable after collection. Isocyanate aerosol cannot simply be collected on a filter because isocyanates can be lost through reaction with other compounds present in the aerosol particle or with those simultaneously collected on the filter. Thus, it is necessary to derivatize isocyanate species rapidly upon collection.

One advantage of impingers and bubblers is that the derivatization reaction can occur rapidly and completely in the impinger fluid. Impingers collect vapors and particles by two mechanisms. Vapors are collected by diffusion of the molecules to the gas-liquid interface during the residence time of the bubbles in the impinger. Large particles are collected by impaction at the bottom of the impinger. However, small particles less than 2 μm in diameter are not efficiently collected by impingers. Bubblers differ from impingers

in that the airstream is dispersed into very small bubbles by passage through sintered glass (frit). Collection results from diffusion of airborne species to the gas-liquid interface,¹ and impaction within the frit to some extent. One study found impingers only 53% as efficient as bubblers for collection of MDI existing as a vapor and condensation aerosol.³ It is possible that bubblers collect very small particles by diffusion more efficiently than impingers. Several studies have evaluated the particle collection efficiency of filters for isocyanate particles, and have found that for reagent-coated glass fiber filters, the efficiencies are high. However, particles (especially the larger ones) may not be efficiently derivatized on the filter.¹

MDI Sampling Protocol

It was decided that the combination of an impinger or bubbler followed by a reagent-coated filter should adequately collect both MDI vapor and condensation aerosol. For comparison purposes, six different sampling trains were used at each location. These sampling trains consisted of either an impinger, bubbler, or two bubblers in series followed by either a 37-mm 1-(2-pyridyl)piperazine [PP]-treated glass fiber filter (OSHA Method 47) or a 13-mm 1-(9-anthracenylmethyl) piperazine [MAP]-treated glass fiber filter. The sampling trains used are listed below.

1. Impinger→MAP-treated glass fiber filter→pump
2. Impinger→PP-treated glass fiber-treated filter→pump
3. Fritted Bubbler→MAP filter→pump
4. Fritted Bubbler→PP filter→pump
5. Fritted Bubbler A→Fritted Bubbler B→MAP filter→pump
6. Fritted Bubbler A→Fritted Bubbler B→PP filter→pump

For sampling train #1 above, for example, air is drawn first into the impinger, which presumably collects the MDI vapor and large particles. The air then passes through tubing to the filter, where the remaining small particles are collected.

Area air sampling for MDI monomer and oligomer was conducted at six foam injection areas: the foam-in-place robotic injection system (outside cage, near instrumentation), two locations near the old cab carousel A & B system (inside machine, between injectors near worker), and three locations around door foam line #1 (near injector, near worker disposing excess foam, and end of line after lamination).

Bubbler and impinger samples were collected with a solution of 20 milliliters (mL) tryptamine in dimethyl sulfoxide (DMSO). For sampling trains containing impingers, the

flow rate was approximately 1 liter per minute (L/min). For bubblers, the flow rate was reduced to 0.5 L/min to prevent excessive foaming. The sampling method is recommended only for area air sampling due to the potential exposure to DMSO solutions. Analyses of impinger and bubbler samples were conducted according to NIOSH Method 5522, Total Isocyanates.⁴ Analyses of tryptamine isocyanate derivative were accomplished by high performance liquid chromatography (HPLC), with fluorescence detection (excitation and emission wavelengths: 275 nm and 320 nm, respectively).

The limits of detection (LOD) and quantification (LOQ) for tryptamine/DMSO samples were 0.4 and 1.2 $\mu\text{g}/\text{sample}$, respectively (for both monomer and oligomer). This translates to a LOD and LOQ of 1 $\mu\text{g}/\text{m}^3$ and 3 $\mu\text{g}/\text{m}^3$, respectively, for impinger samples (400 liter sample), and 2 $\mu\text{g}/\text{m}^3$ and 6 $\mu\text{g}/\text{m}^3$, respectively, for bubbler samples (200 liter sample).

MAP Filters

Experimental 13-mm glass fiber filters treated with 2 mg MAP and 2 μL diethyl phthalate (mounted in Swinnex cassettes) were used in three of the six sampling trains at each location. To ensure all the MDI was derivitized on the filter, the filters were replaced with fresh filters approximately every two hours, at which time the MAP filters were placed in 1 mL solution containing 1 mg MAP in acetonitrile. Three filters were used for each sampling train, and all three were placed in the same vial, becoming a single sample. Field blanks were prepared by placing unused filters in vials containing desorption solution. All 22 samples were stored in the refrigerator until processing.

The filters were analyzed for MDI monomer by HPLC with fluorescence detection (excitation wavelength 250 nm, emission 425 nm). The LOD was 0.3 μg MDI monomer/filter. This translates to about 2 $\mu\text{g}/\text{m}^3$ for the bubbler samples and 1 $\mu\text{g}/\text{m}^3$ for the impinger samples. Because of interferences and artifacts in the samples, the detection limits for the samples were approximately 100 times higher than the instrumental detection limits. Additional information on the analysis protocol can be found in Appendix A.

PP Filters

37-mm PP-treated glass fiber filters were placed in the other three sampling trains at each location. These filters were also replaced in the sampling train approximately every two hours. Immediately after sampling, the filters were removed from the cassettes and

placed in a solution of 1:9 DMSO:acetonitrile. Three filters were used for each sampling train, and all three were placed in the same vial (becoming a single sample). Field blanks were prepared by placing unused filters in vials containing desorption solution. The samples were analyzed for MDI monomer according to OSHA Method 47 by HPLC with fluorescence detection.⁵ The LOD and LOQ was 0.07 and 0.21 $\mu\text{g}/\text{sample}$, respectively. This is equivalent to a LOD of approximately 0.2 $\mu\text{g}/\text{m}^3$ for impinger sampling trains and 0.4 $\mu\text{g}/\text{m}^3$ for bubbler sampling trains.

HCFC-141b

Four PBZ and two area air samples for HCFC-141b were collected by drawing air through coconut shell charcoal tubes (100mg/50mg) at an air flow rate of 50 milliliters per minute (mL/min). The samples were collected using Gillian constant-volume low-flow sampling pumps. One PBZ sample for CFC-11 was collected at the Old Carousel A & B foam injection area. This sample was collected using the same procedure as the HCFC-141b samples.

The charcoal tube samples were prepared and analyzed using a newly modified method for HCFC-141b that is similar to NIOSH Method 2516 for dichlorofluoromethane (Freon®-21).⁴ Each sample was desorbed with 1 mL of carbon disulfide for a minimum of 30 minutes. The samples were analyzed by gas chromatography using a 30-meter DB-1 fused silica capillary column with flame ionization detection.

CFC-11 co-elutes with the HCFC-141b under the conditions used in our analysis. Gas chromatography/mass spectrometry indicated the sample collected at the Old Carousel A & B foam injection area had a detectable peak which was confirmed to be CFC-11. This result was expected since this injection machine still uses CFC-11. For the other samples, the peaks were confirmed to be primarily HCFC-141b. Since CFC-11 was analyzed using HCFC-141b as the standard, the CFC-11 result should be considered a rough estimate only.

The LOD and LOQ for HCFC-141b were 2 $\mu\text{g}/\text{sample}$ and 7 $\mu\text{g}/\text{sample}$, respectively. For a 19 L sample, the LOD and LOQ were approximately 0.02 and 0.08 parts per million (ppm), respectively.

There have been some concerns about possible toxic trace contaminants or breakdown products of HCFC-141b. The two possible contaminants are 1,1-dichloroethene (vinylidene chloride, a potential occupational carcinogen) and a related substance, 1-chloro-1-fluoroethene. To determine if these substances were present, area air samples

were collected with thermal desorption tubes at the 12-Station Foamer, the injection area of the Old Door Foamer, and at the end of the laminator for the Old Door Foamer. Thermal desorption tubes were used because only low-level contaminants were expected. Each stainless steel thermal tube contained three beds of sorbent material: a front layer of Carbotrap C (350 mg), a middle layer of Carbotrap (175 mg), and a back section of Carboxen 569 (150 mg). The samples were collected by drawing air through the tubes at a flow rate of 50 mL/min for 30-60 minutes. The samples were analyzed using the ATD-400® automatic thermal desorption system interfaced directly to a HP5890A gas chromatograph and HP5970 mass selective detector.

EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects if their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a preexisting medical condition, and/or a hypersensitivity (allergy).

In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the evaluation criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent becomes available.

The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH Criteria Documents and Recommended Exposure Limits (RELs), (2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs), and (3) the U.S. Department of Labor/Occupational Safety and Health Administration (OSHA) occupational health standards.⁶⁻⁸ Often, the NIOSH recommendations and ACGIH TLVs are lower than the corresponding OSHA standards. The OSHA standards are required to take into account the feasibility of controlling exposures in various industries where the agents are used; the NIOSH-recommended

standards, by contrast, are based primarily on concerns relating to the prevention of occupational disease. In evaluating the exposure levels and the recommendations for reducing these levels found in this report, it should be noted that industry is required by the Occupational Safety and Health Act of 1970 to meet those levels specified by an OSHA standard.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. Some substances have recommended short-term exposure limits or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from high, short-term exposures.

Following is a discussion of the toxicology and environmental evaluation criteria for the substances evaluated in this survey.

MDI and Isocyanate Group

4,4'-diphenylmethane diisocyanate (MDI), chemical formula $C_{15}H_{10}N_2O_2$, is normally a solid material at room temperature with a white to pale yellow color. This odorless substance, with a molecular weight of 250.3, has a low vapor pressure of 5×10^{-6} mm Hg at 20°C (68°F). Nonvolatile isocyanate species like MDI can present significant vapor hazards when heated or used in exothermic production processes.^{9,10} These isocyanates also may produce condensation aerosols or may be mechanically aerosolized by the production process.

MDI is an aromatic diisocyanate (from a chemical standpoint). Although the majority of studies on aromatic diisocyanates have been done on toluene diisocyanate (TDI), studies done on both chemicals suggest similar health effects.¹⁰ Exposure to MDI and TDI can occur via ingestion, skin contact, and inhalation. Since MDI has a low vapor pressure, fewer respiratory health effects have been reported compared to TDI.

The lung is the primary organ affected by inhaled isocyanates. Adverse reactions include:

- ! upper airway irritation, characterized by cough, and rhinitis;¹¹⁻¹³
- ! acute asthma, manifested as wheezing, breathlessness, and chest tightness occurring immediately after exposure;¹⁴⁻¹⁹
- ! delayed asthma, manifested as wheezing, breathlessness, and chest tightness occurring several hours after exposure;¹⁴⁻¹⁹
- ! dual asthma, manifesting as wheezing, breathlessness, and chest tightness occurring in both an immediate and delayed pattern;^{14-15,19}

- ! hypersensitivity pneumonitis, characterized as chronic fever, malaise, dry cough, and progressive dyspnea;²⁰⁻²²
- ! asymptomatic permanent loss of lung volumes.^{23,24}

Certain individuals may develop isocyanate sensitization, which is usually manifested as a debilitating asthma-like illness caused by very low, even unmeasurable isocyanate concentrations.¹⁰ Other adverse health effects in humans due to isocyanate exposure are skin and eye irritation,^{25,26} and skin hypersensitivity.^{10,26-28} In animals, isocyanates may cause renal toxicity and cancer.¹⁰

The current OSHA standard for monomeric MDI is a ceiling limit of 200 micrograms per cubic meter of air ($\mu\text{g}/\text{m}^3$).⁷ The current NIOSH REL is $50 \mu\text{g}/\text{m}^3$ as a 10-hour time-weighted average (TWA), 40-hour workweek, and a ceiling of $200 \mu\text{g}/\text{m}^3$ for any 10-minute sampling period.^{6,10} The ACGIH TLV is $50 \mu\text{g}/\text{m}^3$ for an 8-hour TWA (no ceiling limit established).⁸

The NIOSH REL for MDI applies to isocyanate monomers only, and not to higher polymers (oligomers) of these compounds. Less information about the toxicological effects of polymeric isocyanates is available.²⁹ Current thinking suggests that unreacted isocyanate groups attached to polymeric isocyanate compounds may also cause effects similar to the monomer.^{29,30}

In 1983 the United Kingdom Health and Safety Commission (HSC) set a "Common Control Limit" for workplace exposure to all isocyanates. This control limit is 20 ug of isocyanate functional group (chemical constituent: -NCO) per cubic meter of air (m^3), expressed as an eight-hour TWA, and $70 \text{ug}/\text{m}^3$, as a 10-minute TWA. The control limit requires that the analytical methods be applicable to "total isocyanate," that is, the sum of all isocyanate species, including monomers and oligomers.³¹

The approach of the HSC is to assume that the isocyanate functional group is inherently responsible for observed health problems associated with exposure, regardless of the organic moiety to which the isocyanate group is attached.³ Thus, $20 \text{ug}/\text{m}^3$ isocyanate functional group applies to any isocyanate-containing compound and is not limited to only a specific monomeric diisocyanate.³²

The following calculation can be used to convert total isocyanate data to appropriate units for comparison to the U.K. standard.³²

Molecular weight of two -NCO groups per molecule = 84 g/mole

MDI molecular weight = 250.26 g/mole

$84/250.26 = 0.34 \text{ g -NCO/g MDI}$

NIOSH Method 5522 base the oligomer calculations on the monomer calibration curve (it is assumed that the oligomers give the same detector response per isocyanate group as the monomer). Therefore, the numbers are added together (monomer + oligomer) to obtain a total estimate, and this number can be converted to the amount of -NCO group to obtain the correct units for comparison to the U.K. standard. Example: a sample contains $3 \text{ug}/\text{m}^3$ monomer, $7 \text{ug}/\text{m}^3$ oligomer = $10 \text{ug}/\text{m}^3$ total MDI. ($10 \mu\text{g MDI}/\text{m}^3$)($0.34 \mu\text{g}$

-NCO/ $\mu\text{g MDI}$) = about 3.4 ug -NCO/ m^3 . This result can then be compared to the U.K. standard of 20 ug/ m^3 .³²

One caution about both NIOSH Methods 5521 and 5522 - during method development, the recovery for oligomer using the monomer calibration curve was estimated between 60% - 75%. This indicates that the fluorescent yield is less for the oligomeric compounds than for the parent monomer compounds. So the oligomer results are an "estimate" (an underestimate) of the amount present.³²

1,1-dichloro-1-fluoroethane (HCFC-141b)

HCFC-141b is a substance currently being used as a replacement for fluorotrichloromethane (CFC-11) as a blowing agent for insulating foams. Several foam injection units at Whirlpool were recently converted from CFC-11 to CFC-141b.

Chlorofluorocarbons can cause narcosis and death from respiratory depression at extremely high concentrations. Additionally, chlorofluorocarbons can cause cardiac arrhythmias or fibrillation following cardiac sensitization.^{33,34} In animal studies, HCFC-141b and CFC-11 appear to have similar thresholds for cardiac sensitization.³⁴ Because of its high vapor pressure, (525 mm Hg at 70 °F),³⁴ HCFC-141b can produce high ambient concentrations of vapor during uncontrolled use. Therefore, HCFC-141b may pose a significant hazard from asphyxiation, particularly in confined spaces.

NIOSH, OSHA, and ACGIH have not established occupational exposure limits for HCFC-141b. The American Industrial Hygiene Association (AIHA), however, has established a Workplace Environmental Exposure Level Guide (WEEL) for HCFC-141b at 500 ppm, expressed as an 8-hour TWA.³⁴ For CFC-11, a Ceiling limit of 1000 ppm (concentration that should not be exceeded at any time) has been established by NIOSH and ACGIH.^{6,8}

RESULTS AND DISCUSSION

MDI Monomer and Oligomer

The area sampling results for MDI monomer and oligomer can be found in Tables 1-6. Since no MDI was detected on the filter samples, the results only reflect MDI found in the bubbler and impinger samples. With one exception, no MDI was found in the back-up bubblers (second bubbler in series).

For easier comparison to the evaluation criteria, arithmetic means of the monomer and oligomer results (combining the impinger and bubbler data) are listed in the tables. Results below the LOD were not included in the calculation of the means. If the data were below the LOQ (values listed in parentheses), the estimated value was used when calculating the mean. Values below the LOQ represent trace concentrations, and the accuracy of concentrations in this range is questionable.

The mean concentrations of monomeric MDI ranged from non-detected (less than $2 \mu\text{g}/\text{m}^3$ for bubbler samples) to a mean of $6 \mu\text{g}/\text{m}^3$, found at the Foam-In-Place Robotic system. These concentrations were below the NIOSH REL and ACGIH TLV TWA criteria of $50 \mu\text{g}/\text{m}^3$. Note that the REL and TLV apply only to the MDI monomer; a REL or TLV for oligomers has not been established.

To calculate the total isocyanate functional group concentrations, the mean monomeric and oligomeric concentrations were added together, and the sums were multiplied by the 0.34 conversion factor, as described in the evaluation criteria. The resulting concentration values were then compared to the 8-hour United Kingdom (U.K.) Common Control Limit for isocyanates ($20 \mu\text{g}/\text{m}^3$). The total -NCO functional group concentrations ranged from below the quantification limit (samples taken inside A & B System Carousel) to $13 \mu\text{g}/\text{m}^3$ (Foam-In-Place unit). These results suggest the concentrations were below the U.K. criteria in all six sampling locations. As discussed in the evaluation criteria, however, the analytical method may underestimate oligomer concentration. Assuming a worst case scenario (60% recovery for oligomers at the Foam-In-Place location), the calculated exposure for total -NCO functional groups may have been as high as $21 \mu\text{g}/\text{m}^3$. Since a recovery study for the particular MDI formulation used at Whirlpool was not conducted, the precise oligomeric concentration at each location cannot be stated with certainty. However, even when considering the reduced recovery for oligomers, it appears likely that all locations were below the U.K. criteria, with the possible exception of the Foam-In-Place location.

In all six sampling locations, the mean concentration of oligomer appeared modestly higher for samples collected with impingers compared to bubblers. Due to insufficient sample size, a statistical difference in concentrations could not be demonstrated, so the significance of this observation remains unknown. Given the LOD for the bubbler samples (about $2 \mu\text{g}/\text{m}^3$), at least some oligomeric MDI should have been found in some back-up bubblers if the bubbler efficiency was significantly less than 100%.

Based on visual observations, some sampling results were unexpected. For example, it was thought that a relatively high MDI concentration might be found inside the A & B

Carousel unit (a location not representative of actual employee exposure). The sampling results indicated this location had the lowest concentration compared to other areas sampled. On the other hand, it was expected that concentrations associated with the Foam-In-Place system might be somewhat lower compared to other areas, since the sampling location was somewhat

removed from the injectors (sampling was conducted 6-8 feet away from the injectors, near the instrument control panels). The Foam-In-Place location actually had the highest MDI concentration.

MDI Condensation Aerosol

The lack of MDI in the filter samples and back-up bubblers (except one) suggests little, if any, MDI was present as a condensation aerosol. This result is consistent with the levels of monomeric MDI found in the impinger and primary (first) bubbler samples, with the highest mean concentration being $6 \mu\text{g}/\text{m}^3$. In this concentration range, most MDI is expected to remain in the vapor form, not forming a condensation aerosol. The vapor concentration of the monomeric species is more important than that of the oligomeric species, since MDI must initially be volatilized before the condensation aerosol can be formed. Oligomeric species have lower vapor pressures compared to monomeric species, so formation of condensation aerosol from oligomer is unlikely.

The oligomer concentrations generally were three to five times higher than the monomeric concentrations. On the basis of vapor pressures, however, the concentration of monomeric vapor should be higher than oligomeric vapor (according to the Material Safety Data Sheet, the starting product MDI is 40-50% monomer and 50-60% oligomer). Two possible explanations account for this apparent discrepancy. First, the collected oligomer may not be in a vapor form. Instead, the airborne oligomeric species may consist of small particles, formed *mechanically* during the injection process. Presumably, these particles are large enough (greater than $2 \mu\text{m}$ in diameter) to be efficiently collected by impingers. Second, MDI monomer may be more reactive compared to the oligomer species. Thus, the monomer may "disappear" before it can be sampled, while the oligomer persists longer in the environment, allowing more of it to be collected.

HCFC-141b

The air sampling results for HCFC-141b can be found in Table 7. The PBZ concentrations ranged from 2 to 9 ppm, which are well below the WEEL guide of 500 ppm. The highest concentration (12 ppm) was found on an area sample collected on the catwalk above the 12-Station Foamer. Less than 1 ppm CFC-11 was found on the PBZ sample collected from a foam operator at the Old Carousel A & B injection area.

Results of the thermal desorption tube analyses indicated the major component on all samples was HCFC-141b. All other substances were present at trace levels compared to HCFC-141b. Other chemicals identified included tetrafluoroethane, propene,

dichlorofluoromethane, fluorotrichloromethane, 1-chloro-1-fluoroethene, methanol, butanes, pentanes, ethanol, acetone, pentanes, isopropanol, 1,1-dichloroethene (vinylidene chloride), and methylene chloride. Some of these compounds (1-chloro-1-fluoroethene and 1,1-dichloroethene) may be present as trace impurities of the HCFC-141b (they were present in our laboratory standard) rather than as decomposition products. The concentrations of these two impurities were so low that they could not be quantified on the charcoal tube samples.

Interviews

During the February 24-25, 1994, NIOSH visit, confidential employee interviews were conducted with seven employees. Five employees were chosen at random, and two employees requested an interview with the NIOSH investigator. Three employees worked in the polyurethane foam injection areas, two employees worked in the plastic thermal forming area, and two employees worked on the door line. None of the employees reported current health symptoms that they believed were related to their work environment. Two employees expressed concern about exposure to second-hand tobacco smoke. Smoking is permitted throughout the facility, except in the painting and degreasing areas. Two employees indicated other employees had to be removed from the foam injection areas in previous years because of health symptoms possibly related to the polyurethane foam operation. Several years ago, polyurethane foam production reportedly utilized toluene diisocyanate (TDI). TDI is no longer used at this Whirlpool plant.

CONCLUSIONS

In all locations sampled, the monomeric MDI concentrations were below the NIOSH REL and ACGIH TLV TWA criteria. With the possible exception of the Foam-In-Place location, the concentrations of total isocyanate functional groups did not exceed the 8-hour TWA U.K. Common Control Limit for isocyanate group. Furthermore, the preheating of the MDI component and the heat generated from the polyurethane formation was not sufficient to produce MDI vapor concentrations which were high enough to form a condensation aerosol. Exposures to blowing agents (HCFC-141b and CFC-11) were effectively controlled.

DISCUSSION AND RECOMMENDATIONS

Paper Tape Monitors

According to MDA representatives, the paper tape monitors for MDI are designed and calibrated to measure monomeric MDI only. In theory, the paper tape monitors should also react with oligomeric MDI, but the relative response of paper tape monitors for oligomeric MDI has not been adequately studied.³⁵ Therefore, it should be recognized that the MDA instrument readings are semi-quantitative, and the instrument has limited utility when MDI oligomer is present (the case at Whirlpool). Since the monitors depend on MDI reacting with a chemical impregnated in the paper tape, MDI in the form of a particulate aerosol may not react completely on the tape, resulting in inaccurate readings. The decision of whether to use the instrument should be made with full knowledge of the instrument's limitations.

Although the focus in this evaluation has been on airborne exposures to MDI, it should be remembered that dermal exposure to unreacted MDI should also be avoided. Coveralls and rubber or polyvinyl chloride gloves should be provided to employees with potential dermal exposure to unreacted MDI.

Environmental Tobacco Smoke

Tobacco smoking in the facility should be eliminated, since it is a health hazard and a potential fire hazard. Workers should not be involuntarily exposed to tobacco smoke. Management and labor should work together to develop appropriate nonsmoking policies that include some or all of the following:³⁶

- ! Prohibit smoking in the workplace and provide sufficient disincentives for those who do not comply.
- ! Distribute information about health promotion and harmful effects of smoking.
- ! Offer smoking-cessation classes to workers.
- ! Establish incentives to encourage workers to stop smoking.

Implementation of a smoking ban might be approached in the following manner. First, a date when the facility is to become smoke free is announced. Sometimes it is convenient for this date to coincide with the end of a re-tooling or shut-down period. During the interim period before the smoking ban, smoking-cessation classes are offered and incentives to stop smoking are established. After the designated date, smoking is strictly

prohibited in the workplace, and sufficient disincentives are implemented for those who do not comply.

The most direct and effective method of eliminating environmental tobacco smoke from the environment is to prohibit smoking in the workplace. Until that is achieved, separate, enclosed areas for smoking, with separate ventilation, may be considered. Air from this area should be exhausted directly outside and not recirculated within the building or mixed with general dilution ventilation for the building. The smoking area should have slight negative pressure to ensure airflow into the area rather than back into the workplace airspace.³⁷

Forklifts

Forklifts in the Whirlpool plant were being operated at a high rate of speed. Considering the number of employees on foot in the facility, the potential for collision between forklifts and employees appeared high. Additional training for forklift operators may be necessary. According to OSHA's regulatory schedule, proposed safety training standards for forklifts and industrial trucks are slated for release in late 1994.³⁸

Miscellaneous

1. As discussed in the interim letter, obstructions to airflow in the paint booth should be removed. Cardboard obstructions, for instance, may affect airflow patterns, possibly resulting in greater exposures to paint solvent.
2. Consider substituting perchloroethylene in the vapor degreaser. NIOSH considers perchloroethylene a potential occupational carcinogen.⁶ Because of environmental restrictions on the use of chlorofluorocarbons, aqueous or terpene cleaners might be considered.
3. Whirlpool's policies regarding hearing protector usage should be enforced in the thermal forming area. During the first NIOSH visit, several employees were not wearing earplugs.

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1. Whirlpool
2. Requester
3. OSHA Region V Office
4. NIOSH Region IV Office
5. Designated State health and safety agencies

For the purpose of informing affected employees, copies of this report shall be posted by the employer in a prominent place accessible to the employees for a period of 30 calendar days.

Definitions and Notes for Tables 1-6

- ! Samples listed within each table were collected during the same time period at the same location. The samples listed are for the bubblers or impingers. All the filter samples were non-detected, and are, therefore, not listed in the tables.
- ! $\mu\text{g}/\text{m}^3$ = micrograms per cubic meter air
- ! For impinger and bubbler samples, values in parentheses are between the detection limit and the quantification limit. The detection and quantification limits for impinger samples were approximately $1 \mu\text{g}/\text{m}^3$ and $3 \mu\text{g}/\text{m}^3$, respectively (400 liter sample). The detection and quantification limits for fritted bubblers were approximately $2 \mu\text{g}/\text{m}^3$ and $6 \mu\text{g}/\text{m}^3$, respectively (200 liter sample).
- ! Flow rates for fritted bubblers were approximately 0.5 L/min, while flow rates for impingers were approximately 0.9 - 1.0 L/min.
- ! NIOSH REL = Recommended Exposure Limit, expressed as a time-weighted average up to 10 hours per day.
- ! ACGIH TLV = American Conference of Governmental Industrial Hygienists Threshold Limit Value, expressed as an 8-hour time-weighted average.
- ! TWA = Time-weighted average, either for up to 10 hours (NIOSH REL) or 8 hours (ACGIH TLV).
- ! For calculating the arithmetic mean, results below the limit of detection were not included in the calculation. All values were rounded to the nearest microgram.

Table 1
 Old Carousel - Inside Machine
 Impinger/Bubbler Sampling Results for
 4,4'-diphenylmethane diisocyanate (MDI)
 Whirlpool Corp.
 June 22, 1994

Sample Number	Flow Rate (L/min)	Sample Volume (L)	Monomer Concentration ($\mu\text{g}/\text{m}^3$)	Oligomer Concentration ($\mu\text{g}/\text{m}^3$)
<i>Impinger-MAP filter-Pump</i>				
IMP-1	0.90	329	-2	4
<i>Impinger-P.Piperazine filter-Pump</i>				
IMP-2	0.95	347	(2)	6
<i>Bubbler-MAP filter-Pump</i>				
BB-21	0.47	172	ND	(3)
<i>Bubbler-P.Piperazine filter-Pump</i>				
BB-22	0.47	172	ND	(4)
<i>Bubbler A-Bubbler B-MAP filter-Pump</i>				
BB-1A	0.50	183	ND	(3)
BB-1B			ND	ND
<i>Bubbler A-Bubbler B-P.Piperazine filter-Pump</i>				
BB-2A	0.48	175	ND	(4)
BB-2B			ND	ND
Arithmetic Mean			(2)	(4)
NIOSH REL and ACGIH TLV as TWA			50	--
Total Isocyanates ($\mu\text{g}/\text{m}^3$)			(6)	
Total -NCO Isocyanate Groups ($\mu\text{g}/\text{m}^3$)			(2)	
United Kingdom Common Control Limit for Total -NCO Isocyanate Groups ($\mu\text{g}/\text{m}^3$)			20	

Table 2

Old Cabinet Line - Between Two Foam Injectors (A & B System)

Impinger/Bubbler Sampling Results for
4,4'-diphenylmethane diisocyanate (MDI)

Whirlpool Corp.

June 22, 1994

Sample Number	Flow Rate (L/min)	Sample Volume (L)	Monomer Concentration ($\mu\text{g}/\text{m}^3$)	Oligomer Concentration ($\mu\text{g}/\text{m}^3$)
<i>Impinger-MAP filter-Pump</i>				
IMP-3	0.95	398	(2)	8
<i>Impinger-P.Piperazine filter-Pump</i>				
IMP-4	0.97	403	(2)	6
<i>Bubbler-MAP filter-Pump</i>				
BB-23	0.49	203	(2)	10
<i>Bubbler-P.Piperazine filter-Pump</i>				
BB-24	0.48	199	ND	6
<i>Bubbler A-Bubbler B-MAP filter-Pump</i>				
BB-3A	0.60	216*	(3)	5
BB-3B			ND	ND
<i>Bubbler A-Bubbler B-P.Piperazine filter-Pump</i>				
BB-4A	0.51	212	(2)	6
BB-4B			ND	ND
Arithmetic Mean			(2)	8
NIOSH REL and ACGIH TLV as TWA			50	--
Total Isocyanates ($\mu\text{g}/\text{m}^3$)				10
Total -NCO Functional Groups ($\mu\text{g}/\text{m}^3$)				3
United Kingdom Common Control Limit for Total -NCO Functional Groups ($\mu\text{g}/\text{m}^3$)				20

* Pump stopped running after 360 minutes

Table 3
 Old Door Foam Line #1, Near Injector
 Impinger/Bubbler Sampling Results for
 4,4'-diphenylmethane diisocyanate (MDI)
 Whirlpool Corp.
 June 22, 1994

Sample Number	Flow Rate (L/min)	Sample Volume (L)	Monomer Concentration ($\mu\text{g}/\text{m}^3$)	Oligomer Concentration ($\mu\text{g}/\text{m}^3$)
<i>Impinger-MAP filter-Pump</i>				
IMP-5	1.00	209*	(3)	12
<i>Impinger-P.Piperazine filter-Pump</i>				
IMP-6	1.00	418	(4)	14
<i>Bubbler-MAP filter-Pump</i>				
BB-25	0.55	230	(3)	11
<i>Bubbler-P.Piperazine filter-Pump</i>				
BB-26	0.50	209	(3)	13
<i>Bubbler A-Bubbler B-MAP filter-Pump</i>				
BB-5A	0.50	209	(4)	11
BB-5B			ND	ND
<i>Bubbler A-Bubbler B-P.Piperazine filter-Pump</i>				
BB-6A	0.50	209	(3)	12
BB-6B			ND	ND
Arithmetic Mean			(3)	12
NIOSH REL and ACGIH TLV as TWA			50	--
Total Isocyanates ($\mu\text{g}/\text{m}^3$)				15
Total -NCO Functional Groups ($\mu\text{g}/\text{m}^3$)				5
United Kingdom Common Control Limit for Total -NCO Functional Groups ($\mu\text{g}/\text{m}^3$)				20

* Estimated volume, pump stopped and was restarted 3 times during the day.

Table 4

Old Door Foam Line #1, Near Worker Disposing Waste Foam
 Impinger/Bubbler Sampling Results for
 4,4'-diphenylmethane diisocyanate (MDI)
 Whirlpool Corp.
 June 22, 1994

Sample Number	Flow Rate (L/min)	Sample Volume (L)	Monomer Concentration ($\mu\text{g}/\text{m}^3$)	Oligomer Concentration ($\mu\text{g}/\text{m}^3$)
<i>Impinger-MAP filter-Pump</i>				
IMP-7	0.93	390	(2)	9
<i>Impinger-P.Piperazine filter-Pump</i>				
IMP-8	0.98	411	(2)	10
<i>Bubbler-MAP filter-Pump</i>				
BB-27	0.53	222	(3)	11
<i>Bubbler-P.Piperazine filter-Pump</i>				
BB-28	0.53	222	(3)	8
<i>Bubbler A-Bubbler B-MAP filter-Pump</i>				
BB-7A	0.50	210	(3)	7
BB-7B			ND	ND
<i>Bubbler A-Bubbler B-P.Piperazine filter-Pump</i>				
BB-8A	0.53	222	(4)	10
BB-8B			(3)	ND
Arithmetic Mean			(3)	9
NIOSH REL and ACGIH TLV as TWA			50	--
Total Isocyanates ($\mu\text{g}/\text{m}^3$)				12
Total -NCO Functional Groups ($\mu\text{g}/\text{m}^3$)				4
United Kingdom Common Control Limit for Total -NCO Functional Groups ($\mu\text{g}/\text{m}^3$)				50

Table 5

Foam-In-Place Robotic Injection System, Outside Cage
 Impinger/Bubbler Sampling Results for
 4,4'-diphenylmethane diisocyanate (MDI)
 Whirlpool Corp.
 June 22, 1994

Sample Number	Flow Rate (L/min)	Sample Volume (L)	Monomer Concentration ($\mu\text{g}/\text{m}^3$)	Oligomer Concentration ($\mu\text{g}/\text{m}^3$)
<i>Impinger-MAP filter-Pump</i>				
IMP-9	0.95	377	5	37
<i>Impinger-P.Piperazine filter-Pump</i>				
IMP-10	1.08	429	4	36
<i>Bubbler-MAP filter-Pump</i>				
BB-29	0.50	199	7	32
<i>Bubbler-P.Piperazine filter-Pump</i>				
BB-30	0.53	210	6	35
<i>Bubbler A-Bubbler B-MAP filter-Pump</i>				
BB-9A	0.55	218	7	28
BB-9B			ND	ND
<i>Bubbler A-Bubbler B-P.Piperazine filter-Pump</i>				
BB-10A	0.50	199	7	28
BB-10B			ND	ND
Arithmetic Mean			6	33
NIOSH REL and ACGIH TLV as TWA			50	--
Total Isocyanates ($\mu\text{g}/\text{m}^3$)			39	
Total -NCO Functional Groups ($\mu\text{g}/\text{m}^3$)			13	
United Kingdom Common Control Limit for Total -NCO Functional Groups as an 8-hour TWA ($\mu\text{g}/\text{m}^3$)			20	

Table 6
 End of Old Door Line #1, After Lamination of Foam
 Impinger/Bubbler Sampling Results for
 4,4'-diphenylmethane diisocyanate (MDI)
 Whirlpool Corp.
 June 22, 1994

Sample Number	Flow Rate (L/min)	Sample Volume (L)	Monomer Concentration ($\mu\text{g}/\text{m}^3$)	Oligomer Concentration ($\mu\text{g}/\text{m}^3$)
<i>Impinger-MAP filter-Pump</i>				
IMP-11	1.0	403	5	38
<i>Impinger-P.Piperazine filter-Pump</i>				
IMP-12	1.0	403	4	25
<i>Bubbler-MAP filter-Pump</i>				
BB-31	0.43	173	(3)	17
<i>Bubbler-P.Piperazine filter-Pump</i>				
BB-32	0.51	206	(5)	22
<i>Bubbler A-Bubbler B-MAP filter-Pump</i>				
BB-11A	0.58	234	(5)	22
BB-11B			ND	ND
<i>Bubbler A-Bubbler B-P.Piperazine filter-Pump</i>				
BB12A	0.58	234	6	23
BB12B			ND	ND
Arithmetic Mean			5	25
NIOSH REL and ACGIH TLV as TWA			50	--
Total Isocyanates ($\mu\text{g}/\text{m}^3$)			30	
Total -NCO Functional Group ($\mu\text{g}/\text{m}^3$)			10	
United Kingdom Common Control Limit for Total -NCO Functional Group ($\mu\text{g}/\text{m}^3$)			20	

Table 7
 Air Sampling Results for
 1,1-dichloro-1-fluoroethane (HCFC-141b)
 Whirlpool Corp.
 June 22, 1994

Job	Location	Sample Time	Concentration HCFC-141b (ppm)^a
Foam Operator	Old Door Line #1	387 minutes (7:35am-2:02pm)	6
Foam Operator	Old Door Line #1	377 minutes (7:42am-2:02pm)	5
Foam Repair Person	North End Door Foamer	345 minutes (8:20am-2:05pm)	2
Foam Operator	12-Station Foamer	370 minutes (8:31am-2:41pm)	9
Area Sample from Catwalk	12-Station Foamer	359 minutes (8:44am-2:43pm)	12
Foam Operator	A & B System	379 minutes (7:52am-2:07pm)	0.3 (Freon-11)
Area Sample	Foam-In-Place	Tubing Disconnected	Invalid Result ^b
Limit of Detection (2 µg/sample)			0.02 ^c
Limit of Quantification (7 µg/sample)			0.08 ^c
HCFC-141b: AIHA Workplace Environmental Exposure Level Guide, as an 8-hour time-weighted average			500
Fluorotrichloromethane: (CFC-11) NIOSH, ACGIH Ceiling Limit (should not be exceeded at any time)			1000

^a ppm = parts per million

^b Tubing connecting sampling pump and charcoal tube was found disconnected.

^c Concentration based on a 19 liter sample.

Appendix A

MAP Filters

10 mL of a solution containing 200 mg MAP reagent and 200 μ L diethyl phthalate in toluene was prepared. A 50 μ L aliquot of this solution was spiked evenly onto a 13 mm binder-free glass fiber filter and allowed to dry in the hood. When dry, a second 50 μ L aliquot was spiked onto it. This gave filters with a total of 2 mg MAP and 2 μ L diethyl phthalate per filter. Approximately 60 filters were prepared in this way. The filters were placed in Swinnex holders and the ends sealed with parafilm. A solution was also prepared to place filters in after sampling. This solution contained MAP at 1 mg/mL in acetonitrile.

In the field, air was drawn through sampling trains possessing MAP filters for about two hours. At this point, the filter assemblies were replaced with new assemblies and the used filters placed in a 4 mL vial containing 1 mL of the desorption solution (contained 1 mg MAP).

Sample workup began by filtering the samples through 0.2 μ m nylon syringe filters. Because particulate material was found in many of the samples after the first filtration, a second filtration was carried out. With washings, the final volume of the samples was approximately 3 mL. To each of these samples was added 10 μ L of acetic anhydride to derivatize the excess MAP (acetylated MAP tails less than free MAP in the HPLC analysis).

The samples were analyzed by injection of 10 μ L (Waters 717Plus Autosampler) onto a 100 x 4.6 mm Alltima C8 reversed-phase column (Alltech). The mobile phase was 62.4% pH 2.5 triethylammonium phosphate buffer / 37.6% acetonitrile run at 1 mL per minute isocratic. The column was maintained at 25 degrees C. The column effluent passed through a Waters Model 486 Tunable Absorbance Detector set at 254 nm, followed by a Spectroflow 980 Programmable Fluorescence Detector set at 250 nm. Detector response ratios were used to assist in peak identification. The fluorescence detector was used for quantitation.

The samples frequently contained a peak at approximately the retention time of the MDI-MAP standard. UV/fluorescence detector response ratio for a pure standard of MDI-MAP was approximately 490. The largest ratio for the sample peak in the retention time window of interest was 49. Therefore, if it was known that only one compound was eluting to give this peak, we could say with certainty that it was not MDI-MAP. The actual retention time and shape of the peak observed in the samples differed slightly from those of the standards, again suggesting it was something else. So, qualitatively, the compound(s) eluting near the retention time of this standard did not appear to be MDI-MAP. NIOSH SOP 018 was used to calculate the LODs for the samples. The LODs given in terms of air concentration vary somewhat because of differences in air sample volume and differences in liquid sample volume. The peak in question, when present in a sample, never gave a fluorescence response greater than the calculated LOD.