TSCA NON-CONFIDENTIAL BUSINESS INFORMATION

DOCUMENT DESCRIPTION	DOCUMENT CONTROL NUMBER	DATE RECEIVED
FYI-1209-01618	85100000001	12/18/09

COMMENTS:

DOES NOT CONTAIN CBI

Bayer MaterialScience

RECEIVED
09 DEC 10 AM 6:01

[redacted]

December 1, 2009

FYI-1209-01618

TSCA Document Processing Center (7407M)
EPA East – Room 6428 Attn: Section 8(e)
U.S. Environmental Protection Agency
1200 Pennsylvania Avenue, NW
Washington, D.C. 20460-0001

8409000007

Re: FYI-0909-01618

To Whom It May Concern:

As you requested in a letter dated October 1, 2009, enclosed are edited versions of five Bayer Material Science (BMS) industrial hygiene reports that describe the spray polyurethane foam (SPF) insulation air monitoring investigations conducted by BMS in 2007 and 2008 (Reports). BMS has edited the Reports out of respect for the privacy of the SPF contractors, their employees and their customers. BMS prepared these Reports with the full cooperation of the contractors and has shared the Reports with the contractors. Importantly, BMS has not edited any data (i.e., information regarding monitoring conditions or results) in the Reports.

Also enclosed are the BMS sampling and analytical methods used for the SPF investigations. Some clarification is necessary. The accompanying edited industrial hygiene Reports make reference to modified NIOSH Method 2516 for 1,1,1,3,3-pentafluoropropane. After completion of the air monitoring investigation, BMS documented the modified method as BMS Method 3.53.0, a copy of which we have enclosed. Next, several of the amine catalysts shown in the Reports are not listed in BMS Method 2.10.3. Though all of the appropriate validation work has been conducted for these particular amines, the written method has not yet been updated to reflect this.

Finally, it is important to note that *none* of the SPF formulations used during the installations referenced in these Reports represent current commercial products. In particular, the [redacted] product has been reformulated to significantly reduce the amount of [redacted] (an amine catalyst); ultimately, [redacted] is scheduled for elimination from the [redacted] product.

Company Sanitized

323475

Please feel free to contact me if you have any questions.

Sincerely,

[redacted]

cc: M.Townsend (cover letter only, via email)
A. Kennedy (cover letter only, via email)

Bayer MaterialScience

August 15, 2007

Mr.
President

Dear :

Please find enclosed the report of the industrial hygiene evaluation conducted by Bayer MaterialScience on June 25, 2007 at
The airborne levels of 2,4- and 4,4-diphenylmethane diisocyanate (MDI), polymeric MDI (PMDI), and several amine catalysts were measured during the installation of spray polyurethane foam insulation.

It was a pleasure being of service to you, and we'd like to express our appreciation for the cooperation that we received from your personnel. Please feel free to contact me if you have any questions.

Sincerely,

Enclosure

PUBLIC COPY

Bayer MaterialScience

An Evaluation of Airborne Methylene Diphenyl Diisocyanate (MDI), Polymeric MDI, and Aliphatic Amines

for

at

Conducted by:

B.F. Karlovich, Sr. Industrial Hygienist, Product Safety & Regulatory Affairs
J.W. Miller, Senior R&D Specialist, Environmental Analytics Laboratory

Reported by:

Reviewed by:

Date of Evaluation: June 25, 2007
Date of Report: August 15, 2007

This Bayer evaluation is provided as a customer service at no charge. Information in this evaluation is, to our knowledge, true and accurate, and is based upon the conditions observed at the time of the evaluation. The recommendations and/or suggestions contained in this evaluation are made as part of our customer service and Bayer makes no warranty, either express or implied, with respect to such recommendations and/or suggestions.

PUBLIC COPY

TABLE OF CONTENTS

PAGE

SUMMARY 1

I. INTRODUCTION 4

II. PROCESS OBSERVATIONS 4

III. CRITERIA 6

IV. SAMPLING AND ANALYTICAL TECHNIQUES 6

V. RESULTS AND DISCUSSION 9

VI. RECOMMENDATIONS 14

TABLE 1 Airborne MDI Concentrations - Personal & Area Samples 16

TABLE 2 Airborne PMDI Concentrations - Personal & Area Samples 17

TABLE 3 Airborne Amine Catalyst Concentrations - Personal & Area Samples 18

PUBLIC COPY

SUMMARY

On June 25, 2007 personal and area monitoring of methylene diphenyl diisocyanate (MDI), polymeric MDI, and several amine catalysts were conducted at [redacted] luring the installation of spray polyurethane foam insulation by [redacted]

Personal samples included full-shift samples for three workers and a short-term sample for one employee. Area samples included stationary full-shift samples on each floor of the structure, mobile samples during spraying (to remain at approximately 10 feet and 20 feet from the applicator), and multiple post-spray samples on each floor of the structure. Sample results are summarized in Tables 1-3.

A supplied air hood or half face air purifying respirator with dual particulate/organic vapor cartridges was worn by all employees during spraying activities. Therefore, the actual worker exposures are likely less than the concentrations reported in Tables 1-3 and in the following paragraphs.

Airborne MDI concentrations were 34 and 48 ug/m^3 for the applicator, 7.2 and 66 ug/m^3 for the applicator assistant, and 25 and 60 ug/m^3 for the helper. When evaluated as a TWA for the entire sampling period (approximately 6 hours), the airborne concentrations were 44 ug/m^3 for the applicator, 22 ug/m^3 for the applicator assistant, and 51 ug/m^3 for the helper. None of the samples collected exceeded the ACGIH TLV-TWA of 51 ug/m^3, though the full shift TWA calculated for the helper equaled the TLV-TWA of 51 ug/m^3. Airborne MDI was detected in the one short-term sample collected in the breathing zone of the applicator assistant during a time when he was spraying foam. The airborne concentration was 176 ug/m^3, which is below the OSHA PEL-C of 200 ug/m^3. Due to sampling equipment issues, the airborne concentrations measured for the applicator and applicator assistant may not be representative of actual airborne MDI concentrations and should be viewed with caution.

Airborne PMDI concentrations were 34 and 47 ug/m^3 for the applicator, 8 and 68 ug/m^3 for the applicator assistant, and 32 and 58 ug/m^3 for the helper. When evaluated as a TWA for the entire sampling period (approximately 6 hours), the airborne concentrations were 44 ug/m^3 for the applicator, 23 ug/m^3 for the applicator assistant, and 52 ug/m^3 for the helper. In addition, airborne PMDI was detected in the one short-term sample collected in the breathing zone of the applicator assistant during a time when he was spraying foam. The airborne concentration was 200 ug/m^3. As was the case for airborne MDI, the airborne PMDI concentrations measured for the applicator and applicator assistant are estimates only. While there is no occupational exposure limit for PMDI, it should be viewed as similar to monomeric MDI as to precautions for handling and use. If the OELs for 4,4'-MDI are used as reference limits, the measured airborne levels of PMDI for the helper exceed the TLV-TWA.

PUBLIC COPY

Airborne ( ) were not detected in the three samples collected in the breathing zones of three individuals. Airborne ( ) was measured at 44 ppb for the applicator, nondetect for the applicator assistant, and 31 ppb for the helper. Airborne ( ) was nondetect for the applicator, 8.7 ppb for the applicator assistant, and nondetect for the helper. Airborne ( ) was measured at 9.0, 8.8, and 8.8 ppb for the applicator, applicator assistant, and helper, respectively. ( )

For the stationary full-shift area samples, airborne MDI concentrations were 4.8 and 13 ug/m^3 in the truck trailer, nondetect and 0.27 ug/m^3 on the first floor, nondetect and 20 ug/m^3 on the second floor, and nondetect and 29 ug/m^3 on the third floor. The measurable values on the second and third floors occurred during the time period that spraying was conducted on those floors, while the nondetects occurred when spraying was being conducted on an alternate floor.

Airborne PMDI concentrations were 0.37 and 0.91 ug/m^3 in the truck trailer, nondetect on the first floor, nondetect and 16 ug/m^3 on the second floor, and nondetect and 17 ug/m^3 on the third floor. Similar to airborne MDI, the measurable airborne PMDI values on the second and third floors occurred during the time period that spraying was conducted on those floors, while the nondetects occurred when spraying was being conducted on an alternate floor.

Airborne ( ) was identified at 5.7 ppb in one of two third floor samples. This sample was collected when spraying was being conducted on the third floor. ( ) was not detected in the samples collected on the second and first floors or in the truck trailer. Airborne ( ) was identified at 53 ppb in the truck trailer, and 105 and 66 ppb on the third floor. The higher value was measured when spraying was conducted on the third floor, while the lower value was measured when spraying was conducted on the second floor. Airborne ( ) was identified at 6.4 ppb in one of two third floor samples. This value was measured when spraying was being conducted on the third floor. This compound was not detected in the samples collected on the second and first floors or the truck trailer. Airborne ( ) was identified at 20 ppb in the truck trailer and 10 ppb in one of the two third floor samples. The 10 ppb sample was collected when spraying was being conducted on the third floor. This compound was not detected in the samples collected on the second and first floors. ( ) was not detected in any sample.

The results of the stationary area samples suggest that MDI, PMDI, and amine catalysts did not migrate from the floor being sprayed to the floor above and/or below it. In addition, the results suggest that airborne MDI, PMDI, and a few amine catalysts were present in the trailer.

For the mobile area samples, airborne MDI was measured at 79 ug/m^3, 10 feet from the applicator, and 71 ug/m^3, 20 feet from the applicator. In addition, the short-term sample collected at 10 feet resulted in an airborne concentration of 264 ug/m^3.

Airborne PMDI was identified at 63 ug/m^3, 10 feet from the applicator, and 61 ug/m^3, 20 feet from the applicator. In addition, the short-term sample collected at 10 feet resulted in an airborne concentration of 243 ug/m^3.

PUBLIC COPY

Airborne [redacted] was measured at 4.1 ppb, 10 feet from the applicator, but was not detected at 20 feet from the applicator. Airborne [redacted] was measured at 137 ppb, 10 feet from the applicator. and 140 ppb, 20 feet from the applicator. Airborne [redacted] was measured at 14 ppb at both 10 feet and 20 feet from the applicator. Neither [redacted] or [redacted] were detected at 10 feet or 20 feet.

The mobile area sample results for MDI, PMDI, and the amine catalysts generally revealed very similar results for the 10-foot and 20-foot samples.

Neither MDI, PMDI, or any of the five amine catalysts were detected in the four post spray samples that were collected at different times on each floor. The periods evaluated started at about 35 minutes post-spray, and ended at about 3 hours and 25 minutes post-spray. These data suggest that, at 35 minutes following the end of spraying, workers could have occupied any level of the structure without needing respiratory protection.

Recommendations based on results and observations at the time of the evaluation appear on Page 14.

PUBLIC COPY

I. INTRODUCTION

At the request of Bayer MaterialScience (BMS) and BaySystems North America (BSNA), and with the cooperation of [redacted] and [redacted] the BMS Product Safety & Regulatory Affairs Department sampled for potential airborne MDI, polymeric MDI (PMDI), and several amine catalysts during the installation of ½ pound per cubic foot spray polyurethane foam insulation at [redacted] These townhomes were under construction at the time of the evaluation. Bayer supplies [redacted] and [redacted] for the manufacture of spray polyurethane foam. [redacted] contains approximately equal amounts of monomeric MDI and PMDI. For the purpose of this report, PMDI refers to molecules containing greater than two methylene-linked-phenyl rings, where each phenyl ring has an isocyanate group and methylene links to one or two other phenyl rings. [redacted] a polyol blend, contains numerous components; however, only the amine catalysts were of interest for this investigation.

II. PROCESS OBSERVATIONS

has a typical mobile spray polyurethane foam insulation system. Major components include a mobile truck trailer, diesel generator, drums of A-side [redacted] and B-side [redacted] material, pumps, preheaters, compressor, proportioner, several hundred feet of hoses (one for A-side, one for B-side, one for compressed air) and an air purge spray gun. The A and B hoses are equipped with heated jackets to maintain the desired temperature. Most of these components are housed in the truck trailer. The hoses are used to deliver A-side and B-side material from the proportioner to the spray gun, where the chemicals mix together just prior to being dispensed as a reacting foam into wall cavities and/or onto the underside of roof decking.

Various equipment and operating parameter details are presented in the following table.

Proportioner type	Gusmer H20/35
Diaphragm pump type	Husky 1040
Gun type	Gap Pro air purge plural component
Preheater temperature for A-side	130 degrees Fahrenheit
Preheater temperature for B-side	145 degrees Fahrenheit
Hose heater temperature	130 degrees Fahrenheit
Pressure	1200 PSI
# Foam passes	1 to 2
Foam thickness	4 to 5 inches
Weather conditions	Sun and clouds High of 85 degrees F
Indoor temperature	High of approximately 95 degrees F

PUBLIC COPY

Ventilation	HVAC system not yet installed; one man door open to outside (between 1st and 2nd floors (split entry)). Also, rear door of truck trailer open to outside.

consisted of three floors. Each floor was approximately 24 feet X 35 feet (840 square feet), with a height of about 10 feet on the first and second floors, and 10 to 12 feet on the third floor, due to the sloping roof. The walls consisted of two by six wood framing with exterior oriented strand board (OSB) sheething. The floors and roof deck were constructed of OSB and wood framing. Only the framing for interior walls was present, such that each floor was essentially one continuous room. Each floor also had a "band joist" that consisted of the upper two feet of each wall. When the unit is fully constructed, this space will separate the ceiling from the floor (or roof) above it, and will presumably function to house utilities such as ductwork.

On the third floor, spray polyurethane foam was applied to the underside of the entire roof deck, the three walls that did not abut walls of adjacent units, and band joist on those three walls. Spraying began at approximately 10 a.m. and finished at approximately 1 p.m. Note that this time period included a 40-minute lunch break. On the second floor, spray foam was applied to three walls, including the band joist on those walls, and a small ceiling area above a bay window. Spraying began at approximately 2 p.m. and was completed by 2:45 p.m. Spraying of the first floor did not occur on the day of the evaluation.

Prior to spraying, preparation activities included attaching plastic sheeting to doors and windows using spray adhesive, applying a one-component foam caulk (aerosol can) around windows, doors, and other cracks, moving hoses, gun, and other equipment into the unit, and adjusting controls and equipment.

Minor amounts of foam present on the face of wall and ceiling framing were periodically scraped or sawed off manually as spraying progressed. Because of the wall stud thickness (nominal six inches), foam typically did not expand beyond the stud face.

Three employees were monitored during this investigation, an applicator, applicator assistant, and helper. The applicator used the spray gun to apply the foam for the entire third floor. However, he functioned as the applicator assistant during the spraying of the second floor. The applicator assistant conducted various activities, including holding the hose for the applicator, moving the mobile scaffold for the applicator when spraying the underside of the roof deck, and using a manual scraper to remove foam from stud faces. The applicator assistant used the spray gun to apply foam to the entire second floor. The helper applied plastic sheeting to windows and doors, installed one component foam around doors and windows, used a manual saw to remove foam from studs, and moved hoses for the applicator. For more than half of the time during spraying, the applicator assistant and helper were near the applicator or on the same floor as the applicator.

PUBLIC COPY

All employees wore jeans, short-sleeved shirts, hardhats, and boots. During spraying of the third floor, the applicator wore a Bullard loose-fitting supplied air hood and fabric gloves. When he was functioning as the applicator assistant, he wore a 3M air purifying respirator with dual particulate/organic vapor cartridges instead of the supplied air hood. During spraying of the third floor by the applicator, the applicator assistant wore a 3M half face air purifying respirator with dual particulate/organic vapor cartridges, Kimberly Clark Konformguard® disposable suit, face shield (by attaching a piece of thin transparent plastic to the brim of his hard hat), and disposable nitrile gloves. When the applicator assistant sprayed foam on the second floor, he wore a Bullard loose-fitting supplied air hood instead of the air purifying respirator. During spraying, the helper wore a 3M half face air purifying respirator with dual particulate/organic vapor cartridges.

III. CRITERIA

MDI/PMDI

The American Conference of Governmental Industrial Hygienists (ACGIH) has adopted a Threshold Limit Value - Time Weighted Average (TLV-TWA) for 4,4'-methylene bisphenyl isocyanate (MDI) of 0.005 parts per million (ppm) (i.e., 5 parts per billion, ppb) or 0.051 milligrams per cubic meter of air (mg/m^3). This is an airborne concentration for a normal 8-hour workday and a 40-hour workweek and represents conditions under which nearly all workers can be exposed without adverse effect. In addition, the federal Occupational Safety and Health Administration (OSHA) has established a Permissible Exposure Limit (PEL) for 4,4'-MDI of 0.02 ppm or 0.2 mg/m^3 as a Ceiling (C) limit. The Ceiling limit is a concentration that should not be exceeded during any part of the day.

At present, neither an ACGIH TLV nor a federal OSHA PEL has been established for 2,4'-MDI or polymeric MDI. However, Bayer MaterialScience recommends that the exposure limits for 4,4'-MDI be used for the 2,4'- MDI isomer. Further, the 4,4'-MDI OELs also should be considered as reference limits for PMDI.

AMINE CATALYSTS

PUBLIC COPY

IV. SAMPLING AND ANALYTICAL TECHNIQUES

Sampling Media

13-mm Impregnated Filter

Prior to any spraying activity, samples of airborne MDI/PMDI were collected using coated 13mm glass fiber filters, mounted in Swinnex holders and connected to SKC Airchek 52 or Buck Basic 5 air sampling pumps. The filters were either attached to the workers' lapels (i.e., personal samples) or placed in the surrounding work area (i.e., area samples). All pumps were calibrated before sample collection to a sampling rate of approximately 1 liter per minute (Lpm) using a Bios DryCal® DC-Lite Primary Air Flow Meter. The sampling rate was reconfirmed after the sampling event, with the average value used in the volume calculation. Prior to mounting the filter to the Swinnex holder, each filter was coated with 2 mg of 1-(2-pyridyl)piperazine and diethyl phthalate. Immediately upon completion of sampling, the filters were removed from the Swinnex holders and desorbed in 2 ml of acetonitrile/dimethyl sulfoxide (90:10 v/v) solution. When airborne MDI/PMDI is drawn through the filter it is converted to a stable urea derivative, which is quantitatively analyzed by High Performance Liquid Chromatography (HPLC) using Bayer MaterialScience Method 1.7.7.

Impinger and 13-mm Impregnated Filter

During and following active spraying, samples of airborne MDI/PMDI were collected using glass impingers containing 15 milliliters of a solution of toluene and 1-(2-pyridyl)piperazine backed up by coated 13mm glass fiber filters, mounted in Swinnex holders and connected to Ametek air sampling pumps. The impinger/filter sampling trains were either attached to the workers' lapels (i.e., personal samples) or placed in the surrounding work area (i.e., area samples). All pumps were calibrated before sample collection to a sampling rate of approximately 1 Lpm, using a Bios DryCal® DC-Lite Primary Air Flow Meter. The sampling rate was reconfirmed after the sampling event, with the average value used in the volume calculation. Prior to mounting the filter to the Swinnex holder, each filter was coated with 2 mg of 1-(2-pyridyl)piperazine and diethyl phthalate. Immediately upon completion of sampling, the filters were removed from the Swinnex holders and desorbed in 2 ml of acetonitrile/dimethyl sulfoxide (90:10 v/v) solution. When airborne MDI/PMDI is drawn through the impinger solution it is converted to a stable urea derivative, which is quantitatively analyzed by HPLC using Bayer MaterialScience Method 1.20.1. The 13mm filters were analyzed according to Bayer MaterialScience Method 1.7.7.

XAD-2 Sorbent Tubes

Samples of amine catalysts were collected using XAD-2 sorbent tubes (8 mm diameter X 110 mm) connected to Gilian LFS-113DC low flow or SKC Airchek 52 air sampling pumps. Sampling devices were either attached to the workers' lapels for breathing zone sampling or placed in fixed locations for area sampling. All pumps were calibrated before and after sample collection to approximately 0.5 Lpm (1.0 Lpm for post-spray samples), using a Bios DryCal®

PUBLIC COPY

DC-Lite Primary Air Flow Meter. Each sample was quantitatively analyzed by Gas Chromatograph / Mass Spectrometer using BMS Industrial Hygiene Laboratory Method 2.10.3.

All samples collected were analyzed at the Bayer MaterialScience Industrial Hygiene Laboratory, which is accredited by the American Industrial Hygiene Association (AIHA).

Background Area Samples

Prior to arrival on site, air samples were collected at the approximate mid-point of the second floor from a height of approximately 4 to 5 feet above the floor. These samples were taken to evaluate background levels of the MDI, PMDI, and amine catalysts. The samples were run for a period of about one hour, and were stopped when arrived on site.

Stationary Area Samples

One sample was collected at approximately the center of each floor from the start of the workday (arrival) until 15, 45, and 50 minutes after the end of spraying for the day for the third, second, and first floors, respectively. The air sampling pumps and associated media were attached to stands such that the samples were drawn from a height of approximately 4 to 5 feet off of the floor. Sample media for each floor were changed out when spraying moved from the third floor to the second floor.

In addition to these samples, samples were collected inside the truck trailer (toward the back away from the door) from a height of approximately 4 to 5 feet off of the floor.

Mobile Area Samples During Spraying

Samples were collected at distances of approximately 10 feet and 20 feet from the applicator during spraying. The air sampling pumps and associated media were attached to stands on small mobile carts such that the samples were drawn from a height of approximately 4 to 5 feet above the floor. The carts were moved periodically to achieve the desired distances from the applicator as the spraying progressed. Due to the near constant movement of the applicator, the 10-foot samples respresented a distance of about 10 to 15 feet, while the 20-foot samples represented a distance of about 20 to 25 feet. Any time spraying had ceased for a period of 15 minutes, the sample pumps were shut off. The pumps were then restarted once spraying resumed. The exception to this was when spraying ended for the day, at which time samples were collected for 40 minutes post spray.

Area Samples Following Spraying

Four samples were collected from the approximate center of each floor of the structure following the end of spraying. The air sampling pumps and associated media were attached to stands such that the samples were drawn from a height of approximately 4 to 5 feet off of the floor. The

PUBLIC COPY

following table depicts the number of minutes following the end of spraying for the four samples at each location. Each sample ran for a duration of about 30 to 40 minutes.

Location	1st Sample (min.)	2nd Sample (min.)	3rd Sample (min.)	4th Sample (min.)
3rd Floor	37	76	113	148
2nd Floor	45	83	120	155
1st Floor	58	94	135	172

V. RESULTS AND DISCUSSION

The analytical results for this evaluation are presented in Tables 1-3. Tables 1 and 2 contain the results for MDI and PMDI, respectively. In both tables, the reported values are a combination of the MDI/PMDI found in the impinger solution and the MDI/PMDI found on the back-up 13mm filter. Table 3 contains the results for the amine catalysts. Each table contains the results of the personal and area samples.

Personal Samples

A supplied air hood or half face air purifying respirator was worn by all employees during spraying activities. Therefore, the actual exposures are likely less than the concentrations reported in Tables 1-3 and in the following paragraphs.

MDI

Airborne MDI was detected in all six of the long term samples collected in the breathing zones of three individuals. Airborne concentrations were 34 and 48 ug/m^3 for the applicator, 7.2 and 66 ug/m^3 for the applicator assistant, and 25 and 60 ug/m^3 for the helper. When evaluated as a TWA for the entire sampling period (approximately 6 hours), the airborne concentrations were 44 ug/m^3 for the applicator, 22 ug/m^3 for the applicator assistant, and 51 ug/m^3 for the helper. While the helper's exposure equaled the ACGIH TLV-TWA of 51 ug/m^3, none of the samples collected exceeded the TLV-TWA. There were occasions, however, when it was discovered that the pumps were not pulling air through the sampling media due to plugging (caused by particulate loading) of the impingers, and other times when portions of the sampling apparatus had become disconnected from the pump tubing. Furthermore, the air flow rates at the end of the sampling period had dropped significantly compared to the flow at the start of the sampling period. Thus, the results for the applicator and applicator assistant may not be representative of the actual airborne MDI concentrations.

Airborne MDI was detected in the one short-term sample collected in the breathing zone of the applicator assistant during the time that he was spraying foam. The airborne concentration was 176 ug/m^3, which is below the OSHA PEL-C of 200 ug/m^3.

PUBLIC COPY

In most cases, MDI was not detected on the back-up 13mm filters, suggesting that the impingers captured the majority of the airborne MDI. Where MDI was identified in the back-up filters, it was measured at very low levels compared to the amount found in the impinger solution.

PMDI

Airborne PMDI was detected in all six of the long term samples collected in the breathing zones of three individuals. Airborne concentrations were 34 and 47 ug/m^3 for the applicator, 8 and 68 ug/m^3 for the applicator assistant, and 32 and 58 ug/m^3 for the helper. When evaluated as a TWA for the entire sampling period (approximately 6 hours), the airborne concentrations were 44 ug/m^3 for the applicator, 23 ug/m^3 for the applicator assistant, and 52 ug/m^3 for the helper. As previously stated, the results for the applicator and applicator assistant may not be representative of the actual airborne PMDI concentrations.

Airborne PMDI was detected in the one short-term sample collected in the breathing zone of the applicator assistant during the time that he was spraying foam. The airborne concentration was 200 ug/m^3.

While there is no OEL for PMDI, it should be viewed as similar to monomeric MDI as to precautions for handling and use. If the OELs for 4,4'-MDI are used as reference limits, the measured airborne levels of PMDI for the helper exceed the TLV-TWA.

In all cases, PMDI was not detected on the back-up 13mm filters, suggesting that the impingers captured all of the airborne PMDI.

Amine Catalysts

Airborne [redacted] were not detected in the three samples collected in the breathing zones of the three workers.

Airborne [redacted] was identified at 44 ppb for the applicator, nondetect for the applicator assistant, and 31 ppb for the helper.

Airborne [redacted] was nondetect for the applicator, 8.7 ppb for the applicator assistant, and nondetect for the helper.

Airborne [redacted] was identified at 9.0, 8.8, and 8.8 ppb for the applicator, applicator assistant, and helper, respectively.

PUBLIC COPY

Area Samples

Background Samples

MDI, PMDI, and amine catalysts were not detected in the background samples.

Full Shift Stationary Samples

MDI

Airborne MDI was detected in five of the eight long term samples collected from four locations. Airborne concentrations were 4.8 and 13 ug/m^3 in the trailer, nondetect and 0.27 ug/m^3 on the first floor, nondetect and 20 ug/m^3 on the second floor, and nondetect and 29 ug/m^3 on the third floor. The measurable values on the second and third floors occurred during the time period that spraying was conducted on those floors, while the nondetects occurred when spraying was being conducted on an alternate floor. These results suggest that MDI did not migrate from the floor being sprayed to the floor above and/or below it. The results also suggest that airborne MDI was present in the trailer.

In most cases, MDI was not detected on the back-up 13mm filters, suggesting that the impingers captured the majority of the airborne MDI. Where MDI was identified in the back-up filters, it was measured at very low levels compared to the amount found in the impinger solution.

PMDI

Airborne PMDI was detected in four of the eight long term samples collected from four locations. Airborne concentrations were 0.37 and 0.91 ug/m^3 in the trailer, nondetect on the first floor, nondetect and 16 ug/m^3 on the second floor, and nondetect and 17 ug/m^3 on the third floor. The measurable values on the second and third floors occurred during the time period that spraying was conducted on those floors, while the nondetects occurred when spraying was being conducted on a different floor. These results suggest that PMDI did not migrate from the floor being sprayed to the floor above and/or below it. The results also suggest that airborne PMDI was present in the trailer.

In all cases, PMDI was not detected on the back-up 13mm filters, suggesting that the impingers captured all of the airborne PMDI.

Amine Catalysts

Airborne was identified at 5.7 ppb in one of two third floor samples. This sample was collected when spraying was being conducted on the third floor. was not detected in the samples collected on the second and first floors.

PUBLIC COPY

Airborne [redacted] was identified at 53 ppb in the truck trailer, and 105 and 66 ppb on the third floor. The higher value was measured when spraying was conducted on the third floor, while the lower value was measured when spraying was conducted on the second floor. Airborne [redacted] was not detected in the samples collected on the second and first floors. The third floor results suggest either the presence of residual airborne chemical from the just-completed spraying of the third floor, or the migration of airborne chemical from the second to the third floor, or both. Because airborne [redacted] was not detected on the second floor during spraying of the second floor, it is more likely that the airborne chemical identified on the third floor was residual from spraying of the third floor.

Airborne [redacted] was identified at 6.4 ppb in one of two third floor samples. This value was measured when spraying was being conducted on the third floor. This chemical was not detected in the samples collected on the second and first floors.

Airborne [redacted] was identified at 20 ppb in the truck trailer, and 10 ppb in one of the two third floor samples. The 10 ppb sample was collected when spraying was being conducted on the third floor. This chemical was not detected in the samples collected on the second and first floors.

Airborne [redacted] was not detected in any sample.

These amine catalyst results suggest that the catalysts did not migrate beyond the floor being sprayed. Further, the results suggest that airborne amine catalysts were present in the trailer.

Mobile Samples During Spraying

MDI

Airborne MDI was identified at 79 ug/m^3, 10 feet from the applicator, and 71 ug/m^3, 20 feet from the applicator. In addition, the short-term sample collected at 10 feet indicated an airborne concentration of 264 ug/m^3. These results suggest that if a worker would have been consistently positioned at 10 feet or 20 feet away from the applicator, he/she would likely have been exposed to airborne MDI concentrations above the ACGIH TLV-TWA of 51 ug/m^3 and OSHA PEL-C of 200 ug/m^3.

In most cases, MDI was not detected on the back-up 13mm filters, suggesting that the impingers captured the majority of the airborne MDI. Where MDI was identified in the back-up filters, it was measured at very low levels compared to the amount found in the impinger solution.

PMDI

Airborne PMDI was identified at 63 ug/m^3 at 10 feet from the applicator, and 61 ug/m^3 at 20 feet from the applicator. In addition, the short-term sample collected at 10 feet indicated an airborne concentration of 243 ug/m^3. If the OELs for 4,4'-MDI are used as reference limits, these results

PUBLIC COPY

suggest that if a worker would have been consistently positioned at 10 feet or 20 feet away from the applicator, he/she would likely have been exposed to airborne PMDI concentrations above the TLV-TWA and OSHA PEL-C.

In all cases, PMDI was not detected on the back-up 13mm filters, suggesting that the impingers captured all of the airborne PMDI.

Amine Catalysts

Airborne [redacted] was identified at 4.1 ppb at 10 feet from the applicator, but was not detected at 20 feet from the applicator.

Airborne [redacted] was identified at 137 ppb, 10 feet from the applicator, and 140 ppb, 20 feet from the applicator.

Airborne [redacted] was identified at 14 ppb at both 10 feet and 20 feet from the applicator.

Neither [redacted] were detected at 10 feet or 20 feet.

The MDI, PMDI, and amine catalyst results generally reveal very similar results for the 10-foot and 20-foot samples.

Post Spray Samples

Neither MDI, PMDI, or any of the five amine catalysts was detected in the four samples that were collected at different times on each floor. The period evaluated started at about 35 minutes post-spray (start of first sample), and ended at about 3 hours and 25 minutes post-spray (end of last sample).

These data suggest that, at 35 minutes following the end of spraying, workers could have occupied any level of the structure without needing respiratory protection.

PUBLIC COPY

VI. RECOMMENDATIONS

The following recommendations are based on the sampling results and observations that occurred during the day of this evaluation.

1. During spraying, respiratory protection should continue to be worn by the applicator and all other employees who are working on the same floor as the applicator. The minimum level of protection for employees who are not spraying should be an air-purifying respirator (APR) equipped with a combination organic vapor and P100 cartridge. Given that the MDI/PMDI personal air sampling results for the applicator may underestimate actual airborne concentrations, it is prudent for the applicator to continue to wear a supplied air respirator (loose fitting hood) during spraying. Advantages to wearing the hood are that it provides a greater level of protection (i.e., its assigned protection factor is greater than for an air purifying respirator), and it protects the eyes and face from sprays/drips of reacting foam.

2. During spraying, the applicator should wear a disposable long-sleeve suit that provides protection against reacting foam that may be accidentally sprayed onto or that may drip onto the body. The suit should also provide protection against solid and liquid aerosols.

3. During spraying, the applicator should wear disposable boot/shoe covers made of polyethylene, vinyl, or Tyvek®-like material.

4. The fabric gloves worn by the applicator should be substituted or supplemented with gloves made of nitrile, neoprene, or butyl to provide chemical protection, particularly against unreacted MDI/PMDI. An alternative may be to utilize a hybrid glove that is made of fabric that is coated in nitrile, neoprene, or butyl.

5. It was observed that some horizontal surfaces in the work area (e.g., industrial hygienist's notepad, hardhat, and some air sampling equipment) developed a slightly rough or grainy feel, presumably from the deposition of reacting aerosols. Where the square footage/volume (per floor) of a space being sprayed is similar to or smaller than that in this investigation, all employees working on the same floor as the applicator should wear a disposable long-sleeve suit that provides protection against solid and liquid aerosols during spraying, in addition to respiratory protection.

6. If not already done so, a respirator cartridge change-out schedule should be implemented.

7. If not already done so, worker medical evaluations and respirator fit tests should be carried out on an annual basis.

8. If the weather and job site conditions permit, consider the use of ventilation during spraying by opening windows and/or doors on opposite sides of the structure.

PUBLIC COPY

9. Because measureable airborne concentrations of MDI, PMDI, and some amine catalysts were identified in the truck trailer, ensure that all drums of chemicals are tightly closed, connections between pumps, drums, hoses, etc. are tight, and that any drips/leaks are promptly addressed.

PUBLIC COPY

TABLE 1
AIRBORNE METHYLENE DIPHENYL DIISOCYANATE (MDI) CONCENTRATIONS
Personal & Area Samples -
(, - June 25, 2007

Sample Number	Location/ Job Description	Sampling Period	Sample Volume (liters)	2,4'-MDI (ug/m³)	4,4'-MDI (ug/m³)	Total MDI[6] (ug/m³)	TWA[1] (ug/m³)
PERSONAL SAMPLES							
19036-1[2]	, Applicator	09:00-13:23	177.3	6.77	41.3	48	44
19036-2		13:26-14:57	101.3	5.23	28.6	34	
22780-1	, Helper	09:00-13:23	259.6	8.09	51.5	60	51
22780-2		13:27-14:54	81.0	4.94	19.8	25	
22781-1	, Applicator Assistant	09:00-13:23	291.1	1.06	6.18	7.2	22
22781-2[2]		13:28-14:56	59.5	10.1	55.5	66	
23524-1	Applies foam to walls **(short term sample)**	14:26-14:44	16.8	20.8	155	176	--
AREA SAMPLES - STATIONARY							
302-1	2nd Floor - Background	06:21-07:32	73.8	ND[3]	ND	ND	--
888-1	Truck Trailer	08:33-12:30	248.4	1.81	11.4	13	--
888-2		12:30-14:57	154.1	0.74	4.02	4.8	--
19022-1	1st Floor	07:40-14:10	447.7	ND	0.27	0.27	--
19022-2		14:15-15:35	87.4	ND	ND	ND	--
19020-1	2nd Floor	07:35-13:45	404.0	ND	ND	ND	--
19020-2		13:50-15:30	107.5	4.28	15.8	20	--
18437-1	3rd Floor	07:27-13:58	526.3	5.89	23.2	29	--
18437-2		14:04-15:03	63.2	ND	ND	ND	--
AREA SAMPLES - MOBILE							
22787-1	10 feet	09:55-15:25[4]	276.7	13.7	65.1	79	--
19031-1	10 feet (short term sample)	12:40-12:55	15.4	42.9	221	264	--
23516-1	20 feet	09:55-15:25[4]	275.6	12.7	58.4	71	--
AREA SAMPLES – POST SPRAY							
19022-3	1st Floor	15:43-16:14	34.7	ND	ND	ND	--
19022-4		16:19-16:55	37.0	ND	ND	ND	--
19022-5		17:00-17:32	33.9	ND	ND	ND	--
19022-6		17:37-18:09	30.8	ND	ND	ND	--
19020-3[5]	2nd Floor	15:30-16:03	31.8	ND	ND	ND	--
19020-4		16:08-16:41	30.9	ND	ND	ND	--
19020-5		16:45-17:16	31.1	ND	ND	ND	--
19020-6		17:20-17:52	29.2	ND	ND	ND	--
18437-3	3rd Floor	15:22-15:55	33.6	ND	ND	ND	--
18437-4		16:01-16:32	29.6	ND	ND	ND	--
18437-5		16:38-17:08	30.5	ND	ND	ND	--
18437-6		17:13-17:43	28.6	ND	ND	ND	--

(1) Time Weighted Average (TWA) based on the combined sampling times
(2) Sample result is an estimate only – see Results section for further details.
(3) ND (Non-detectable) – concentrations were less than the analytical Limit of Quantitation (LOQ) of 0.1 μg/sample
(4) Sample pump was turned off twice and then back on twice during this time period to coincide with the ceasing/resuming of spraying. Total sample time is 262 minutes.
(5) Small amount of impinger solution was spilled – reported result may slightly underestimate actual airborne concentration.
(6) Reported values are a combination of MDI found in the impinger solution and MDI found on the back-up 13mm filter.

PUBLIC COPY

TABLE 2
AIRBORNE POLYMERIC METHYLENE DIPHENYL DIISOCYANATE (PMDI) CONCENTRATIONS
Personal & Area Samples -
([redacted])- June 25, 2007

Sample Number	Location/ Job Description	Sampling Period	Sample Volume (liters)	PMDI[6] (ug/m^3)	TWA[1] (ug/m^3)
PERSONAL SAMPLES					
19036-1[2]	, Applicator	09:00-13:23	177.3	47	44
19036-2		13:26-14:57	101.3	34	
22780-1	, Helper	09:00-13:23	259.6	58	52
22780-2		13:27-14:54	81.0	32	
22781-1	, Applicator Assistant	09:00-13:23	291.1	8	23
22781-2[2]		13:28-14:56	59.5	68	
23524-1	Applies foam to walls **(short term sample)**	14:26-14:44	16.8	200	--
AREA SAMPLES – STATIONARY					
302-1	2nd Floor - Background	06:21-07:32	73.8	ND[3]	--
888-1	Truck Trailer	08:33-12:30	248.4	0.91	0.7
888-2		12:30-14:57	154.1	0.37	
19022-1	1st Floor	07:40-14:10	447.7	ND	--
19022-2		14:15-15:35	87.4	ND	--
19020-1	2nd Floor	07:35-13:45	404.0	ND	--
19020-2		13:50-15:30	107.5	16	--
18437-1	3rd Floor	07:27-13:58	526.3	17	--
18437-2		14:04-15:03	63.2	ND	--
AREA SAMPLES - MOBILE					
22787-1	10 feet	09:55-15:25[4]	276.7	63	-
19031-1	10 feet **(short term sample)**	12:40-12:55	15.4	243	-
23516-1	20 feet	09:55-15:25[4]	275.6	61	-
AREA SAMPLES – POST SPRAY					
19022-3	1st Floor	15:43-16:14	34.7	ND	-
19022-4		16:19-16:55	37.0	ND	-
19022-5		17:00-17:32	33.9	ND	-
19022-6		17:37-18:09	30.8	ND	-
19020-3[5]	2nd Floor	15:30-16:03	31.8	ND	-
19020-4		16:08-16:41	30.9	ND	-
19020-5		16:45-17:16	31.1	ND	-
19020-6		17:20-17:52	29.2	ND	-
18437-3	3rd Floor	15:22-15:55	33.6	ND	-
18437-4		16:01-16:32	29.6	ND	-
18437-5		16:38-17:08	30.5	ND	-
18437-6		17:13-17:43	28.6	ND	-

(1) Time Weighted Average (TWA) based on the combined sampling times
(2) Sample result is an estimate only – see Results section for further details.
(3) ND (Non-detectable) – concentrations were less than the analytical Limit of Quantitation (LOQ) of 3 μg/sample
(4) Sample pump was turned off twice and then back on twice during this time period to coincide with the ceasing/resuming of spraying. Total sample time is 262 minutes.
(5) Small amount of impinger solution was spilled – reported result may slightly underestimate actual airborne concentration.
(6) Reported values are a combination of PMDI found in the impinger solution and PMDI found on the back-up 13mm filter.

PUBLIC COPY

TABLE 3
AIRBORNE AMINE CATALYST CONCENTRATIONS
Personal & Area Samples - [redacted] - June 25, 2007

Sample Number	Location/ Job Description	Sampling Period	Sample Volume (liters)	[redacted] (ppb)	[redacted] (ppb)	[redacted] (ppb)	[redacted] (ppb)	[redacted] (ppb)
PERSONAL SAMPLES								
6019-1	, Applicator	09:00-14:57	178.1	ND[1]	ND	44	ND	9.0
6018-1	, Helper	09:00-14:54	177.7	ND	ND	31	ND	8.8
6017-1	, Applicator Assistant	09:00-14:56	179.1	ND	ND	ND	8.7	8.8
AREA SAMPLES - STATIONARY								
193-1	2nd Floor - Background	06:21-07:37	38.7	ND	ND	ND	ND	ND
608-1	Truck Trailer	08:33-14:55	82.9	ND	ND	53	ND	20
400-1	1st Floor	07:40-14:15	155.2	ND	ND	ND	ND	ND
400-2		14:15-15:36	31.8	ND	ND	ND	ND	ND
193-2	2nd Floor	07:37-13:45	187.3	ND	ND	ND	ND	ND
193-3		13:50-15:30	50.9	ND	ND	ND	ND	ND
195-1	3rd Floor	07:25-14:06	191.3	5.7	ND	105	6.4	10
195-2		14:06-15:04	27.7	ND	ND	66	ND	ND
AREA SAMPLES - MOBILE								
606-1	10 feet	09:55-15:25[2]	114.2	4.1	ND	137	ND	14
197-1	20 feet	09:55-15:25[2]	123.4	ND	ND	140	ND	14
AREA SAMPLES – POST SPRAY								
954-1	1st Floor	15:39-16:15	38.1	ND	ND	ND	ND	ND
954-2		16:18-16:56	40.5	ND	ND	ND	ND	ND
954-3		17:00-17:33	35.8	ND	ND	ND	ND	ND
954-4		17:37-18:07	32.3	ND	ND	ND	ND	ND
985-1	2nd Floor	15:30-16:03	34.8	ND	ND	ND	ND	ND
985-2		16:06-16:42	38.9	ND	ND	ND	ND	ND
985-3		16:46-17:17	33.5	ND	ND	ND	ND	ND
985-4		17:20-17:52	34.7	ND	ND	ND	ND	ND
949-1	3rd Floor	15:22-15:55	35.0	ND	ND	ND	ND	ND
949-2		16:01-16:33	34.9	ND	ND	ND	ND	ND
949-3		16:38-17:09	33.7	ND	ND	ND	ND	ND
949-4		17:13-17:43	32.7	ND	ND	ND	ND	ND

(1) ND (Non-detectable) - concentrations were less than the analytical Limit of Quantitation (LOQ).
(2) Sample pump was turned off twice and then back on twice during this time period to coincide with the ceasing/resuming of spraying. Total sample time is 262 minutes.

PUBLIC COPY

Bayer MaterialScience

October 16, 2007

Mr.
President

Dear :

Please find enclosed the report of the industrial hygiene evaluation conducted by Bayer MaterialScience on August 6, 2007 at a single-family home at The airborne levels of 2,4- and 4,4-diphenylmethane diisocyanate (MDI), polymeric MDI (PMDI), three amine catalysts, and 1,1,1,3,3-pentafluoropropane were measured during the installation of spray polyurethane foam insulation.

It was a pleasure being of service to you, and we'd like to express our appreciation for the cooperation that we received from your personnel. Please feel free to contact me if you have any questions.

Sincerely,

Enclosure

PUBLIC COPY

Bayer MaterialScience

An Evaluation of Airborne Methylene Diphenyl Diisocyanate (MDI), Polymeric MDI, Amines, and 1,1,1,3,3-Pentafluoropropane

for

at

Conducted by:

Reported by:

Reviewed by:

Date of Evaluation: August 6, 2007
Date of Report: October 16, 2007

This Bayer evaluation is provided as a customer service at no charge. Information in this evaluation is, to our knowledge, true and accurate, and is based upon the conditions observed at the time of the evaluation. The recommendations and/or suggestions contained in this evaluation are made as part of our customer service and Bayer makes no warranty, either express or implied, with respect to such recommendations and/or suggestions.

PUBLIC COPY

TABLE OF CONTENTS

PAGE

SUMMARY 1

I. INTRODUCTION 5

II. PROCESS OBSERVATIONS 5

III. CRITERIA 7

IV. SAMPLING AND ANALYTICAL TECHNIQUES 7

V. RESULTS AND DISCUSSION 10

VI. RECOMMENDATIONS 15

TABLE 1 Airborne MDI Concentrations - Personal & Area Samples 17

TABLE 2 Airborne PMDI Concentrations - Personal & Area Samples 18

TABLE 3 Airborne 1,1,1,3,3-Pentafluoropropane Concentrations - Personal & Area Samples 19

TABLE 4 Airborne Amine Catalyst Concentrations - Personal & Area Samples 20

PUBLIC COPY

SUMMARY

On August 6, 2007 personal and area monitoring of methylene diphenyl diisocyanate (MDI), polymeric MDI, three amine catalysts, and 1,1,1,3,3-pentafluoropropane were conducted at a single family home located at ( ) during the installation of spray polyurethane foam insulation by

Personal (breathing zone) Samples

Personal samples included full-shift samples for three workers and a short-term sample for one employee. Area samples included stationary full-shift samples on each floor of the structure, mobile samples during spraying (to remain at approximately 10 feet, 20 feet, and 30 feet from the applicator), and multiple post-spray samples on each floor of the structure. Sample results are summarized in Tables 1-4.

A supplied air hood was worn by the applicator, and a half face air purifying respirator with dual particulate/organic vapor cartridges was worn by the applicator assistant during spraying activities (when on the same floor as the applicator). Therefore, the actual exposures for these employees are likely less than the concentrations reported in Tables 1-4 and in the following paragraphs.

Airborne MDI concentrations were 7.6 and 37 ug/m^3 for the applicator, 9.3 and 35 ug/m^3 for the applicator assistant, and 6.6 and 6.9 ug/m^3 for the helper. When evaluated as a TWA for the entire sampling period (approximately 5 hours), the airborne concentrations were 71 ug/m^3 for the applicator, 23 ug/m^3 for the applicator assistant, and 6.7 ug/m^3 for the helper. The airborne concentration measured for the applicator exceeds the ACGIH TLV-TWA of 51 ug/m^3. Airborne MDI was detected in the one short-term sample collected in the breathing zone of the applicator during a time when he was spraying foam. The airborne concentration was 799 ug/m^3, which is greater than the OSHA PEL-C of 200 ug/m^3. Due to sampling equipment issues, one of the airborne concentrations measured for the applicator (37 ug/m^3) may not be representative of actual airborne MDI concentration and should be viewed with caution (see Table 1).

Airborne PMDI concentrations were nondetect and 67 ug/m^3 for the applicator, 18 and 25.4 ug/m^3 for the applicator assistant, and nondetect and 9.9 ug/m^3 for the helper. When evaluated as a TWA for the entire sampling period (approximately 5 hours), the airborne concentrations were 56 ug/m^3 for the applicator, 22 ug/m^3 for the applicator assistant, and 4.9 ug/m^3 for the helper. In addition, airborne PMDI was detected in the one short-term sample collected in the breathing zone of the applicator during a time when he was spraying foam. The airborne concentration was 305 ug/m^3 (see Table 2). As was the case for airborne MDI, one of the airborne PMDI concentrations measured for the applicator (67 ug/m^3) is an estimate only due to sampling equipment issues. While there is no occupational exposure limit for PMDI, it should be viewed as similar to monomeric MDI as to the precautions for handling and use. If the OELs for 4,4'-MDI are used as

PUBLIC COPY

reference limits, the measured airborne levels of PMDI for the applicator exceeded both the TLV-TWA and PEL-C.

Airborne 245fa concentrations were 89.6 and 281 ppm for the applicator, 29.9 and 126 ppm for the applicator assistant, and 22.6 and 21.9 ppm for the helper. When evaluated as a TWA for the entire sampling period (approximately 6 hours), the airborne concentrations were 148 ppb for the applicator, 56 ppb for the applicator assistant, and 22 ppb for the helper. None of these values exceed the AIHA WEEL of 300 ppm (see Table 3). It is of note that the air flow rates at the end of the sampling period had increased significantly compared to the flow at the start of the sampling period. Thus, the results may not be representative of the actual airborne 245fa concentrations. Furthermore, the airborne concentration measured for the applicator assistant may be underestimated.

Airborne [redacted] was identified at 15 ppb for the applicator, 13 ppb for the applicator assistant, and 11 ppb for the helper. Airborne [redacted] was identified at 9.8 ppb for the applicator, 6.8 ppb for the applicator assistant, and nondetect for the helper. Airborne [redacted] was not detected in any sample (see Table 4). There are no OELs for these three amine catalysts. [redacted]

Stationary Area Samples

For the stationary full-shift area samples, airborne MDI concentrations were nondetect in the truck trailer, nondetect and 1 ug/m^3 in the basement, nondetect and 2.3 ug/m^3 on the first floor, and nondetect and 45 ug/m^3 on the second floor. The measurable values in the basement and on the first and second floors occurred during the time period that spraying was conducted on the second floor, while the nondetects occurred prior to the start of spraying.

Airborne PMDI concentrations were nondetect in the truck trailer, nondetect and 5.4 ug/m^3 in the basement, nondetect and 16.8 ug/m^3 on the first floor, and nondetect and 40.1 ug/m^3 on the second floor. The measurable values in the basement and on the first and second floors occurred during the time period that spraying was conducted on the second floor, while the nondetects occurred prior to the start of spraying.

Airborne [redacted] was identified at 11 ppb in the truck trailer, and 33 ppb in one of two second floor samples. The 33 ppb sample was collected when spraying was being conducted on the second floor. Airborne [redacted] was not detected in the samples collected in the basement and on the first floor. Airborne [redacted] was identified at 13 ppb in one of two second floor samples. This sample was collected when spraying was being conducted on the second floor. Airborne [redacted] was not detected in the samples collected in the basement, on the first floor, or in the truck trailer. Airborne [redacted] was not detected in any sample.

PUBLIC COPY

Airborne 245fa concentrations were nondetect and 0.94 ppm in the truck trailer, 1.24 and 19.7 ppm in the basement, 0.79 and 18.5 ppm on the first floor, and 16.5 and 209 ppm on the second floor. The larger concentrations in the basement and on the first and second floors occurred during the time period that spraying was conducted on the second floor, while the lower concentrations were measured prior to the start of spraying. As previously stated, the 245fa concentrations should be viewed as estimates only. Also, the airborne concentration measured in two of the samples may be underestimated.

The results of the stationary area samples suggest that MDI, PMDI, and blowing agent migrated from the floor being sprayed to the floors below it. In addition, the results suggest that minor quantities of airborne blowing agent and one amine catalyst were present in the trailer.

Mobile Area Samples

For the mobile area samples, airborne MDI was measured at 44 ug/m^3 10 feet from the applicator, 36 ug/m^3 20 feet from the applicator, and 36 ug/m^3 30 feet from the applicator. In addition, short-term samples collected at 10, 20 and 30 feet indicated airborne concentrations of 49, 23, and 7.5 ug/m^3, respectively.

Airborne PMDI was identified at 30.5 ug/m^3 10 feet from the applicator, 31.5 ug/m^3 20 feet from the applicator, and 36.1 ug/m^3 30 feet from the applicator. In addition, airborne PMDI was not detected in the short-term samples collected at 10, 20, and 30 feet.

Airborne [redacted] was identified at 62 ppb 10 feet from the applicator, 48 ppb 20 feet from the applicator, and 56 ppb 30 feet from the applicator. Airborne [redacted] was identified at 24 ppb 10 feet from the applicator, 22 ppb 20 feet from the applicator, and 25 ppb 30 feet from the applicator. Airborne [redacted] was not detected at any distance.

Airborne 245fa was identified at 238 ppm at 10 feet from the applicator, 279 ppb 20 feet from the applicator, and 259 ppm 30 feet from the applicator.

The mobile area sample results for MDI, PMDI, amine catalysts, and blowing agent generally revealed very similar results for the 10, 20, and 30-foot samples. In other words, distance did not make a significant difference in the measured level.

Post Spray Samples

Neither PMDI nor any of the three amine catalysts was detected in the four samples (two samples for the attic) that were collected at different times on each floor. The period evaluated started at about 15 minutes post-spray (start of first sample), and ended at about 3 hours post-spray (end of last sample). Airborne MDI was detected on the second floor at 4.7 ug/m^3 in the first post spray sample, but not in the other post spray samples. Airborne 245fa was identified in the basement at 23.3 and 13.3 ppb in the first two post-spray samples, but was nondetect in the third sample (the fourth sample was invalid). Airborne 245fa was identified on the first floor at 20.9, 10.2, 5.77, and

PUBLIC COPY

2.95 ppb in the first through fourth post-spray samples. Airborne 245fa was identified on the second floor at 278, 173, 94.9, and 43.9 ppb in the first through fourth post-spray samples. Airborne 245fa was identified in the attic at 192 and 77.6 ppb in the first and second post-spray samples. As previously stated, the 245fa concentrations should be viewed as estimates only. Also, the airborne concentration measured in two of the samples may be underestimated. These results suggest a consistent decline in airborne concentrations with time following the end of spraying. In addition, the data resulting from this survey suggest that, at approximately 15 minutes following the end of spraying, workers could have occupied any level of the structure without the use of respiratory protection.

Recommendations based on results and observations at the time of the evaluation appear on Page 15.

PUBLIC COPY

I. INTRODUCTION

At the request of Bayer MaterialScience (BMS) and BaySystems North America (BSNA), and with the cooperation of the BMS Product Safety & Regulatory Affairs Department sampled for potential airborne MDI, polymeric MDI (PMDI), three amine catalysts, and blowing agent (1,1,1,3,3-pentafluoropropane) during the installation of 2 pound per cubic foot spray polyurethane foam insulation at a single-family home, located at The home was in the process of being renovated at the time of the evaluation. Bayer supplies for the manufacture of spray polyurethane foam. contains approximately equal amounts of monomeric MDI and PMDI. For the purpose of this report, PMDI refers to molecules containing greater than two methylene-linked-phenyl rings, where each phenyl ring has an isocyanate group and methylene links to one or two other phenyl rings. BaySeal 2.0, a polyol blend, contains numerous components; however, only the amine catalysts and blowing agent were of interest for this investigation.

II. PROCESS OBSERVATIONS

has a typical mobile spray polyurethane foam insulation system. Major components include a mobile truck trailer, diesel generator, drums of A-side and B-side material, pumps, preheaters, compressor, proportioner, several hundred feet of hoses (one for A-side, one for B-side, one for compressed air) and an air purge spray gun. The A and B hoses are equipped with heated jackets to maintain the desired temperature. Most of these components are housed in the truck trailer. The hoses are used to deliver A-side and B-side material from the proportioner to the spray gun, where the chemicals mix together just prior to being dispensed as a reacting foam into wall cavities and/or onto the underside of roof decking.

Various equipment and operating parameter details are presented in the following table.

Proportioner type	Graco Reactor E-30 Plural Component
Diaphragm pump type	Husky 1040
Gun type	Gap Pro air purge plural component
Preheater temperature for A-side	110 degrees Fahrenheit
Preheater temperature for B-side	110 degrees Fahrenheit
Hose heater temperature	110 degrees Fahrenheit
Pressure	1100 PSI
# Foam passes	3 to 4 (upon completion)
Foam thickness	3 to 3 1/2 inches (upon completion)
Weather conditions	Fog (a.m.), Hazy sun (p.m.) 09:55 - 77 degrees F / 85% RH 17:05 - 86 degrees F / 73% RH
Indoor temperature and relative humidity	09:55 - 78 degrees F / 77% RH 17:05 - 84 degrees F / 74% RH

PUBLIC COPY

Ventilation	HVAC system not operating; First floor front and back man doors open to outside; Basement back man door open to outside; Also, rear door of truck trailer open to outside.

The single-family home consisted of four floors – a basement, first floor, second floor, and an attic that was accessible via the central stairwell. Each floor was approximately 45 feet (in its longest dimension) by 45 to 50 feet (in its longest dimension). The height was approximately 8 feet in the basement and 10 feet on the first and second floors. The wall system consisted of two by four wood framing on the second floor, two by four and other dimensional wood framing on the first floor, and plaster and brick exterior walls. The floors and roof deck were constructed of wood framing and decking. Only the framing for interior walls was present, such that each floor was essentially one continuous room.

Spray polyurethane foam was applied to all four exterior walls. Spraying began at approximately 11:15 a.m. and finished at approximately 2:30 p.m. Note that this time period included a 55-minute lunch break taken outside (the MDI/PMDI samples were stopped during this period). The second floor was not completed on the day of the evaluation, and additional layers of foam were scheduled to be applied to the second floor walls to achieve the desired thickness on the following day. Spraying of the first floor walls was scheduled to occur on the following day. The underside of the roof deck in the attic was scheduled to be sprayed with a ½ pound foam on the following day as well.

Prior to spraying, preparation activities included attaching plastic sheeting to doors and windows using spray adhesive, laying down plastic sheeting on floors, applying a one-component foam caulk/sealant (aerosol can) around windows, doors, and other cracks, moving hoses, gun, and other equipment into the home, and adjusting controls and equipment in the truck trailer.

Three employees were monitored during this investigation, an applicator, applicator assistant, and helper. The applicator used the spray gun to apply the foam. The applicator assistant conducted various activities, including applying plastic sheeting to floors, and at times holding a cardboard shield over the windows to prevent overspray from contacting them. The helper primarily applied plastic sheeting to windows and doors and installed one component foam around doors and windows,. For the majority of the time during spraying, the applicator assistant was not on the same floor as the applicator. At no time was the helper on the same floor as the applicator during spraying.

All employees wore jeans, short-sleeved shirts, and boots. During spraying, the applicator wore a Bullard loose-fitting supplied air hood, a Kimberly Clark Konformguard® disposable suit, and fabric gloves. The applicator assistant wore a 3M half face air purifying respirator with dual particulate/organic vapor cartridges when on the same floor as the applicator during spraying. The helper wore no PPE, as he was never on the same floor as the applicator during spraying.

PUBLIC COPY

III. CRITERIA

MDI/PMDI

The American Conference of Governmental Industrial Hygienists (ACGIH) has adopted a Threshold Limit Value - Time Weighted Average (TLV-TWA) for 4,4'-methylene bisphenyl isocyanate (MDI) of 0.005 parts per million (ppm) (i.e., 5 parts per billion, ppb) or 0.051 milligrams per cubic meter of air (mg/m^3). This is an airborne concentration for a normal 8-hour workday and a 40-hour workweek and represents conditions under which nearly all workers can be exposed without adverse effect. In addition, the federal Occupational Safety and Health Administration (OSHA) has established a Permissible Exposure Limit (PEL) for 4,4'-MDI of 0.02 ppm or 0.2 mg/m^3 as a Ceiling (C) limit. The Ceiling limit is a concentration that should not be exceeded during any part of the day.

At present, neither an ACGIH TLV nor a federal OSHA PEL has been established for 2,4'-MDI or polymeric MDI. However, Bayer MaterialScience recommends that the exposure limits for 4,4'-MDI be used for the 2,4'- MDI isomer. Further, the 4,4'-MDI OELs also should be considered as reference limits for PMDI.

AMINE CATALYSTS

At present, none of the three amine catalysts have occupational exposure limits (OELs).

IV. SAMPLING AND ANALYTICAL TECHNIQUES

Sampling Media

13-mm Impregnated Filter

Prior to any spraying activity, samples of airborne MDI/PMDI were collected using coated 13mm glass fiber filters, mounted in Swinnex holders, and connected to SKC Airchek 52 air sampling pumps. The filters were either attached to the workers' lapels (i.e., personal samples) or placed in the surrounding work area (i.e., area samples). All pumps were calibrated before sample collection to a sampling rate of approximately 1 liter per minute (Lpm) using a Bios DryCal® DC-Lite Primary Air Flow Meter. The sampling rate was reconfirmed after the sampling event, with the average value used in the volume calculation. Prior to mounting the filter to the Swinnex holder, each filter was coated with 2 mg of 1-(2-pyridyl)piperazine and diethyl phthalate. Immediately upon completion of sampling, the filters were removed from the Swinnex holders and desorbed in 2 ml of acetonitrile/dimethyl sulfoxide (90:10 v/v) solution. When airborne MDI/PMDI is drawn through the filter it is converted to a stable urea derivative,

PUBLIC COPY

which is quantitatively analyzed by High Performance Liquid Chromatography (HPLC) using Bayer MaterialScience Method 1.7.7.

Impinger and 13-mm Impregnated Filter

During and following active spraying, samples of airborne MDI/PMDI were collected using glass impingers containing 15 milliliters of a solution of toluene and 1-(2-pyridyl)piperazine backed up by coated 13mm glass fiber filters, mounted in Swinnex holders, and connected to Ametek air sampling pumps. The impinger/filter sampling trains were either attached to the workers' lapels (i.e., personal samples) or placed in the surrounding work area (i.e., area samples). All pumps were calibrated before sample collection to a sampling rate of approximately 1 Lpm, using a Bios DryCal® DC-Lite Primary Air Flow Meter. The sampling rate was reconfirmed after the sampling event, with the average value used in the volume calculation. Prior to mounting the filter to the Swinnex holder, each filter was coated with 2 mg of 1-(2-pyridyl)piperazine and diethyl phthalate. Immediately upon completion of sampling, the filters were removed from the Swinnex holders and desorbed in 2 ml of acetonitrile/dimethyl sulfoxide (90:10 v/v) solution. When airborne MDI/PMDI is drawn through the impinger solution it is converted to a stable urea derivative, which is quantitatively analyzed by HPLC using Bayer MaterialScience Method 1.20.1. The 13mm filters were analyzed according to Bayer MaterialScience Method 1.7.7.

XAD-2 Sorbent Tubes

Samples of amine catalysts were collected using XAD-2 sorbent tubes (8 mm diameter X 110 mm) connected to SKC Airchek 52 air sampling pumps. Sampling devices were either attached to the workers' lapels for breathing zone sampling or placed in fixed locations for area sampling. All pumps were calibrated before and after sample collection to approximately 0.5 Lpm (1.0 Lpm for post-spray samples), using a Bios DryCal® DC-Lite Primary Air Flow Meter. Each sample was quantitatively analyzed by Gas Chromatograph / Mass Spectrometer using BMS Industrial Hygiene Laboratory Method 2.10.3.

Anasorb Coconut Shell Charcoal Tubes

Samples of blowing agent (1,1,1,3,3-pentafluoropropane) were collected using two charcoal tubes in series (8 mm diameter X 110 mm) connected to Gilian LFS-113DC low flow air sampling pumps. Sampling devices were either attached to the workers' lapels for breathing zone sampling or placed in fixed locations for area sampling. All pumps were calibrated before and after sample collection to approximately 0.01 Lpm, using a Bios DryCal® DC-Lite Primary Air Flow Meter. Each sample was quantitatively analyzed by Gas Chromatograph / Flame Ionization Detector using modified NIOSH Method 2516.

All samples collected were analyzed at the Bayer MaterialScience Industrial Hygiene Laboratory, which is accredited by the American Industrial Hygiene Association (AIHA).

PUBLIC COPY

Background Area Samples

Prior to arrival on site, air samples were collected at the approximate mid-point of the first floor from a height of approximately 4 to 5 feet above the floor. These samples were taken to evaluate background levels of MDI, PMDI, amine catalysts, and blowing agent. The samples were run for a period of 105 minutes, and were stopped when arrived on site.

Stationary Area Samples

With the exception of the attic, one sample was collected at approximately the center of each floor from the start of the workday (arrival) until 15 to 20 minutes after the end of spraying for the day. The air sampling pumps and associated media were attached to stands such that the samples were drawn from a height of approximately 4 to 5 feet above the floor. Sample media for each floor were changed out when spraying began for the day.

In addition to these samples, samples were collected inside the truck trailer (toward the back away from the door) from a height of approximately 4 to 5 feet above the floor.

Mobile Area Samples During Spraying

Samples were collected at distances of approximately 10 feet, 20 feet, and 30 feet from the applicator during spraying. The air sampling pumps and associated media were attached to stands on small mobile carts such that the samples were drawn from a height of approximately 4 to 5 feet above the floor. The carts were moved periodically to achieve the desired distances from the applicator as the spraying progressed. Due to the near constant movement of the applicator, the 10-foot samples represented a distance of about 10 to 15 feet, the 20-foot samples represented a distance of about 20 to 25 feet, and the 30-foot samples represented a distance of about 30 to 35 feet. Any time spraying had ceased for a period of 15 minutes or more, the sample pumps were shut off. The pumps were then restarted once spraying resumed.

Area Samples Following Spraying

Four samples were collected from the approximate center of the basement, first floor, and second floor following the end of spraying. Two samples were collected from the approximate center of the attic following the end of spraying. The air sampling pumps and associated media were attached to stands such that the samples were drawn from a height of approximately 4 to 5 feet above the floor. The following table depicts the number of minutes following the end of spraying for the four samples at each location. Each sample ran for a duration of about 30 to 40 minutes.

Location	1st Sample (min.)	2nd Sample (min.)	3rd Sample (min.)	4th Sample (min.)
Attic	15	55	--	--
2nd Floor	21	60	93	130
1st Floor	28	68	99	135
Basement	33	77	110	146

PUBLIC COPY

V. RESULTS AND DISCUSSION

The analytical results for this evaluation are presented in Tables 1-4. Tables 1 and 2 contain the results for MDI and PMDI, respectively. In both tables, the reported values are a combination of the MDI/PMDI found in the impinger solution and the MDI/PMDI found on the back-up 13mm filter. Table 3 contains the results for the blowing agent. Table 4 contains the results for the amine catalysts. Each table contains the results of the personal and area samples.

Personal Samples

A supplied air hood was worn by the applicator, and a half face air purifying respirator was worn by the applicator assistant during spraying activities (when on the same floor as the applicator). Therefore, the actual exposures for these employees are likely less than the concentrations reported in Tables 1-4 and in the following paragraphs.

MDI

Airborne MDI was detected in all six of the long term samples collected in the breathing zones of three individuals. Airborne concentrations were 7.6 and 37 ug/m^3 for the applicator, 9.3 and 35 ug/m^3 for the applicator assistant, and 6.6 and 6.9 ug/m^3 for the helper. When evaluated as a TWA for the entire sampling period (approximately 5 hours), the airborne concentrations were 71 ug/m^3 for the applicator, 23 ug/m^3 for the applicator assistant, and 6.7 ug/m^3 for the helper. Only the applicator's exposure exceeded the ACGIH TLV-TWA of 51 ug/m^3. It is of note that one of the airborne concentrations measured for the applicator (37 ug/m^3) may not be representative of actual airborne MDI concentration because the air flow rate at the end of the sampling period had dropped significantly compared to the flow at the start of the sampling period.

Airborne MDI was detected in the one short-term sample collected in the breathing zone of the applicator during a time when he was spraying foam. The airborne concentration was 799 ug/m^3, which is above the OSHA PEL-C of 200 ug/m^3.

In some cases, MDI was identified on the back-up 13mm filters, but typically at very low levels compared to the amount found in the impinger solution.

PMDI

Airborne PMDI was detected in four of the six long term samples collected in the breathing zones of three individuals. Airborne concentrations were nondetect and 67 ug/m^3 for the applicator, 18 and 25.4 ug/m^3 for the applicator assistant, and 9.9 ug/m^3 and nondetect for the helper. When evaluated as a TWA for the entire sampling period (approximately 5 hours), the airborne concentrations were 56 ug/m^3 for the applicator, 22 ug/m^3 for the applicator assistant, and 4.9 ug/m^3 for the helper. As was the case for airborne MDI, one of the airborne PMDI concentrations

PUBLIC COPY

measured for the applicator (67 ug/m^3) is an estimate only due to a significant decline in air flow rate.

Airborne PMDI was detected in the one short-term sample collected in the breathing zone of the applicator during a time that he was spraying foam. The airborne concentration was 305 ug/m^3.

While there is no OEL for PMDI, it should be viewed as similar to monomeric MDI as to precautions for handling and use. If the OELs for 4,4'-MDI are used as reference limits, the measured airborne levels of PMDI for the applicator would have exceeded both the TLV-TWA and PEL-C.

In some cases, PMDI was identified on the back-up 13mm filters, but typically at lower levels than the amount found in the impinger solution.

Amine Catalysts

Airborne [redacted] was identified at 15 ppb for the applicator, 13 ppb for the applicator assistant, and 11 ppb for the helper. Airborne [redacted] was identified at 9.8 ppb for the applicator, 6.8 ppb for the applicator assistant, and nondetect for the helper. Airborne [redacted] was not detected in any sample.

There are no OELs for these three amine catalysts. [redacted]

Blowing Agent

Airborne 245fa was detected in all six of the long term samples collected in the breathing zones of three individuals. Airborne concentrations were 89.6 and 281 ppm for the applicator, 29.9 and 126 ppm for the applicator assistant, and 22.6 and 21.9 ppm for the helper. When evaluated as a TWA for the entire sampling period (approximately 6 hours), the airborne concentrations were 148 ppb for the applicator, 56 ppb for the applicator assistant, and 22 ppb for the helper. None of these values exceed the AIHA WEEL of 300 ppm. It is of note that the air flow rates at the end of the sampling period had increased significantly compared to the flow at the start of the sampling period. Thus, the results may not be representative of the actual airborne 245fa concentrations. In addition, analytical results for one sample showed greater amounts of 245fa on the back-up charcoal tube than on the first-stage charcoal tube; therefore, the result reported for the applicator assistant (126 ppb) may underestimate the true airborne concentration. It is possible that some 245fa migrated through and was lost from the sampling media.

PUBLIC COPY

Area Samples

Background Samples

Airborne MDI, PMDI, 245fa, and amine catalysts were not detected in the background samples.

Full Shift Stationary Samples

MDI

Airborne MDI was detected in three of the eight long term samples collected from four locations. Airborne concentrations were nondetect and 1 ug/m^3 in the basement, nondetect and 2.3 ug/m^3 on the first floor, and nondetect and 45 ug/m^3 on the second floor. The measurable values in the basement and on the first and second floors occurred during the time period that spraying was conducted on the second floor, while the nondetects occurred prior to the start of spraying. These results suggest a slight migration of MDI from the floor being sprayed to the floors below it. Airborne MDI was not detected in the trailer.

In all but one case, MDI was not detected on the back-up 13mm filters, suggesting that the impingers were effective at capturing the airborne MDI. For the one sample where MDI was identified on the back-up filter, it was measured at a very low level compared to the amount found in the impinger solution.

PMDI

Airborne PMDI was detected in three of the eight long term samples collected from four locations. Airborne concentrations were nondetect and 5.4 ug/m^3 in the basement, nondetect and 16.8 ug/m^3 on the first floor, and nondetect and 40.1 ug/m^3 on the second floor. The measurable values in the basement and on the first and second floors occurred during the time period that spraying was conducted on the second floor, while the nondetects occurred prior to the start of spraying. These results suggest a migration of PMDI from the floor being sprayed to the floors below it. Airborne PMDI was not detected in the trailer.

In most cases, PMDI was not detected on the back-up 13mm filters, suggesting that the impingers were effective at capturing the airborne PMDI. For one sample, the amount of PMDI identified on the back-up filter was greater than the amount detected in the impinger solution. This suggests that for this sample, the majority of the aerosol may have been less than 2 microns in diameter (the size at which impingers are least efficient).

Amine Catalysts

Airborne [redacted] was identified at 11 ppb in the truck trailer, and 33 ppb in one of two second floor samples. The 33 ppb sample was collected when spraying was being conducted

PUBLIC COPY

on the second floor. Airborne [redacted] was not detected in the samples collected in the basement and on the first floor.

Airborne [redacted] as identified at 13 ppb in one of two second floor samples. This sample was collected when spraying was being conducted on the second floor. Airborne [redacted] was not detected in the samples collected in the basement, on the first floor, or in the truck trailer.

Airborne [redacted] was not detected in any sample.

These amine catalyst results suggest that the catalysts did not migrate beyond the floor being sprayed. Further, the results indicate the presence of one airborne amine catalyst in the trailer.

Blowing Agent

Airborne 245fa was detected in seven of the eight long term samples collected from four locations. Airborne concentrations were nondetect and 0.94 ppm in the truck trailer, 1.24 and 19.7 ppm in the basement, 0.79 and 18.5 ppm on the first floor, and 16.5 and 209 ppm on the second floor. The larger concentrations in the basement and on the first and second floors occurred during the time period that spraying was conducted on the second floor, while the lower concentrations were measured prior to the start of spraying. These results suggest a migration of 245fa from the floor being sprayed to the floors below it. The results also indicate a low concentration of airborne 245fa in the trailer.

It is of note that the air flow rates at the end of the sampling period had increased significantly compared to the flow at the start of the sampling period. Thus, the results may not be representative of the actual airborne 245fa concentrations. In addition, analytical results for two samples showed greater amounts of 245fa on the back-up charcoal tube than on the first-stage charcoal tube; therefore, the results reported for the basement (19.7 ppb) and 2nd floor (16.5 ppb) may underestimate the true airborne concentrations. It is possible that some 245fa migrated through and was lost from the sampling media.

Mobile Samples During Spraying

MDI

Airborne MDI was identified at 44 ug/m^3 10 feet from the applicator, 36 ug/m^3 20 feet from the applicator, and 36 ug/m^3 30 feet from the applicator. In addition, short-term samples collected at 10, 20 and 30 feet indicated airborne concentrations of 49, 23, and 7.5 ug/m^3, respectively.

In some cases, MDI was not detected on the back-up 13mm filters, while in other cases it was identified at very low levels compared to the amount found in the impinger solution. These results suggest that the majority of the airborne MDI was captured by the impinger.

PUBLIC COPY

PMDI

Airborne PMDI was identified in the long-term samples at 30.5 ug/m^3 10 feet from the applicator, 31.5 ug/m^3 20 feet from the applicator, and 36.1 ug/m^3 30 feet from the applicator; however, airborne PMDI was not detected in the short-term samples collected at 10, 20, and 30 feet.

In all cases, PMDI was detected on the back-up 13mm filters at levels greater than those identified in the impinger solution. This suggests that for these samples, the majority of the aerosol may have been less than 2 microns in diameter.

Amine Catalysts

Airborne [redacted] was identified at 62 ppb 10 feet from the applicator, 48 ppb 20 feet from the applicator, and 56 ppb 30 feet from the applicator.

Airborne [redacted] was identified at 24 ppb, 10 feet from the applicator, 22 ppb, 20 feet from the applicator, and 25 ppb, 30 feet from the applicator.

Airborn [redacted] was not detected at any distance.

Blowing Agent

Airborne 245fa was identified at 238 ppm at 10 feet from the applicator, 279 ppb 20 feet from the applicator, and 259 ppm 30 feet from the applicator.

It is of note that the air flow rates at the end of the sampling period had increased significantly compared to the flow at the start of the sampling period. Thus, the results may not be representative of the actual airborne 245fa concentrations. In addition, analytical results for one sample showed greater amounts of 245fa on the back-up charcoal tube than on the first-stage charcoal tube; therefore, the result reported for the 30 foot sample (259 ppb) may underestimate the true airborne concentration. It is possible that some 245fa migrated through and was lost from the sampling media.

The MDI, PMDI, amine catalyst, and 245fa results generally reveal very similar results for the 10, 20, and 30-foot samples. In other words, distance did not make a significant difference in the measured levels.

Post Spray Samples

Neither PMDI nor any of the three amine catalysts was detected in the four samples (two samples for the attic) that were collected at different times on each floor. The period evaluated started at

PUBLIC COPY

about 15 minutes post-spray (start of first sample), and ended at about 3 hours post-spray (end of last sample).

Airborne MDI was detected on the second floor at 4.7 ug/m^3 in the first post spray sample, but not in the other post spray samples.

Airborne 245fa was identified in the basement at 23.3 and 13.3 ppb in the first two post-spray samples, but was nondetect in the third sample (the fourth sample was invalid). Airborne 245fa was identified on the first floor at 20.9, 10.2, 5.77, and 2.95 ppb in the first through fourth post-spray samples. Airborne 245fa was identified on the second floor at 278, 173, 94.9, and 43.9 ppb in the first through fourth post-spray samples. Airborne 245fa was identified in the attic at 192 and 77.6 ppb in the first and second post-spray samples. These results demonstrate a consistent decline in airborne concentrations with time.

It is of note that, for the blowing agent samples, the air flow rates at the end of the sampling period had increased significantly compared to the flow at the start of the sampling period. Thus, the results may not be representative of the actual airborne 245fa concentrations. In addition, analytical results for two samples showed greater amounts of 245fa on the back-up charcoal tube than on the first-stage charcoal tube; therefore, the results reported for one second floor sample (278 ppb) and one attic sample (192 ppb) may underestimate the true airborne concentrations. It is possible that some 245fa migrated through and was lost from the sampling media.

The post-spray sampling results for this survey suggest that, at approximately 15 minutes following the end of spraying, workers could have occupied any level of the structure without the use of respiratory protection.

VI. RECOMMENDATIONS

The following recommendations are based on the sampling results and observations that occurred during the day of this evaluation.

1. During spraying, respiratory protection should continue to be worn by the applicator and all other employees who are working on the same floor as the applicator. The minimum level of protection for employees who are not spraying should be an air-purifying respirator (APR) equipped with a combination organic vapor and P100 cartridge. Given that the MDI/PMDI personal air sampling results for the applicator may underestimate actual airborne concentrations, it is prudent for the applicator to continue to wear a supplied air respirator (loose fitting hood) during spraying. Advantages to wearing the hood are that it provides a greater level of protection (i.e., its assigned protection factor is greater than for an air purifying respirator), and it protects the eyes and face from sprays/drips of reacting foam.

2. During spraying, the applicator should wear disposable boot/shoe covers made of polyethylene, vinyl, or Tyvek®-like material.

PUBLIC COPY

3. The fabric gloves worn by the applicator should be substituted or supplemented with gloves made of nitrile, neoprene, or butyl to provide chemical protection, particularly against unreacted MDI/PMDI. An alternative may be to utilize a hybrid glove that is made of fabric that is coated in nitrile, neoprene, or butyl.

4. If not in place, a respirator cartridge change-out schedule should be implemented. Further, worker medical evaluations and respirator fit tests should be carried out on an annual basis.

5. If the weather and job site conditions permit, consider the use of ventilation during spraying by opening windows and/or doors on opposite sides of the structure.

6. Because measurable airborne concentrations of one amine catalyst and the blowing agent were identified in the truck trailer, ensure that all drums of chemicals are tightly closed, connections between pumps, drums, hoses, etc. are tight, and that any drips/leaks are promptly addressed.

PUBLIC COPY

TABLE 1
AIRBORNE METHYLENE DIPHENYL DIISOCYANATE (MDI) CONCENTRATIONS
Personal & Area Samples – Single Family Home
August 6, 2007

Sample Number	Location/ Job Description	Sampling Period	Sample Volume (liters)	2,4'-MDI (ug/m^3)	4,4'-MDI (ug/m^3)	Total MDI[1] (ug/m^3)	TWA[2] (ug/m^3)
		PERSONAL SAMPLES					
951-1	, Applicator	09:28-11:02	98.8	ND[3]	7.59	7.6	71
23524-1		11:02-12:10 13:05-14:07 14:23-14:40	106.2	5.65	31.1	37[4]	
22787-4	Applies foam to walls **(short term sample)**	14:08-14:23	16.1	72.7	727	799	
442-1	, Applicator Assistant	8:40-11:05	149.8	ND	9.35	9.3	23
23525-1		11:05-12:10 13:02-14:40	182.3	3.57	31.5	35	
348-1	, Helper	08:30-11:07	167.7	ND	6.56	6.6	6.7
22781-1		11:07-12:10 13:00-14:40	181.7	ND	6.88	6.9	
		AREA SAMPLES – STATIONARY					
302-1	1st Floor - Background	06:20-08:05	108.9	ND	ND	ND	--
347-1	Truck Trailer	09:18-12:45	211.3	ND	ND	ND	--
347-2		12:45-14:35	112.3	ND	ND	ND	--
18437-1	Basement	08:00-10:25	208.5	ND	ND	ND	--
18437-2		10:25-15:00	336.6	ND	0.98	1.0	--
19020-1	1st Floor	08:00-10:20	133.4	ND	ND	ND	--
19020-2		10:20-14:55	272.8	ND	2.31	2.3	--
19022-1	2nd Floor	08:00-10:30	138.0	ND	ND	ND	--
19022-2		10:30-14:47	248.3	3.88	41.6	45	--
		AREA SAMPLES - MOBILE					
19031-1	10 feet	11:14-14:45[5]	160.6	3.80	39.9	44	--
22787-1	10 feet (short term sample)	11:49-12:04	15.4	ND	49.4	49	--
23516-1	20 feet	11:14-14:45[5]	168.5	3.50	32.5	36	
22787-2	20 feet (short term sample)	13:18-13:33	14.5	ND	23.4	23	
23526-1	30 feet	11:14-14:45[5]	147.1	3.24	32.9	36	
22787-3	30 feet (short term sample)	13:38-13:53	14.7	ND	7.48	7.5	--
		AREA SAMPLES – POST SPRAY					
18437-3	Basement	15:03-15:43	43.6	ND	ND	ND	--
18437-4		15:47-16:17	29.9	ND	ND	ND	--
18437-5		16:20-16:54	34.1	ND	ND	ND	--
18437-6		16:56-17:28	32.4	ND	ND	ND	--
19020-3	1st Floor	14:58-15:35	38.0	ND	ND	ND	--
19020-4		15:38-16:06	29.1	ND	ND	ND	--
19020-5		16:09-16:42	33.3	ND	ND	ND	--
19020-6		16:45-17:23	42.6	ND	ND	ND	--
19022-3	2nd Floor	14:51-15:28	34.2	ND	4.68	4.7	--
19022-4		15:30-16:01	25.8	ND	ND	ND	--
19022-5		16:03-16:37	29.6	ND	ND	ND	--
19022-6		16:40-17:17	32.6	ND	ND	ND	
22787-5	Attic	14:45-15:17	33.8	ND	ND	ND	
22787-6		15:20-15:50	34.1	ND	ND	ND	--

(1) Reported values are a combination of MDI found in the impinger solution and MDI found on the back-up 13mm filter.
(2) Time Weighted Average (TWA) based on the combined sampling times
(3) ND (Non-detectable) – concentrations were less than the analytical Limit of Quantitation (LOQ) of 0.1 μg/sample
(4) Sample result is an estimate only – see Results section for further details.
(5) Sample pump was turned off once and then back on once during this time period to coincide with the ceasing/resuming of spraying. Total sample time is 157 minutes.

PUBLIC COPY

TABLE 2

AIRBORNE POLYMERIC METHYLENE DIPHENYL DIISOCYANATE (PMDI) CONCENTRATIONS

Personal & Area Samples – Single Family Home

August 6, 2007

Sample Number	Location/ Job Description	Sampling Period	Sample Volume (liters)	PMDI[1] (ug/m^3)	TWA[2] (ug/m^3)
	PERSONAL SAMPLES				
951-1	, Applicator	09:28-11:02	98.8	ND[3]	56
23524-1		11:02-12:10	106.2	67[4]	
		13:05-14:07			
		14:23-14:40			
22787-4	Applies foam to walls **(short term sample)**	14:08-14:23	16.1	305	
442-1	, Applicator Assistant	8:40-11:05	149.8	18.0	22
23525-1		11:05-12:10	182.3	25.4	
		13:02-14:40			
348-1	, Helper	08:30-11:07	167.7	9.9	4.9
22781-1		11:07-12:10	181.7	ND	
		13:00-14:40			
	AREA SAMPLES – STATIONARY				
302-1	1st Floor - Background	06:20-08:05	108.9	ND	--
347-1	Truck Trailer	09:18-12:45	211.3	ND	--
347-2		12:45-14:35	112.3	ND	--
18437-1	Basement	08:00-10:25	208.5	ND	--
18437-2		10:25-15:00	336.6	5.4	--
19020-1	1st Floor	08:00-10:20	133.4	ND	--
19020-2		10:20-14:55	272.8	16.8	--
19022-1	2nd Floor	08:00-10:30	138.0	ND	--
19022-2		10:30-14:47	248.3	40.1	--
	AREA SAMPLES – MOBILE				
19031-1	10 feet	11:14-14:45[5]	160.6	30.5	-
22787-1	10 feet (short term sample)	11:49-12:04	15.4	ND	-
23516-1	20 feet	11:14-14:45[5]	168.5	31.5	
22787-2	20 feet (short term sample)	13:18-13:33	14.5	ND	
23526-1	30 feet	11:14-14:45[5]	147.1	36.1	
22787-3	30 feet (short term sample)	13:38-13:53	14.7	ND	-
	AREA SAMPLES – POST SPRAY				
18437-3	Basement	15:03-15:43	43.6	ND	-
18437-4		15:47-16:17	29.9	ND	-
18437-5		16:20-16:54	34.1	ND	-
18437-6		16:56-17:28	32.4	ND	-
19020-3	1st Floor	14:58-15:35	38.0	ND	-
19020-4		15:38-16:06	29.1	ND	-
19020-5		16:09-16:42	33.3	ND	-
19020-6		16:45-17:23	42.6	ND	-
19022-3	2nd Floor	14:51-15:28	34.2	ND	-
19022-4		15:30-16:01	25.8	ND	-
19022-5		16:03-16:37	29.6	ND	-
19022-6		16:40-17:17	32.6	ND	
22787-5	Attic	14:45-15:17	33.8	ND	
22787-6		15:20-15:50	34.1	ND	-

(1) Reported values are a combination of MDI found in the impinger solution and MDI found on the back-up 13mm filter.
(2) Time Weighted Average (TWA) based on the combined sampling times
(3) ND (Non-detectable) -- concentrations were less than the analytical Limit of Quantitation (LOQ) of 3 µg/sample
(4) Sample result is an estimate only – see Results section for further details.
(5) Sample pump was turned off once and then back on once during this time period to coincide with the ceasing/resuming of spraying. Total sample time is 157 minutes.

PUBLIC COPY

TABLE 3
AIRBORNE 1,1,1,3,3-PENTAFLUOROPROPANE CONCENTRATIONS
Personal & Area Samples – Single Family Home
( )– August 6, 2007

Sample Number	Location/ Job Description	Sampling Period	Sample Volume (liters)	245fa (ppm)	TWA[1] (ppm)
PERSONAL SAMPLES					
400-1	, Applicator	09:28-13:05	7.0	89.6	148
400-2		13:05-14:40	3.1	281	
197-1	, Applicator Assistant	08:40-13:02	14.1	29.9	56
197-2		13:02-14:40	5.3	126[2]	
195-1	, Helper	08:30-13:00	6.8	22.6	22
195-2		13:00-14:40	2.5	21.9	
AREA SAMPLES – STATIONARY					
193-1	1st Floor - Background	06:20-08:05	5.5	ND[3]	--
193-2	Truck Trailer	09:18-12:45	2.6	0.94	--
193-3		12:45-14:35	1.4	ND	--
606-1	Basement	08:00-10:25	10.8	1.24	--
606-2		10:25-15:00	20.4	19.7[2]	--
401-1	1st Floor	08:00-10:20	5.2	0.79	--
401-2		10:20-14:55	10.2	18.5	--
608-1	2nd Floor	08:00-10:30	6.6	16.5[2]	--
608-2		10:30-14:47	11.2	209	--
AREA SAMPLES – MOBILE					
6017-1	10 feet	11:14-14:45[4]	8.0	238	-
6018-1	20 feet	11:14-14:45[4]	10.1	279	
6019-1	30 feet	11:14-14:45[4]	10.7	259[2]	
AREA SAMPLES – POST SPRAY					
606-3	Basement	15:03-15:43	3.0	23.3	-
606-4		15:47-16:17	2.2	13.3	-
606-5		16:20-16:54	2.2	ND	-
401-3	1st Floor	14:58-15:35	1.4	20.9	-
401-4		15:38-16:06	1.0	10.2	-
401-5		16:09-16:42	1.2	5.77	-
401-6		16:45-17:25	1.5	2.95	-
608-3	2nd Floor	14:51-15:28	1.6	278[2]	-
608-4		15:30-16:01	1.4	173	-
608-5		16:03-16:37	1.5	94.9	-
608-6		16:40-17:17	1.6	43.9	
193-4	Attic	14:45-15:20	0.5	192[2]	
193-5		15:25-15:55	0.4	77.6	-

(1) Time Weighted Average (TWA) based on the combined sampling times
(2) Result may underestimate true airborne concentration – see Results section.
(3) ND (Non-detectable) – concentrations were less than the analytical Limit of Quantitation (LOQ)
(4) Sample pump was turned off once and then back on once during this time period to coincide with the ceasing/resuming of spraying. Total sample time is 157 minutes.

PUBLIC COPY

TABLE 4
AIRBORNE AMINE CATALYST CONCENTRATIONS
Personal & Area Samples – Single Family Home
[illegible] - August 6, 2007

Sample Number	Location/ Job Description	Sampling Period	Sample Volume (liters)	[illegible] (ppb)	[illegible] (ppb)	[illegible] (ppb)
PERSONAL SAMPLES						
916-1	, Applicator	09:28-14:40	156.2	15	9.8	ND[1]
949-1	, Applicator Assistant	08:40-14:40	207.8	13	6.8	ND
888-1	, Helper	08:30-14:40	193.5	11	ND	ND
AREA SAMPLES - STATIONARY						
902-1	1st Floor - Background	06:20-08:05	58.7	ND	ND	ND
902-2	Truck Trailer	09:18-14:35	185.6	11	ND	ND
954-1	Basement	08:00-10:25	78.4	ND	ND	ND
954-2		10:25-15:00	148.6	ND	ND	ND
955-1	1st Floor	08:00-10:20	85.0	ND	ND	ND
955-2		10:20-14:55	167.0	ND	ND	ND
985-1	2nd Floor	08:00-10:30	80.0	ND	ND	ND
985-2		10:30-14:47	137.0	33	13	ND
AREA SAMPLES - MOBILE						
2129-1	10 feet	11:14-14:45[2]	82.7	62	24	ND
2173-1	20 feet	11:14-14:45[2]	79.6	48	22	ND
2326-1	30 feet	11:14-14:45[2]	81.6	56	25	ND
AREA SAMPLES - POST SPRAY						
954-3	Basement	15:03-15:43	21.6	ND	ND	ND
954-4		15:47-16:17	30.9	ND	ND	ND
954-5		16:20-16:54	35.0	ND	ND	ND
954-6		16:56-17:29	34.0	ND	ND	ND
955-3	1st Floor	14:58-15:35	22.5	ND	ND	ND
955-4		15:38-16:06	30.1	ND	ND	ND
955-5		16:09-16:42	35.5	ND	ND	ND
985-3	2nd Floor	14:51-15:28	19.7	ND	ND	ND
985-4		15:30-16:01	32.9	ND	ND	ND
985-5		16:03-16:37	36.0	ND	ND	ND
985-6		16:40-17:18	40.3	ND	ND	15
902-3	Attic	14:45-15:20	21.7	ND	ND	ND
902-4		15:25-15:55	31.7	ND	ND	ND

(1) ND (Non-detectable) - concentrations were less than the analytical Limit of Quantitation (LOQ).
(2) Sample pump was turned off once and then back on once during this time period to coincide with the ceasing/resuming of spraying. Total sample time is 157 minutes.

PUBLIC COPY

Bayer MaterialScience

October 23, 2007

Mr.
President

Dear :

Please find enclosed the report of the industrial hygiene evaluation conducted by Bayer MaterialScience on August 27, 2007 at the . The airborne levels of 2,4- and 4,4-diphenylmethane diisocyanate (MDI), polymeric MDI (PMDI), and five amine catalysts were measured during the installation of spray polyurethane foam insulation.

It was a pleasure being of service to you, and we'd like to express our appreciation for the cooperation that we received from your personnel. Please feel free to contact me if you have any questions.

Sincerely,

Enclosure

PUBLIC COPY

Bayer MaterialScience

An Evaluation of Airborne Methylene Diphenyl Diisocyanate (MDI), Polymeric MDI, and Amines

for

at

Conducted by:

Reported by:

Reviewed by:

Date of Evaluation: August 27, 2007
Date of Report: October 23, 2007

This Bayer evaluation is provided as a customer service at no charge. Information in this evaluation is, to our knowledge, true and accurate, and is based upon the conditions observed at the time of the evaluation. The recommendations and/or suggestions contained in this evaluation are made as part of our customer service and Bayer makes no warranty, either express or implied, with respect to such recommendations and/or suggestions.

TABLE OF CONTENTS

PAGE

SUMMARY 1

I. INTRODUCTION 4

II. PROCESS OBSERVATIONS 4

III. CRITERIA 6

IV. SAMPLING AND ANALYTICAL TECHNIQUES 7

V. RESULTS AND DISCUSSION 9

VI. RECOMMENDATIONS 13

TABLE 1 Airborne MDI Concentrations - Personal & Area Samples 14

TABLE 2 Airborne PMDI Concentrations - Personal & Area Samples 16

TABLE 3 Airborne Amine Catalyst Concentrations - Personal & Area Samples 18

PUBLIC COPY

SUMMARY

On August 27, 2007 personal and area monitoring of methylene diphenyl diisocyanate (MDI), polymeric MDI, and five amine catalysts ( ) were conducted at ( ) during the installation of spray polyurethane foam insulation by ( )

Personal samples included full-shift samples for three employees and short-term samples for two employees. Area samples included stationary full-shift samples on each floor of the structure, mobile samples during spraying (to remain at approximately 10 feet and 20 feet from the applicator), and multiple post-spray samples on each floor of the structure. Sample results are summarized in Tables 1-3.

Personal Samples

A supplied air hood or half face air purifying respirator with dual particulate/organic vapor cartridges was worn by all employees during spraying activities. Therefore, the actual worker exposures are likely less than the concentrations reported in Tables 1-3 and in the following paragraphs.

Airborne MDI concentrations in the long term samples were 125 and 79 ug/m^3 for the applicator/helper, 29 and 168 ug/m^3 for the helper/applicator, and 250 and 4.6 ug/m^3 for the applicator assistant. When evaluated as a TWA for the entire sampling period (approximately 7 hours), the airborne concentrations were 86 ug/m^3 for the applicator/helper, 144 ug/m^3 for the helper/applicator, and 39 ug/m^3 for the applicator assistant. The airborne concentrations measured for both applicators exceeded the ACGIH TLV-TWA of 51 ug/m^3. Airborne MDI was detected in both short-term samples that were collected in the breathing zones of the helper/applicator (during a time when he was spraying foam) and the applicator assistant (when he was on the same floor as the applicator). The airborne concentrations were 183 and 9.0 ug/m^3, respectively, both of which are less than the OSHA PEL-C of 200 ug/m^3. Due to sampling equipment complications, the airborne concentrations measured for the applicator/helper and helper/applicator should be viewed as estimates.

Airborne PMDI concentrations in the long term samples were nondetect and 73 ug/m^3 for the applicator/helper, nondetect and 157 ug/m^3 for the helper/applicator, and nondetect for the applicator assistant. When evaluated as a TWA for the entire sampling period (approximately 7 hours), the airborne concentrations were 61 ug/m^3 for the applicator/helper, 130 ug/m^3 for the helper/applicator, and nondetect for the applicator assistant. In addition, airborne PMDI was not detected in either short-term sample collected in the breathing zones of the helper/applicator during a time that he was spraying foam, or the applicator assistant, when he was on the same floor as the

PUBLIC COPY

applicator. As was the case for airborne MDI, the airborne PMDI concentrations measured for the applicator/helper and helper/applicator should be viewed as estimates.

While there is no occupational exposure limit for PMDI, it should be viewed as similar to monomeric MDI as to precautions for handling and use. If the OELs for 4,4'-MDI are used as reference limits, the measured airborne levels of PMDI for the applicator/helper and helper/applicator exceeded the TLV-TWA.

Airborne [redacted] was identified at 7.5 ppb for the helper/applicator, 11 ppb for the applicator assistant, and nondetect for the applicator/helper. There is no OEL for [redacted] Results for the remaining four amine catalysts were nondetect.

Stationary Area Samples

Airborne MDI concentrations were nondetect in the truck trailer, nondetect on the first floor, nondetect and 2.4 ug/m^3 on the second floor; nondetect, 2.2 ug/m^3, and 6.5 ug/m^3 on the third floor; and nondetect, 126 ug/m^3, and 1.6 ug/m^3 on the fourth floor. The measurable values on the second, third, and fourth floors coincide with time periods when spraying was conducted on those floors. The nondetects and relatively lower values per floor occurred as follows: prior to the start of spraying (for the second floor sample at 2.2 ug/m^3), and during the spraying of the third floor (for the fourth floor sample at 1.6 ug/m^3).

Airborne PMDI concentrations were nondetect for the first, second, and third floors, and nondetect and 99 ug/m^3 on the fourth floor. The measurable value for the fourth floor coincided with the spraying of the fourth floor. The nondetects occurred prior to the start of spraying and during the spraying of the other floors.

Airborne [redacted] was identified in only one of 18 samples, at a level of 46 ppb. This sample was collected on the fourth floor during the time that spraying was being conducted on that floor. Airborne [redacted] was identified in two of 18 samples, at 17 ppb on the fourth floor and 14 ppb on the third floor. These samples were collected during the time that the third floor was being sprayed. The three remaining amine catalysts were not detected in any sample.

The results of the stationary area samples suggest that one amine catalyst, [redacted], may have migrated from the floor being sprayed to the floor above it.

Mobile Area Samples

Airborne MDI was identified at 25 ug/m^3 10 feet from the applicator and 6.5 ug/m^3 20 feet from the applicator. In addition, short-term samples collected at 10 and 20 feet from the applicator indicated airborne concentrations of 14 ug/m^3 and nondetect, respectively.

COPY

Airborne PMDI was not detected in the samples collected at 10 feet and 20 feet from the applicator. In addition, airborne PMDI was not detected in the short-term samples collected at 10 and 20 feet.

Airborne [redacted] was not detected at 10 feet from the applicator, but was identified at 50 ppb 20 feet from the applicator. Results for the remaining four amine catalysts were nondetect at 10 and 20 feet from the applicator.

Post Spray Samples

None of the five amine catalysts were detected in the post spray samples. In addition, PMDI was not identified in any of the post spray samples. MDI was identified in only one post spray sample, at 4.7 ug/m^3 in the third of four samples collected on the third floor, approximately two hours following the end of spraying. The period evaluated for the post-spray samples started at about 15 minutes post-spray (start of first sample), and ended at about 3 hours post-spray (end of last sample). These data suggest that, at approximately 15 to 30 minutes following the end of spraying, workers could have occupied any level of the structure without the use of respiratory protection.

Recommendations based on results and observations at the time of the evaluation appear on Page 14.

I. INTRODUCTION

At the request of Bayer MaterialScience (BMS)/BaySystems North America (BSNA), and with the cooperation of the BMS Product Safety & Regulatory Affairs Department sampled for potential airborne MDI, polymeric MDI (PMDI), and five amine catalysts during the installation of 1/2 pound per cubic foot spray polyurethane foam insulation at The townhome was in the process of being constructed at the time of the evaluation. Bayer supplies and to for the manufacture of spray polyurethane foam. it contains approximately equal amounts of monomeric MDI and PMDI. For the purpose of this report, PMDI refers to molecules containing greater than two methylene-linked-phenyl rings, where each phenyl ring has an isocyanate group and methylene links to one or two other phenyl rings. a polyol blend, contains numerous components; however, only the amine catalysts were of interest for this investigation.

II. PROCESS OBSERVATIONS

has a typical mobile spray polyurethane foam insulation system. Major components include a mobile truck trailer, diesel generator, drums of A-side and B-side material, pumps, preheaters, compressor, proportioner, several hundred feet of hoses (one for A-side, one for B-side, one for compressed air) and an air purge spray gun. The A and B hoses are equipped with heated jackets to maintain the desired temperature. Most of these components are housed in the truck trailer. The hoses are used to deliver A-side and B-side material from the proportioner to the spray gun, where the chemicals mix together just prior to being dispensed as a reacting foam into wall cavities and/or onto the underside of roof decking.

Various equipment and operating parameter details are presented in the following table.

Proportioner type	Gusmer H-20/35
Diaphragm pump type	Husky 1040
Gun type	Gap Pro air purge plural component
Preheater temperature for A-side	115 degrees Fahrenheit
Preheater temperature for B-side	125 degrees Fahrenheit
Hose heater temperature	130 degrees Fahrenheit
Pressure	1100 PSI
# Foam passes	1 to 2
Foam thickness	5 to 6 inches
Weather conditions	Mostly Sunny 09:30 - 71 degrees F / 63% RH 17:40 - 83 degrees F / 48% RH
Indoor temperature and relative humidity	09:30 - 75 degrees F / 65% RH 17:40 - 85 degrees F / 50% RH

Ventilation	HVAC system not installed; First floor rear man door open to outside; Fourth floor window and door open to outside (at some point in the p.m. following spraying of that floor); Also, rear door of truck trailer open to outside.

The townhome that was the subject of this investigation had four floors. Each floor was approximately 25 feet by 30 feet (750 square feet), with a height of about 10 feet on each floor. The fourth floor was approximately 15 feet by 16 feet in the main area (240 square feet), and 7 feet by 8 feet at the top of the stairs. The walls consisted of two by six wood framing with exterior oriented strand board (OSB) sheathing. The floors and roof deck were constructed of OSB and wood framing. Only the framing for interior walls was present, such that each floor was essentially one continuous room. Each floor also had a "band joist" that consisted of the upper two feet of each wall. When the unit is fully constructed, this space will separate the ceiling from the floor (or roof) above it, and will presumably function to house utilities such as ductwork.

On the fourth floor, spray polyurethane foam was applied to the underside of the entire roof deck and the band joist for all four walls. Spraying began at approximately 10:00 a.m. and finished at approximately 11:00 a.m. On the third floor, spray foam was applied to the underside of the perimeter roof deck (about 500 square feet) and the band joist of the three walls that did not abut the adjoining townhome. Spraying began at approximately 1:00 p.m. and was completed by 2:30 p.m. On the second floor, spray foam was applied only to the band joist of the three walls that did not abut the adjoining townhome. Spraying began at approximately 3:00 p.m. and was completed by 3:30 p.m. Spraying of the first floor did not occur on the day of the evaluation.

Prior to spraying, preparation activities included attaching plastic sheeting to doors and windows using spray adhesive, moving hoses, gun, and other equipment into the unit, adjusting controls and equipment in the truck trailer, transferring the intake tube from one drum of Mondur MR Light to another, and discharging a small amount of residual chemicals through the spray gun into a 5-gallon bucket in the truck trailer.

Very minor amounts of foam present on the face of wall and ceiling framing were periodically scraped or sawed off manually as spraying progressed. Because of the wall stud thickness (nominal six inches), foam typically did not expand beyond the stud face. In addition, the application of a one-component foam caulk/sealant (aerosol can) around some of the windows, doors, and other cracks was conducted after spraying had started.

Three employees were monitored during this investigation, an applicator, applicator assistant, and helper. The applicator and helper swapped roles at mid day, such that the applicator became the helper, and the helper became the applicator. From this point forward, applicator/helper and helper/applicator will be used to describe these employees. The applicator/helper and

PUBLIC COPY

helper/applicator used the spray gun to apply the foam (when functioning as the applicator), and primarily applied plastic sheeting to windows and doors (when functioning as the helper). The applicator assistant conducted various activities, including using a manual scraper to remove foam drips from floors, and applying a one component foam around doors and windows. For the majority of the time during spraying, the helper was not on on the same floor as the applicator. At times, the applicator assistant was present on the same floor as the applicator during spraying.

All employees wore jeans or pants, short-sleeved shirts, and shoes or boots. During spraying, the applicator wore a Bullard loose-fitting supplied air hood, Kimberly Clark Konformguard® disposable suit, and fabric gloves. The applicator assistant wore a 3M half face air purifying respirator with dual particulate/organic vapor cartridges when on the same floor as the applicator during spraying. The helper wore a 3M half face air purifying respirator with dual particulate/organic vapor cartridges when on the same floor as the applicator during spraying.

III. CRITERIA

MDI/PMDI

The American Conference of Governmental Industrial Hygienists (ACGIH) has adopted a Threshold Limit Value - Time Weighted Average (TLV-TWA) for 4,4'-methylene bisphenyl isocyanate (MDI) of 0.005 parts per million (ppm) (i.e., 5 parts per billion, ppb) or 0.051 milligrams per cubic meter of air (mg/m^3). This is an airborne concentration for a normal 8-hour workday and a 40-hour workweek and represents conditions under which nearly all workers can be exposed without adverse effect. In addition, the federal Occupational Safety and Health Administration (OSHA) has established a Permissible Exposure Limit (PEL) for 4,4'-MDI of 0.02 ppm or 0.2 mg/m^3 as a Ceiling (C) limit. The Ceiling limit is a concentration that should not be exceeded during any part of the day.

At present, neither an ACGIH TLV nor a federal OSHA PEL has been established for 2,4'-MDI or polymeric MDI. However, Bayer MaterialScience recommends that the exposure limits for 4,4'-MDI be used for the 2,4'- MDI isomer. Further, the 4,4'-MDI OELs also should be considered as reference limits for PMDI.

AMINE CATALYSTS

PUBLIC COPY

IV. SAMPLING AND ANALYTICAL TECHNIQUES

Sampling Media

13-mm Impregnated Filter

Prior to any spraying activity, samples of airborne MDI/PMDI were collected using coated 13mm glass fiber filters, mounted in Swinnex holders and connected to SKC Airchek 52 air sampling pumps. The filters were either attached to the workers' lapels (i.e., personal samples) or placed in the surrounding work area (i.e., area samples). All pumps were calibrated before sample collection to a sampling rate of approximately 1 liter per minute (Lpm) using a Bios DryCal® DC-Lite Primary Air Flow Meter. The sampling rate was reconfirmed after the sampling event, with the average value used in the volume calculation. Prior to mounting the filter to the Swinnex holder, each filter was coated with 2 mg of 1-(2-pyridyl)piperazine and diethyl phthalate. Immediately upon completion of sampling, the filters were removed from the Swinnex holders and desorbed in 2 ml of acetonitrile/dimethyl sulfoxide (90:10 v/v) solution. When airborne MDI/PMDI is drawn through the filter it is converted to a stable urea derivative, which is quantitatively analyzed by High Performance Liquid Chromatography (HPLC) using Bayer MaterialScience Method 1.7.7.

Impinger and 13-mm Impregnated Filter

During and following active spraying, samples of airborne MDI/PMDI were collected using glass impingers containing 15 milliliters of a solution of toluene and 1-(2-pyridyl)piperazine backed up by coated 13mm glass fiber filters, mounted in Swinnex holders and connected to Ametek P2500B air sampling pumps. The impinger/filter sampling trains were either attached to the workers' lapels (i.e., personal samples) or placed in the surrounding work area (i.e., area samples). All pumps were calibrated before sample collection to a sampling rate of approximately 1 Lpm, using a Bios DryCal® DC-Lite Primary Air Flow Meter. The sampling rate was reconfirmed after the sampling event, with the average value used in the volume calculation. Prior to mounting the filter to the Swinnex holder, each filter was coated with 2 mg of 1-(2-pyridyl)piperazine and diethyl phthalate. Immediately upon completion of sampling, the filters were removed from the Swinnex holders and desorbed in 2 ml of acetonitrile/dimethyl sulfoxide (90:10 v/v) solution. When airborne MDI/PMDI is drawn through the impinger solution it is converted to a stable urea derivative, which is quantitatively analyzed by HPLC using Bayer MaterialScience Method 1.20.1. The 13mm filters were analyzed according to Bayer MaterialScience Method 1.7.7.

XAD-2 Sorbent Tubes

Samples of amine catalysts were collected using XAD-2 sorbent tubes (8 mm diameter X 110 mm) connected to SKC Airchek 52 air sampling pumps. Sampling devices were either attached to the workers' lapels for breathing zone sampling or placed in fixed locations for area sampling. All pumps were calibrated before and after sample collection to approximately 0.5 Lpm (1.0 Lpm

for post-spray samples), using a Bios DryCal® DC-Lite Primary Air Flow Meter. Each sample was quantitatively analyzed by Gas Chromatograph / Mass Spectrometer using BMS Industrial Hygiene Laboratory Method 2.10.3.

All samples collected were analyzed at the Bayer MaterialScience Industrial Hygiene Laboratory, which is accredited by the American Industrial Hygiene Association (AIHA).

Background Area Samples

Prior to arrival on site, air samples were collected at the approximate mid-point of the second floor from a height of approximately 4 to 5 feet above the floor. These samples were taken to evaluate background levels of MDI, PMDI, and amine catalysts. The samples were run for a period of 80 minutes, and were stopped when arrived on site.

Stationary Area Samples

One sample was collected at approximately the center of each floor from the start of the workday (arrival) until 15 to 30 minutes after the end of spraying for the day. The air sampling pumps and associated media were attached to stands such that the samples were drawn from a height of approximately 4 to 5 feet off of the floor. Sample media for each floor were changed out when spraying began for the day.

In addition to these samples, samples were collected inside the truck trailer (toward the back away from the door) from a height of approximately 4 to 5 feet off of the floor.

Mobile Area Samples During Spraying

Samples were collected at distances of approximately 10 and 20 feet from the applicator during spraying. The air sampling pumps and associated media were attached to stands on small mobile carts such that the samples were drawn from a height of approximately 4 to 5 feet above the floor. The carts were moved periodically to achieve the desired distances from the applicator as the spraying progressed. Due to the near constant movement of the applicator, the 10-foot samples respresented a distance of about 10 to 15 feet, and the 20-foot samples represented a distance of about 20 to 25 feet. Any time spraying had ceased for a period of 15 minutes or more, the sample pumps were shut off. The pumps were then restarted once spraying resumed.

Area Samples Following Spraying

Four samples were collected from the approximate center of each floor following the end of spraying. The air sampling pumps and associated media were attached to stands such that the samples were drawn from a height of approximately 4 to 5 feet off of the floor. The following table depicts the number of minutes following the end of spraying for the four samples at each location. Each sample ran for a duration of about 30 to 40 minutes.

Location	1st Sample (min.)	2nd Sample (min.)	3rd Sample (min.)	4th Sample (min.)
4th Floor	18	55	94	132
3rd Floor	23	61	100	136
2nd Floor	30	65	103	142
1st Floor	35	67	107	147

V. RESULTS AND DISCUSSION

The analytical results for this evaluation are presented in Tables 1-3. Tables 1 and 2 contain the results for MDI and PMDI, respectively. In both tables, the reported values are a combination of the MDI/PMDI found in the impinger solution and the MDI/PMDI found on the back-up 13mm filter. Table 3 contains the results for the amine catalysts. Each table contains the results of the personal and area samples.

Personal Samples

A supplied air hood or half face air purifying respirator was worn by all employees during spraying activities. Therefore, the actual airborne concentrations are likely less than the concentrations reported in Tables 1-3 and in the following paragraphs.

MDI

Airborne MDI was detected in all six of the long term samples collected in the breathing zones of three individuals. Airborne concentrations were 125 and 79 ug/m^3 for the applicator/helper, 29 and 168 ug/m^3 for the helper/applicator, and 250 and 4.6 ug/m^3 for the applicator assistant. Note that the higher values for the applicator/helper and applicator assistant occurred prior to spraying, and may be explained by the intake tube transfer and gun purging activities that they jointly conducted in the truck trailer near the start of the work day. When evaluated as a TWA for the entire sampling period (approximately 7 hours), the airborne concentrations were 86 ug/m^3 for the applicator/helper, 144 ug/m^3 for the helper/applicator, and 39 ug/m^3 for the applicator assistant. The airborne concentrations measured for both the applicator/helper and helper/applicator exceeded the ACGIH TLV-TWA of 51 ug/m^3. However, it is of note that the air flow sampling rates at the end of the sampling period for both of these employees had dropped significantly compared to the air flow sampling rates at the start of the sampling period. Thus, the results for the applicator/helper and helper/applicator may not be representative of the actual airborne MDI concentrations.

Airborne MDI was detected in both short-term samples that were collected in the breathing zones of the helper/applicator (during a time when he was spraying foam), and the applicator assistant (when he was on the same floor as the applicator). The airborne concentrations were 183 and 9.0 ug/m^3, respectively, both of which are less than the OSHA PEL-C of 200 ug/m^3.

In some cases, MDI was identified on the back-up 13mm filters, typically at very low levels compared to the amount found in the impinger solution.

PMDI

Airborne PMDI was detected in two of the six long term samples collected in the breathing zones of three individuals. Airborne concentrations were nondetect and 73 ug/m^3 for the applicator/helper, nondetect and 157 ug/m^3 for the helper/applicator, and nondetect for the applicator assistant. When evaluated as a TWA for the entire sampling period (approximately 7 hours), the airborne concentrations were 61 ug/m^3 for the applicator/helper, 130 ug/m^3 for the helper/applicator, and nondetect for the applicator assistant. As previously stated, the results for both employees may not be representative of the actual airborne PMDI concentrations.

Airborne PMDI was not detected in either short-term sample collected in the breathing zones of the helper/applicator during a time that he was spraying foam, or the applicator assistant when he was on the same floor as the applicator.

While there is no OEL for PMDI, it should be viewed as similar to monomeric MDI as to precautions for handling and use. If the OELs for 4,4'-MDI are used as reference limits, the measured airborne levels of PMDI in the long term samples collected for the applicator/helper and helper/applicator exceeded the TLV-TWA.

In one sample, PMDI was identified on the back-up 13mm filter, but at a much lower level than the amount found in the impinger solution.

Amine Catalysts

Airborne [illegible] was identified at 7.5 ppb for the helper/applicator, 11 ppb for the applicator assistant, and nondetect for the applicator/helper. There is no OEL for [illegible]

None of the other four amine catalysts were detected. These include [illegible]

Area Samples

Background Samples

MDI, PMDI, and all five amine catalysts were not detected in the background samples.

Full Shift Stationary Samples

MDI

PUBLIC COPY

Airborne MDI was detected in five of the 18 long term samples collected from five locations. Airborne concentrations were nondetect in the trailer, nondetect on the first floor, nondetect and 2.4 ug/m^3 on the second floor; nondetect, 2.2 ug/m^3, and 6.5 ug/m^3 on the third floor; and nondetect, 126 ug/m^3, and 1.6 ug/m^3 on the fourth floor. The measurable values on the second, third, and fourth floors coincide with time periods when spraying was conducted on those floors, while the nondetects and relatively lower values per floor occurred as follows: prior to the start of spraying (for second floor sample 2.2 ug/m^3), and during the spraying of the third floor (for fourth floor sample 1.6 ug/m^3). These results suggest that airborne MDI generally did not migrate from the floor being sprayed to the floors above and/or below it.

In all cases, MDI was not detected on the back-up 13mm filters, suggesting that the impingers efficiently captured the airborne MDI.

PMDI

Airborne PMDI was detected in only one of 18 long term samples collected from five locations. Airborne concentrations were nondetect in the trailer, as well as nondetect on the first, second, and third floors. Airborne concentrations were nondetect and 99 ug/m^3 on the fourth floor. The measurable value coincided with the spraying of the fourth floor, while the nondetects occurred prior to the start of spraying and during the spraying of the other floors. These results suggest that PMDI did not migrate from the floor being sprayed to the floors above and/or below it.

In the one sample in which PMDI was identified, PMDI was not detected on the back-up 13mm filter, suggesting that the impinger efficiently captured the airborne PMDI.

Amine Catalysts

Airborne [redacted] was identified in only one of 18 samples, at a level of 46 ppb. This sample was collected on the fourth floor during the time that spraying was being conducted on that floor.

Airborne [redacted] was identified in two of 18 samples, at 17 ppb on the fourth floor and 14 ppb on the third floor. These samples were collected during the time that the third floor was being sprayed.

The other three amine catalysts were not detected in any sample.

These results may suggest a migration of [redacted] om the third to the fourth floor.

Mobile Samples During Spraying

MDI

Airborne MDI was identified at 25 ug/m^3 10 feet from the applicator and 6.5 ug/m^3 20 feet from the applicator. In addition, short-term samples collected at 10 and 20 feet from the applicator indicated airborne concentrations of 14 ug/m^3 and nondetect, respectively.

In all cases, MDI was not detected on the back-up 13mm filters, suggesting that the airborne MDI was efficiently captured by the impingers.

PMDI

Airborne PMDI was not detected in the samples collected at 10 feet and 20 feet from the applicator. In addition, airborne PMDI was not detected in the short-term samples collected at 10 and 20 feet.

Amine Catalysts

Airborne was not detected at 10 feet from the applicator, but was identified at 50 ppb 20 feet from the applicator.

Results for the four remaining amine catalysts were nondetect at 10 and 20 feet from the applicator. These include

Post Spray Samples

None of the five amine catalysts were detected in any of the post spray samples. In addition, PMDI was not identified in any of the post spray samples. MDI was identified in only one post spray sample, at 4.7 ug/m^3 in the third of four samples collected on the third floor, approximately two hours following the end of spraying. The period evaluated for the post-spray samples started at about 15 minutes post-spray (start of first sample), and ended at about 3 hours post-spray (end of last sample).

These data suggest that, at approximately 15 to 30 minutes following the end of spraying, workers could have occupied any level of the structure without the use of respiratory protection.

VI. RECOMMENDATIONS

The following recommendations are based on the sampling results and observations that occurred during the day of this evaluation.

1. During spraying, respiratory protection should continue to be worn by the applicator and all other employees who are working on the same floor as the applicator. The minimum level of protection for employees who are not spraying should be an air-purifying respirator (APR) equipped with a combination organic vapor and P100 cartridge. Airborne MDI/PMDI personal air sampling results for the applicator/helper and helper/applicator should be viewed as estimates given the sampling pump complications that occurred during this survey. However, the concentrations measured do indicate the need for respiratory protection, with the supplied air respirator offering a greater level of protection during spraying. Advantages to wearing the supplied air hood are that it provides a greater level of protection (i.e., its assigned protection factor is greater than for an air purifying respirator), and it protects the eyes and face from sprays/drips of reacting foam.

2. When residual spray foam chemicals are purged from the spray gun into a bucket or other container, employees should wear an APR equipped with a combination organic vapor and P100 cartridge.

3. During spraying, the applicator should wear disposable boot/shoe covers made of polyethylene, vinyl, or Tyvek®-like material.

4. The fabric gloves worn by the applicator should be substituted or supplemented with gloves made of nitrile, neoprene, or butyl to provide chemical protection, particularly against unreacted MDI/PMDI. An alternative may be to utilize a hybrid glove that is made of fabric that is coated in nitrile, neoprene, or butyl.

5. Facial hair that may have interfered with the seal of the respirator to the face was observed for one employee. Employees should be reminded to be clean shaven in the areas where the respirator seals to the face.

6. If not in place, a respirator cartridge change-out schedule should be implemented. Further, worker medical evaluations and respirator fit tests should be carried out on an annual basis.

7. If the weather and job site conditions permit, consider the use of ventilation during spraying by opening windows and/or doors on opposite sides of the structure.

PUBLIC COPY

TABLE 1
AIRBORNE METHYLENE DIPHENYL DIISOCYANATE (MDI) CONCENTRATIONS
Personal & Area Samples –
– August 27, 2007

Sample Number	Location/ Job Description	Sampling Period	Sample Volume (liters)	2,4'-MDI (ug/m^3)	4,4'-MDI (ug/m^3)	Total MDI[1] (ug/m^3)	TWA[2] (ug/m^3)
PERSONAL SAMPLES – LONG TERM							
902-1	, Applicator Assistant	8:44-9:42	60.4	34.8	215	250	39
23524-1		9:42-15:35	356.8	0.70	3.92	4.6	
347-1	, Applicator (a.m.)/Helper (p.m.)	8:42-9:47	65.8	18.2	106	125	86
23525-1		9:52-15:35	186.2	8.06	70.5	79[3]	
225-1	, Helper (a.m.)/Applicator (p.m.)	8:33-9:45	73.4	4.22	24.5	29	144
18437-1		9:45-15:35	207.6	15.4	153	168[3]	
PERSONAL SAMPLES – SHORT TERM							
19020-2	, Applicator Assistant Observes spraying on 2nd Floor	15:02-15:17	15.6	ND[4]	8.97	9.0	--
19022-1	, Applicator Sprays foam on 3rd Floor	12:59-13:14	8.8	12.5	170	183[3]	--
AREA SAMPLES – STATIONARY							
302-1	2nd Floor - Background	06:50-08:10	80.2	ND	ND	ND	--
951-1	Truck Trailer	8:51-12:00	176.4	ND	ND	ND	--
951-2		12:00-15:35	225.8	ND	ND	ND	--
22781-1	1st Floor	8:26-10:06	103.6	ND	ND	ND	--
22781-2		10:06-11:24	115.1	ND	ND	ND	--
22781-3		11:24-14:48	248.1	ND	ND	ND	--
22781-4		14:48-15:57	76.0	ND	ND	ND	--
22787-1	2nd Floor	8:21-10:04	91.2	ND	ND	ND	--
22787-2		10:04-11:18	77.6	ND	ND	ND	--
22787-3		11:18-14:47	208.8	ND	ND	ND	--
22787-4		14:47-15:51	67.5	ND	2.37	2.4	--
19036-1	3rd Floor	8:19-10:00	103.7	ND	2.22	2.2	--
19036-2		10:00-11:13	72.1	ND	ND	ND	--
19036-3		11:13-14:44	234.2	0.94	5.55	6.5	--
19036-4		14:44-15:45	68.1	ND	ND	ND	--
23526-1	4th Floor	8:18-9:55	82.3	ND	ND	ND	--
23526-2		9:55-11:10	76.4	15.7	110	126	--
23526-3		11:10-14:34	203.6	ND	1.57	1.6	--
23526-4		14:35-15:41	65.3	ND	ND	ND	--
AREA SAMPLES - MOBILE							
19031-1	10 feet	13:00-15:40[5]	144.7	2.56	22.1	25	--
22780-1	10 feet (short term sample)	13:00-13:15	14.6	ND	14.4	14	--
23516-1	20 feet	13:00-15:40[5]	134.8	0.96	5.56	6.5	--

PUBLIC COPY

Sample Number	Location/ Job Description	Sampling Period	Sample Volume (liters)	2,4'-MDI (ug/m^3)	4,4'-MDI (ug/m^3)	Total MDI[1] (ug/m^3)	TWA[2] (ug/m^3)
19020-1	20 feet (short term sample)	13:00-13:15	15.5	ND	ND	ND	
AREA SAMPLES – POST SPRAY							
22781-5	1st Floor	16:00-16:31	32.9	ND	ND	ND	--
22781-6		16:32-17:10	40.4	ND	ND	ND	--
22781-7		17:12-17:50	41.2	ND	ND	ND	--
22781-8		17:52-18:22	32.0	ND	ND	ND	--
22787-5	2nd Floor	15:55-16:27	31.8	ND	ND	ND	--
22787-6		16:30-17:06	39.2	ND	ND	ND	--
22787-7		17:08-17:45	38.3	ND	ND	ND	--
22787-8		17:47-18:17	30.3	ND	ND	ND	--
19036-5	3rd Floor	15:48-16:22	33.5	ND	ND	ND	--
19036-6		16:26-17:03	35.3	ND	ND	ND	--
19036-7		17:05-17:39	36.2	ND	4.70	4.7	--
19036-8		17:41-18:13	32.1	ND	ND	ND	--
23526-5	4th Floor	15:43-16:16	34.1	ND	ND	ND	--
23526-6		16:20-16:55	36.4	ND	ND	ND	--
23526-7		16:59-17:35	33.4	ND	ND	ND	--
23526-8		17:37-18:10	35.5	ND	ND	ND	--

(1) Reported values are a combination of MDI found in the impinger solution and MDI found on the back-up 13mm filter.
(2) Time Weighted Average (TWA) based on the combined sampling times
(3) Sample result is an estimate only – see Results section for further details.
(4) ND (Non-detectable) – concentrations were less than the analytical Limit of Quantitation (LOQ) of 0.1 μg/sample
(5) Sample pump was turned off once and then back on once during this time period to coincide with the ceasing/resuming of spraying. Total sample time is 142 minutes.

PUBLIC COPY

TABLE 2
AIRBORNE POLYMERIC METHYLENE DIPHENYL DIISOCYANATE (PMDI) CONCENTRATIONS
Personal & Area Samples –
– August 27, 2007

Sample Number	Location/ Job Description	Sampling Period	Sample Volume (liters)	PMDI[1] (ug/m^3)	TWA[2] (ug/m^3)
PERSONAL SAMPLES – LONG TERM					
902-1	, Applicator Assistant	8:44-9:42	60.4	ND[4]	ND
23524-1		9:42-15:35	356.8	ND	
347-1	, Applicator (a.m.)/Helper (p.m.)	8:42-9:47	65.8	ND	61
23525-1		9:52-15:35	186.2	73[3]	
225-1	, Helper (a.m.)/Applicator (p.m.)	8:33-9:45	73.4	ND	130
18437-1		9:45-15:35	207.6	157[3]	
PERSONAL SAMPLES – SHORT TERM					
19020-2	, Applicator Assistant Observes spraying on 2nd Floor	15:02-15:17	15.6	ND	--
19022-1	, Applicator Sprays foam on 3rd Floor	12:59-13:14	8.8	ND[3]	--
AREA SAMPLES – STATIONARY					
302-1	2nd Floor - Background	06:50-08:10	80.2	ND	--
951-1	Truck Trailer	8:51-12:00	176.4	ND	--
951-2		12:00-15:35	225.8	ND	--
22781-1	1st Floor	8:26-10:06	103.6	ND	--
22781-2		10:06-11:24	115.1	ND	--
22781-3		11:24-14:48	248.1	ND	--
22781-4		14:48-15:57	76.0	ND	--
22787-1	2nd Floor	8:21-10:04	91.2	ND	--
22787-2		10:04-11:18	77.6	ND	--
22787-3		11:18-14:47	208.8	ND	--
22787-4		14:47-15:51	67.5	ND	--
19036-1	3rd Floor	8:19-10:00	103.7	ND	--
19036-2		10:00-11:13	72.1	ND	--
19036-3		11:13-14:44	234.2	ND	--
19036-4		14:44-15:45	68.1	ND	--
23526-1	4th Floor	8:18-9:55	82.3	ND	--
23526-2		9:55-11:10	76.4	99	--
23526-3		11:10-14:34	203.6	ND	--
23526-4		14:35-15:41	65.3	ND	--
AREA SAMPLES – MOBILE					
19031-1	10 feet	13:00-15:40[5]	144.7	ND	--
22780-1	10 feet (short term sample)	13:00-13:15	14.6	ND	--
23516-1	20 feet	13:00-15:40[5]	134.8	ND	--

Sample Number	Location/ Job Description	Sampling Period	Sample Volume (liters)	PMDI[1] (ug/m^3)	TWA[2] (ug/m^3)
19020-1	20 feet (short term sample)	13:00-13:15	15.5	ND	--
AREA SAMPLES – POST SPRAY					
22781-5	1st Floor	16:00-16:31	32.9	ND	--
22781-6		16:32-17:10	40.4	ND	--
22781-7		17:12-17:50	41.2	ND	--
22781-8		17:52-18:22	32.0	ND	--
22787-5	2nd Floor	15:55-16:27	31.8	ND	--
22787-6		16:30-17:06	39.2	ND	--
22787-7		17:08-17:45	38.3	ND	--
22787-8		17:47-18:17	30.3	ND	--
19036-5	3rd Floor	15:48-16:22	33.5	ND	--
19036-6		16:26-17:03	35.3	ND	--
19036-7		17:05-17:39	36.2	ND	--
19036-8		17:41-18:13	32.1	ND	--
23526-5	4th Floor	15:43-16:16	34.1	ND	--
23526-6		16:20-16:55	36.4	ND	--
23526-7		16:59-17:35	33.4	ND	--
23526-8		17:37-18:10	35.5	ND	--

(1) Reported values are a combination of MDI found in the impinger solution and MDI found on the back-up 13mm filter.
(2) Time Weighted Average (TWA) based on the combined sampling times
(3) Sample result is an estimate only – see Results section for further details.
(4) ND (Non-detectable) – concentrations were less than the analytical Limit of Quantitation (LOQ) of 3 μg/sample
(5) Sample pump was turned off once and then back on once during this time period to coincide with the ceasing/resuming of spraying. Total sample time is 142 minutes.

PUBLIC COPY

TABLE 3
AIRBORNE AMINE CATALYST CONCENTRATIONS
Personal & Area Samples – August 27, 2007

Sample Number	Location/ Job Description	Sampling Period	Sample Volume (liters)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)
PERSONAL SAMPLES								
985-1	, Helper (a.m.)/Applicator (p.m.)	8:33-15:35	226.6	ND[1]	ND	7.5	ND	ND
2130-1	, Applicator (a.m.)/Helper (p.m.)	8:42-15:35	215.6	ND	ND	ND	ND	ND
2129-1	, Applicator Assistant	8:44-15:35	195.6	ND	ND	11	ND	ND
AREA SAMPLES – STATIONARY								
888-1	2nd Floor - Background	6:50-8:10	45.5	ND	ND	ND	ND	ND
2173-1	Truck Trailer	8:51-12:00	98.5	ND	ND	ND	ND	ND
2173-2		12:00-15:35	112.0	ND	ND	ND	ND	ND
954-1	1st Floor	8:26-10:06	54.2	ND	ND	ND	ND	ND
954-2		10:06-11:24	42.3	ND	ND	ND	ND	ND
954-3		11:24-14:48	110.6	ND	ND	ND	ND	ND
954-4		14:48-15:57	37.4	ND	ND	ND	ND	ND
888-2	2nd Floor	8:23-10:04	57.5	ND	ND	ND	ND	ND
888-3		10:04-11:18	42.1	ND	ND	ND	ND	ND
888-4		11:18-14:46	118.4	ND	ND	ND	ND	ND
888-5		14:46-15:51	37.0	ND	ND	ND	ND	ND
442-1	3rd Floor	8:18-10:00	61.0	ND	ND	ND	ND	ND
442-2		10:00-11:13	43.7	ND	ND	ND	ND	ND
442-3		11:13-14:40	123.8	ND	ND	14	ND	ND
442-4		14:40-15:45	38.9	ND	ND	ND	ND	ND
348-1	4th Floor	8:18-9:55	57.9	ND	ND	ND	ND	ND
348-2		9:55-11:10	44.8	46	ND	ND	ND	ND
348-3		11:10-14:36	123.0	ND	ND	17	ND	ND
348-4		14:36-15:41	38.8	ND	ND	ND	ND	ND
AREA SAMPLES - MOBILE								
916-1	10 feet	13:00-15:40[2]	71.1	ND	ND	ND	ND	ND
949-1	20 feet	13:00-15:40[2]	78.2	ND	ND	50	ND	ND

Sample Number	Location/ Job Description	Sampling Period	Sample Volume (liters)	(ppb)	(ppb)	(ppb)	(ppb)	(ppb)
AREA SAMPLES – POST SPRAY								
954-5	1st Floor	16:00-16:31	33.6	ND	ND	ND	ND	ND
954-6		16:32-17:10	41.2	ND	ND	ND	ND	ND
954-7		17:12-17:50	41.2	ND	ND	ND	ND	ND
954-8		17:52-18:22	32.5	ND	ND	ND	ND	ND
888-6	2nd Floor	15:55-16:28	34.6	ND	ND	ND	ND	ND
888-7		16:30-17:06	37.7	ND	ND	ND	ND	ND
888-8		17:08-17:45	38.7	ND	ND	ND	ND	ND
888-9		17:47-18:17	31.4	ND	ND	ND	ND	ND
442-5	3rd Floor	15:46-16:22	41.4	ND	ND	ND	ND	ND
442-6		16:26-17:03	42.5	ND	ND	ND	ND	ND
442-7		17:05-17:39	39.1	ND	ND	ND	ND	ND
442-8		17:41-18:13	36.8	ND	ND	ND	ND	ND
348-5	4th Floor	15:43-16:16	33.5	ND	ND	ND	ND	ND
348-6		16:20-16:55	35.5	ND	ND	ND	ND	ND
348-7		16:59-17:35	36.5	ND	ND	ND	ND	ND
348-8		17:37-18:10	33.5	ND	ND	ND	ND	ND

(1) ND (Non-detectable) - concentrations were less than the analytical Limit of Quantitation (LOQ).
(2) Sample pump was turned off once and then back on once during this time period to coincide with the ceasing/resuming of spraying. Total sample time is 142 minutes.

PUBLIC COPY

Bayer MaterialScience

February 18, 2008

Mr.
President

Dear :

Please find enclosed the report of the industrial hygiene evaluation conducted by Bayer MaterialScience on December 19, 2007 at a single-family home at ,) The airborne levels of 2,4- and 4,4-diphenylmethane diisocyanate (MDI), polymeric MDI (PMDI), three amine catalysts, and 1,1,1,3,3-pentafluoropropane were measured during the installation of spray polyurethane foam insulation.

It was a pleasure being of service to you, and we'd like to express our appreciation for the cooperation that we received from your personnel. Please feel free to contact me if you have any questions.

Sincerely,

Enclosure

PUBLIC COPY

Bayer MaterialScience

An Evaluation of Airborne Methylene Diphenyl Diisocyanate (MDI), Polymeric MDI, Amines, and 1,1,1,3,3-Pentafluoropropane

for

at

Conducted by:

Reported by:

Reviewed by:

Date of Evaluation: December 19, 2007
Date of Report: February 18, 2008

This Bayer evaluation is provided as a customer service at no charge. Information in this evaluation is, to the best of our knowledge, true and accurate, and is based upon the conditions observed at the time of the evaluation. The recommendations and/or suggestions contained in this evaluation are made as part of our customer service and Bayer makes no warranty, either express or implied, with respect to such recommendations and/or suggestions.

PUBLIC COPY

TABLE OF CONTENTS

PAGE

SUMMARY 1

I. INTRODUCTION 4

II. PROCESS OBSERVATIONS 4

III. CRITERIA 6

IV. SAMPLING AND ANALYTICAL TECHNIQUES 6

V. RESULTS AND DISCUSSION 9

VI. RECOMMENDATIONS 13

TABLE 1 Airborne MDI Concentrations - Personal & Area Samples 14

TABLE 2 Airborne PMDI Concentrations - Personal & Area Samples 15

TABLE 3 Airborne 1,1,1,3,3-Pentafluoropropane Concentrations - Personal & Area Samples 16

TABLE 4 Airborne Amine Catalyst Concentrations - Personal & Area Samples 17

PUBLIC COPY

SUMMARY

On December 19, 2007 personal and area monitoring of methylene diphenyl diisocyanate (MDI), polymeric MDI, three amine catalysts, and 1,1,1,3,3-pentafluoropropane were conducted at a single family home located at [redacted] during the installation of spray polyurethane foam insulation by [redacted]

Personal samples included full-shift samples for two workers and a short-term sample for one employee. Area samples included stationary full-shift samples on each floor of the structure, mobile samples during spraying (to remain at approximately 10 feet, 20 feet, and 30 feet from the applicator), and multiple post-spray samples on each floor of the structure. Sample results are summarized in Tables 1-4.

Half face air purifying respirators with dual particulate/organic vapor cartridges were worn by the applicator (at times) and applicator assistant during spraying activities (when on the same floor as the applicator). Therefore, the actual exposures for these employees are likely less than the concentrations reported in Tables 1-4 and in the following paragraphs.

Personal (breathing zone) Samples

Three long-term samples collected for airborne MDI were 199 and 998 ug/m^3 for the applicator, and 189 ug/m^3 for the applicator assistant. When evaluated as a time-weighted average (TWA) for the entire sampling period (approximately 3 hours), the airborne concentrations were 471 ug/m^3 for the applicator, and 189 ug/m^3 for the applicator assistant. The airborne MDI concentrations for both the applicator and applicator assistant exceed the ACGIH TLV-TWA of 51 ug/m^3. Airborne MDI was detected in the one short-term sample collected in the breathing zone of the applicator during a time when he was spraying foam. The airborne concentration was 451ug/m^3, which is greater than the OSHA PEL-C of 200 ug/m^3 (see Table 1).

Two long-term samples collected for airborne PMDI were 216 and 1228 ug/m^3 for the applicator, and 203 ug/m^3 for the applicator assistant. When evaluated as a TWA for the entire sampling period (approximately 3 hours), the airborne concentrations were 572 ug/m^3 for the applicator, and 203 ug/m^3 for the applicator assistant. In addition, airborne PMDI was detected in the one short-term sample collected in the breathing zone of the applicator during a time when he was spraying foam. The airborne concentration was 672 ug/m^3 (see Table 2). While there is no occupational exposure limit for PMDI, it should be viewed as similar to monomeric MDI as to the precautions for handling and use. If the OELs for 4,4'-MDI are used as reference limits, the measured airborne levels of PMDI for both the applicator and applicator assistant exceed both the ACGIH TLV-TWA and the OSHA PEL-C.

Two long-term samples collected for airborne 245fa (1,1,1,3,3-pentafluoropropane) were 131 ppm for the applicator, and 109 ppm for the applicator assistant. Neither of these values exceeds the AIHA WEEL-TWA of 300 ppm (see Table 3).

PUBLIC COPY

None of the amine catalysts [redacted] was identified in any sample (see Table 4).

Stationary Area Samples

For the stationary area samples, airborne MDI concentrations were 2.2 ug/m^3 on the first floor, 5.9 ug/m^3 on the second floor, 36 ug/m^3 on the third floor, and nondetect in the truck trailer.

Airborne PMDI was only identified on the third floor, at a concentration of 34 ug/m^3.

None of the amine catalysts [redacted] was identified in any sample.

Airborne 245fa concentrations were nondetect and 31.3 ppm in the truck trailer, 21.3 ppm on the first floor, 48.7 ppm on the second floor, and 83.8 ppm on the third floor.

The results of the stationary area samples suggest that airborne MDI and 245fa migrated from the floor being sprayed (3rd) to the floors below it. In addition, the results suggest the presence of airborne 245fa in the trailer.

Mobile Area Samples

For the mobile area samples, airborne MDI was identified at 84 ug/m^3 10 feet from the applicator, 17 ug/m^3 20 feet from the applicator, and 11 ug/m^3 30 feet from the applicator. In addition, short-term samples collected at 10, 20 and 30 feet indicated airborne concentrations of 221, 34, and 18 ug/m^3, respectively. These results suggest that if a worker had been consistently positioned at 10 feet from the applicator, the airborne concentrations would have exceeded both the ACGIH TLV-TWA and the OSHA PEL-C.

Airborne PMDI was identified in the long-term samples at 76 ug/m^3 10 feet from the applicator, 12.3 ug/m^3 20 feet from the applicator, and nondetect at 30 feet from the applicator. In addition, short-term samples collected at 10, 20, and 30 feet indicated airborne concentrations of 224 ug/m^3, nondetect, and nondetect, respectively.

Airborne [redacted] was not detected at 10 feet from the applicator, however it was identified at 19.4 ppb 20 feet from the applicator, and 27.4 ppb 30 feet from the applicator. Neither airborne [redacted] no [redacted] was detected at any distance.

Airborne 245fa was identified at 108 ppm at both 10 and 20 feet from the applicator, and at 107 ppm 30 feet from the applicator.

The MDI and PMDI results suggest a decline in airborne concentration with distance away from the applicator, while the amine catalyst results indicate an increase in airborne concentration with distance away from the applicator. The blowing agent results suggest that distance did not make a difference in the measured levels.

PUBLIC COPY

Post Spray Samples

Neither MDI, PMDI, blowing agent, nor any of the three amine catalysts was detected in the four samples that were collected at different times on each floor. The period evaluated started at about 30 minutes post-spray (start of first sample), and ended at about 3 hours post-spray (end of last sample). These data suggest that, at approximately 30 minutes following the end of spraying, workers could have occupied any level of the structure without the use of respiratory protection.

Recommendations based on results and observations at the time of the evaluation appear on Page 13.

PUBLIC COPY

I. INTRODUCTION

At the request of Bayer MaterialScience (BMS) and BaySystems North America (BSNA), and with the cooperation of the BMS Product Safety & Regulatory Affairs Department sampled for potential airborne MDI, polymeric MDI (PMDI), three amine catalysts, and blowing agent (1,1,1,3,3-pentafluoropropane) during the installation of 2 pound per cubic foot spray polyurethane foam insulation at a single-family home, located at , The home was in the process of being renovated at the time of the evaluation. Bayer supplies and for the manufacture of spray polyurethane foam contains approximately equal amounts of monomeric MDI and PMDI. For the purpose of this report, PMDI refers to molecules containing greater than two methylene-linked-phenyl rings, where each phenyl ring has an isocyanate group and methylene links to one or two other phenyl rings. a polyol blend, contains numerous components; however, only the amine catalysts and blowing agent were of interest for this investigation.

II. PROCESS OBSERVATIONS

has a typical mobile spray polyurethane foam insulation system. Major components include a mobile truck trailer, diesel generator, drums of A-side and B-side material, pumps, preheaters, compressor, proportioner, several hundred feet of hoses (one for A-side, one for B-side, one for compressed air) and an air purge spray gun. The A and B hoses are equipped with heated jackets to maintain the desired temperature. Most of these components are housed in the truck trailer. The hoses are used to deliver A-side and B-side material from the proportioner to the spray gun, where the chemicals mix together just prior to being dispensed as a reacting foam into wall cavities and/or onto the underside of roof decking.

Various equipment and operating parameter details are presented in the following table.

Proportioner type	Gusmer H-20/35
Diaphragm pump type	Husky 1040
Gun type	Gap Pro air purge plural component; 0.02 tip
Preheater temperature for A-side	115 degrees Fahrenheit
Preheater temperature for B-side	115 degrees Fahrenheit
Hose heater temperature	115 degrees Fahrenheit
Pressure	1500 PSI
# Foam passes	1 to 2
Foam thickness	Approximately 2 inches
Weather conditions	Light snow/rain mix (a.m.), cloudy (p.m.) 35- 40 degrees F
Indoor temperature and relative humidity	35- 40 degrees F

PUBLIC COPY

Ventilation	HVAC system not operating; First floor front and side man doors open to outside during spraying; post-spray, only side man door open; One window slightly open; Also, rear doors of truck trailer partially open to outside.

The single-family home consisted of four floors – a basement, first floor, second floor, and third floor/attic. A portion of each of the first, second, and third floors had a newly-constructed addition. Each floor was approximately 45 feet (in its longest dimension) by 45 to 55 feet (in its longest dimension). The height was approximately 8 to 9 feet on the first and second floors, and 16 feet at the highest point on the third floor. The perimeter wall systems consisted of two-inch by four-inch or two-inch by six-inch wood framing, with exterior walls constructed of either two-inch by eight-inch boards or oriented strand board (new addition). The floors and roof deck were constructed of wood framing and wooden decking (boards or oriented strand board). Only the framing for interior walls was present, such that each floor was essentially one continuous room.

Spray polyurethane foam was applied to the inside surface of all four exterior walls of the third floor on the day of the evaluation. Spraying began at approximately 10:35 a.m. and finished at approximately 1:20 p.m. Spraying of the roof deck and first and second floor walls was scheduled to occur over the next two days.

Prior to spraying, preparation activities included attaching plastic sheeting to doors and windows using spray adhesive, applying a one-component foam caulk/sealant (aerosol can) around windows, doors, and other cracks, moving hoses, gun, and other equipment into the home, and adjusting controls and equipment in the truck trailer.

Two employees were monitored during this investigation, an applicator and applicator assistant. The applicator predominantly used the spray gun to apply the foam. The applicator assistant applied plastic sheeting to windows and doors, installed one component foam around doors and windows, and periodically used a manual saw to scrape minor amounts of foam off of stud faces. On a few occasions he also sprayed foam, but only for a few minutes each time. At times, the applicator assistant was on the same floor as the applicator, while at other times, he was not.

Both employees wore long pants, shirts, jackets, and boots or shoes. During spraying, the applicator wore a half face air purifying respirator (APR) with combination particulate/organic vapor cartridges (at times), fabric head and neck cover, make-shift face shield (overhead transparency sheets taped to the head and neck cover), a Kimberly Clark Komfortguard® disposable suit, disposable boot covers, and fabric gloves. The applicator assistant wore a half face APR with dual organic vapor cartridges when on the same floor as the applicator during spraying.

PUBLIC COPY

III. CRITERIA

MDI/PMDI

The American Conference of Governmental Industrial Hygienists (ACGIH) has adopted a Threshold Limit Value - Time Weighted Average (TLV-TWA) for 4,4'-methylene bisphenyl isocyanate (MDI) of 0.005 parts per million (ppm) (i.e., 5 parts per billion, ppb) or 0.051 milligrams per cubic meter of air (mg/m^3). This is an airborne concentration for a normal 8-hour workday and a 40-hour workweek and represents conditions under which nearly all workers can be exposed without adverse effect. In addition, the federal Occupational Safety and Health Administration (OSHA) has established a Permissible Exposure Limit (PEL) for 4,4'-MDI of 0.02 ppm or 0.2 mg/m^3 as a Ceiling (C) limit. The Ceiling limit is a concentration that should not be exceeded during any part of the day.

At present, neither an ACGIH TLV nor a federal OSHA PEL has been established for 2,4'-MDI or polymeric MDI. However, Bayer MaterialScience recommends that the exposure limits for 4,4'-MDI be used for the 2,4'- MDI isomer. Further, the 4,4'-MDI OELs also should be considered as reference limits for PMDI.

AMINE CATALYSTS

At present, none of the three amine catalysts [illegible] have published occupational exposure limits (OELs).

BLOWING AGENT (245fa or 1,1,1,3,3-pentafluoropropane)

The American Industrial Hygiene Association has established a Workplace Environmental Exposure Level (WEEL) for 1,1,1,3,3-pentafluoropropane of 300 parts per million (ppm) as an 8-hour TWA concentration.

IV. SAMPLING AND ANALYTICAL TECHNIQUES

Sampling Media

13-mm Impregnated Filter

For the truck trailer location, samples of airborne MDI/PMDI were collected using coated 13mm glass fiber filters, mounted in Swinnex holders, and connected to SKC Airchek 52 air sampling pumps. The filters were either attached to the workers' lapels (i.e., personal samples) or placed in the surrounding work area (i.e., area samples). All pumps were calibrated before sample collection to a sampling rate of approximately 1 liter per minute (Lpm) using a Bios DryCal® DC-Lite Primary Air Flow Meter. The sampling rate was reconfirmed after the sampling event, with the average value used in the volume calculation. Prior to mounting the filter to the

PUBLIC COPY

Swinnex holder, each filter was coated with 2 mg of 1-(2-pyridyl)piperazine and diethyl phthalate. Immediately upon completion of sampling, the filters were removed from the Swinnex holders and desorbed in 2 ml of acetonitrile/dimethyl sulfoxide (90:10 v/v) solution. When airborne MDI/PMDI is drawn through the filter it is converted to a stable urea derivative, which is quantitatively analyzed by High Performance Liquid Chromatography (HPLC) using Bayer MaterialScience Method 1.7.7.

Impinger and 13-mm Impregnated Filter

During and following active spraying, samples of airborne MDI/PMDI were collected using glass impingers containing 15 milliliters of a solution of toluene and 1-(2-pyridyl)piperazine backed up by coated 13mm glass fiber filters, mounted in Swinnex holders, and connected to Ametek air sampling pumps. The impinger/filter sampling trains were either attached to the workers' lapels (i.e., personal samples) or placed in the surrounding work area (i.e., area samples). All pumps were calibrated before sample collection to a sampling rate of approximately 1 Lpm, using a Bios DryCal® DC-Lite Primary Air Flow Meter. The sampling rate was reconfirmed after the sampling event, with the average value used in the volume calculation. Prior to mounting the filter to the Swinnex holder, each filter was coated with 2 mg of 1-(2-pyridyl)piperazine and diethyl phthalate. Immediately upon completion of sampling, the filters were removed from the Swinnex holders and desorbed in 2 ml of acetonitrile/dimethyl sulfoxide (90:10 v/v) solution. When airborne MDI/PMDI is drawn through the impinger solution it is converted to a stable urea derivative, which is quantitatively analyzed by HPLC using Bayer MaterialScience Method 1.20.1. The 13mm filters were analyzed according to Bayer MaterialScience Method 1.7.7.

XAD-2 Sorbent Tubes

Samples of amine catalysts were collected using XAD-2 sorbent tubes (8 mm diameter X 110 mm) connected to SKC Airchek 52 air sampling pumps. Sampling devices were either attached to the workers' lapels for breathing zone sampling or placed in fixed locations for area sampling. All pumps were calibrated before and after sample collection to approximately 0.5 Lpm (1.0 Lpm for post-spray samples), using a Bios DryCal® DC-Lite Primary Air Flow Meter. Each sample was quantitatively analyzed by Gas Chromatograph / Mass Spectrometer using BMS Industrial Hygiene Laboratory Method 2.10.3.

Anasorb Coconut Shell Charcoal Tubes

Samples of blowing agent (1,1,1,3,3-pentafluoropropane or 245fa) were collected using two charcoal tubes in series (8 mm diameter X 110 mm) connected to Gilian LFS-113DC or SKC 222 low flow air sampling pumps. Sampling devices were either attached to the workers' lapels for breathing zone sampling or placed in fixed locations for area sampling. All pumps were calibrated before and after sample collection to approximately 0.02 Lpm, using a Bios DryCal® DC-Lite Primary Air Flow Meter. Each sample was quantitatively analyzed by Gas Chromatograph / Flame Ionization Detector using modified NIOSH Method 2516.

PUBLIC COPY

All samples collected were analyzed at the Bayer MaterialScience Industrial Hygiene Laboratory, which is accredited by the American Industrial Hygiene Association (AIHA).

Background Area Samples

Because and Bayer arrived at the site at the same time, background samples were not collected.

Stationary Area Samples

One sample was collected at approximately the center of each floor from one hour prior to the start of spraying until approximately 15 minutes after the end of spraying for the day. The air sampling pumps and associated media were attached to stands such that the samples were drawn from a height of approximately 4 to 5 feet above the floor.

In addition to these samples, samples were collected inside the truck trailer (toward the back away from the door) from a height of approximately 4 to 5 feet above the floor.

Mobile Area Samples During Spraying

Samples were collected at distances of approximately 10 feet, 20 feet, and 30 feet from the applicator during spraying. The air sampling pumps and associated media were attached to stands such that the samples were drawn from a height of approximately 4 to 5 feet above the floor. The stands were moved periodically to achieve the desired distances from the applicator as the spraying progressed. Due to the near constant movement of the applicator, the 10-foot samples represented a distance of about 10 to 15 feet, the 20-foot samples represented a distance of about 20 to 25 feet, and the 30-foot samples represented a distance of about 30 to 35 feet. Any time spraying had ceased for a period of 15 minutes or more, the sample pumps were shut off. The pumps were then restarted once spraying resumed.

Area Samples Following Spraying

Four samples were collected from the approximate center of the first, second, and third floors following the end of spraying. The air sampling pumps and associated media were attached to stands such that the samples were drawn from a height of approximately 4 to 5 feet above the floor. The following table depicts the number of minutes following the end of spraying for the four samples at each location. Each sample ran for a duration of about 30 to 40 minutes.

Location	1st Sample (min.)	2nd Sample (min.)	3rd Sample (min.)	4th Sample (min.)
1st Floor	49	83	113	143
2nd Floor	40	75	109	147
3rd Floor	30	70	103	134

PUBLIC COPY

V. RESULTS AND DISCUSSION

The analytical results for this evaluation are presented in Tables 1-4. Tables 1 and 2 contain the results for MDI and PMDI, respectively. In both tables, the reported values are a combination of the MDI/PMDI found in the impinger solution and the MDI/PMDI found on the back-up 13mm filter. Table 3 contains the results for the blowing agent. Table 4 contains the results for the amine catalysts. Each table contains the results of the personal and area samples.

Personal Samples

A half mask air purifying respirator was worn by the applicator at times during spraying activities. Similarly, a half face air purifying respirator was worn by the applicator assistant during spraying activities (when on the same floor as the applicator). Therefore, the actual exposures for these employees are likely less than the concentrations reported in Tables 1-4 and in the following paragraphs.

MDI

Airborne MDI was detected in all three of the long term samples collected in the breathing zones of the two workers. Airborne concentrations were 199 and 998 ug/m^3 for the applicator, and 189 ug/m^3 for the applicator assistant. When evaluated as a TWA for the entire sampling period (approximately 3 hours), the airborne concentrations were 471 ug/m^3 for the applicator and 189 ug/m^3 for the applicator assistant. The airborne MDI concentration for both the applicator and applicator assistant exceeded the ACGIH TLV-TWA of 51 ug/m^3. This is true even if the assumption of zero exposure is made for the portion of the work day that was not sampled. It is of note that the airborne concentrations measured for the applicator (199 and 998 ug/m^3) may not be representative of actual airborne MDI concentration because the air flow rates at the end of the sampling periods had dropped significantly compared to the flow rates at the start of the sampling periods.

Airborne MDI was detected in the one short-term sample collected in the breathing zone of the applicator during a time when he was spraying foam. The airborne concentration was 451 ug/m^3, which is above the OSHA PEL-C of 200 ug/m^3.

In all cases, MDI was identified on the back-up 13mm filters, but typically at very low levels compared to the amount found in the impinger solution.

PMDI

Airborne PMDI was detected in all three long term samples collected in the breathing zones of the two workers. Airborne concentrations were 216 and 1228 ug/m^3 for the applicator, and 203 ug/m^3 for the applicator assistant. When evaluated as a TWA for the entire sampling period (approximately 3 hours), the airborne concentrations were 572 ug/m^3 for the applicator, and 203 ug/m^3 for the applicator assistant. As was the case for airborne MDI, the airborne concentrations measured for the applicator are estimates only due to significant declines in air flow rate.

PUBLIC COPY

Airborne PMDI was detected in the one short-term sample collected in the breathing zone of the applicator during a time that he was spraying foam. The airborne concentration was 672 ug/m^3.

While there is no OEL for PMDI, it should be viewed as similar to monomeric MDI as to precautions for handling and use. If the OELs for 4,4'-MDI are used as reference limits, the measured airborne levels of PMDI for both the applicator and applicator assistant would have exceeded both the ACGIH TLV-TWA and PEL-C.

In most cases, PMDI was identified on the back-up 13mm filters, but typically at lower levels than the amount found in the impinger solution.

Amine Catalysts

None of the amine catalysts [redacted] was detected in any sample.

Blowing Agent

Airborne 245fa (1,1,1,3,3-pentafluoropropane) was detected in both long term samples collected in the breathing zones of the two employees. Airborne concentrations were 131 ppm for the applicator, and 109 ppm for the applicator assistant. Neither of these values exceeds the AIHA WEEL TWA of 300 ppm.

Area Samples

Stationary Samples

MDI

Airborne MDI was detected in three of the five long term samples collected from four locations. Airborne concentrations were 2.2 ug/m^3 on the first floor, 5.9 ug/m^3 on the second floor, and 36 ug/m^3 on the third floor. These results suggest a slight migration of MDI from the floor being sprayed (3rd) to the floors below it. Airborne MDI was not detected in the truck trailer.

In two of the three samples where MDI was identified, MDI was detected on the back-up 13mm filters, but at very low levels compared to the amounts found in the impinger solution.

PMDI

Airborne PMDI was detected in one of the five long term samples collected from four locations. The airborne MDI concentration on the third floor was 34 ug/m^3. These results suggest that PMDI did not migrate from the floor being sprayed (3rd) to the floors below it. Airborne PMDI was not detected in the truck trailer.

PUBLIC COPY

For the one sample in which PMDI was identified, PMDI was not detected on the back-up 13mm filter, suggesting that the impinger was effective at capturing the airborne PMDI.

Amine Catalysts

None of the amine catalysts [redacted] was identified in any sample.

Blowing Agent

Airborne 245fa (1,1,1,3,3-pentafluoropropane) was detected in four of the five long term samples collected from four locations. Airborne concentrations were nondetect and 31.3 ppm in the truck trailer, 21.3 ppm on the first floor, 48.7 ppm on the second floor, and 83.8 ppm on the third floor. These results suggest a migration of 245fa from the floor being sprayed (3rd) to the floors below it. The results also indicate the presence of airborne 245fa in the truck trailer.

Mobile Samples During Spraying

MDI

Airborne MDI was identified in the long term samples at 84 ug/m^3 10 feet from the applicator, 17 ug/m^3 20 feet from the applicator, and 11 ug/m^3 30 feet from the applicator. In addition, short-term samples collected at 10, 20 and 30 feet indicated airborne concentrations of 221, 34, and 18 ug/m^3, respectively. These results suggest that if a worker had been consistently positioned at 10 feet from the applicator, the airborne concentrations would have exceeded both the ACGIH TLV-TWA and the OSHA PEL-C.

In some cases, MDI was not detected on the back-up 13mm filters, while in other cases it was identified at very low levels compared to the amount found in the impinger solution. These results suggest that the majority of the airborne MDI was captured by the impinger.

PMDI

Airborne PMDI was identified in the long-term samples at 76 ug/m^3 10 feet from the applicator, 12.3 ug/m^3 20 feet from the applicator, and nondetect at 30 feet from the applicator. In addition, short-term samples collected at 10, 20, and 30 feet indicated airborne concentrations of 224 ug/m^3, nondetect, and nondetect, respectively.

PMDI was not detected on the back-up 13mm filters, suggesting that the impingers were effective at capturing the airborne PMDI.

PUBLIC COPY

Amine Catalysts

Airborne [redacted] was not detected at 10 feet from the applicator, however it was identified at 19.4 ppb 20 feet from the applicator, and 27.4 ppb 30 feet from the applicator.

Neither airborne [redacted] nor [redacted] was detected at any distance.

Blowing Agent

Airborne 245fa was identified at 108 ppm at both 10 and 20 feet from the applicator, and at 107 ppm 30 feet from the applicator.

The MDI and PMDI results suggest a decline in airborne concentration with distance away from the applicator, while the amine catalyst results indicate an increase in airborne concentration with distance away from the applicator. The blowing agent results suggest that distance did not make a difference in the measured levels.

Post Spray Samples

Neither MDI, PMDI, blowing agent, nor any of the three amine catalysts was detected in the four samples that were collected at different times on each floor. The period evaluated started at about 30 minutes post-spray (start of first sample), and ended at about 3 hours post-spray (end of last sample).

The post spray samples collected for 245fa on the second and third floors were invalid due to sampling pump problems.

The post-spray sampling results for this survey suggest that, at approximately 30 minutes following the end of spraying, workers could have occupied any level of the structure without the use of respiratory protection.

PUBLIC COPY

VI. RECOMMENDATIONS

The following recommendations are based on the sampling results and observations that occurred during the day of this evaluation.

1. Respiratory protection should be worn at all times during spraying. Further, given the level of airborne MDI/PMDI identified for the applicator, it is prudent for the applicator to wear a supplied air respirator (e.g., loose fitting hood) during spraying. Advantages to wearing the hood are that it provides a greater level of protection (i.e., its assigned protection factor is greater than for an air purifying respirator), and it protects the eyes and face from sprays/drips of reacting foam.

2. Respiratory protection should continue to be worn by the applicator assistant and all other employees who are working on the same floor as the applicator. The minimum level of protection for employees who are not spraying should be an air-purifying respirator (APR) equipped with combination organic vapor/P100 cartridges, rather than organic vapor cartridges that are not combined with particulate filtering media.

3. The applicator assistant should wear safety glasses with side shields or goggles during spraying activities.

4. Recent observations suggest that loosely-woven disposable suits, like that worn by the applicator, may not be as protective against accidental sprays of foam as compared to more tightly-woven suits, such as Tyvek®. Therefore, a disposable suit made of a more tightly-woven material should be worn by the applicator during spraying.

5. The fabric gloves worn by the applicator should be substituted or supplemented with gloves made of nitrile, neoprene, or butyl to provide an effective barrier between the skin and unreacted MDI/PMDI material. An alternative may be to utilize a hybrid glove that is made of fabric coated with nitrile, neoprene, or butyl rubber.

6. If not in place, a respirator cartridge change-out schedule should be implemented. Further, worker medical evaluations and respirator fit tests should be carried out on an annual basis.

7. If the weather and job site conditions permit, consider the use of ventilation during spraying by opening windows and/or doors on opposite sides of the structure.

8. Because measurable airborne concentrations of blowing agent were identified in the truck trailer, ensure that all drums of chemicals are tightly closed, connections between pumps, drums, hoses, etc. are tight, and that any drips/leaks are promptly addressed.

PUBLIC COPY

TABLE 1
AIRBORNE METHYLENE DIPHENYL DIISOCYANATE (MDI) CONCENTRATIONS
Personal & Area Samples – Single Family Home
December 19, 2007

Sample Number	Location/ Job Description	Sampling Period	Sample Volume (liters)	2,4'-MDI (ug/m^3)	4,4'-MDI (ug/m^3)	Total MDI[1] (ug/m^3)	TWA[2] (ug/m^3)
PERSONAL SAMPLES							
23526-1	, Applicator (23526-2 is a short term sample)	10:28-11:20	39.1	106	893	998[4]	471
23526-2		11:24-11:39	15.4	44.2	406	451	
23526-3		11:40-13:20	81.0	26.5	173	199[4]	
23525-1	, Applicator Assistant	10:25-13:20	158.2	19.6	170	189	189
AREA SAMPLES – STATIONARY							
916-1	Truck Trailer	08:25-12:28	207.3	ND[3]	ND	ND	--
916-2		12:28-13:30	52.9	ND	ND	ND	--
19036-1	1st Floor	09:24-13:35	277.6	0.47	1.69	2.2	--
19020-1	2nd Floor	09:25-13:35	190.0	ND	5.89	5.9[4]	--
22780-1	3rd Floor	09:26-13:40	254.5	3.93	32.3	36	--
AREA SAMPLES - MOBILE							
22781-1	10 feet	10:35-13:35	190.4	8.93	74.8	84	--
19031-1	10 feet (short term sample)	11:18-11:33	15.4	26.0	195	221	--
23516-1	20 feet	10:35-13:35	134.1	ND	17.2	17[4]	
23524-1	20 feet (short term sample)	11:38-11:56	18.6	ND	34.4	34	
18437-1	30 feet	10:35-13:35	194.4	1.54	9.41	11	
23524-2	30 feet (short term sample)	12:10-12:25	15.3	ND	17.6	18	--
AREA SAMPLES – POST SPRAY							
19036-2	1st Floor	14:09-14:40	33.0	ND	ND	ND	--
19036-3		14:43-15:11	30.8	ND	ND	ND	--
19036-4		15:13-15:41	30.1	ND	ND	ND	--
19036-5		15:43-16:19	36.3	ND	ND	ND	--
19020-2	2nd Floor	14:00-14:32	32.4	ND	ND	ND	--
19020-3		14:35-15:07	30.9	ND	ND	ND	--
19020-4		15:09-15:35	26.6	ND	ND	ND	--
19020-5		15:37-16:13	36.0	ND	ND	ND	--
22780-2	3rd Floor	13:50-14:25	29.0	ND	ND	ND	--
22780-3		14:30-15:01	32.4	ND	ND	ND	--
22780-4		15:03-15:32	30.1	ND	ND	ND	--
22780-5		15:34-16:07	35.4	ND	ND	ND	

(1) Reported values are a combination of MDI found in the impinger solution and MDI found on the back-up 13mm filter.
(2) Time Weighted Average (TWA) based on the combined sampling times.
(3) ND (Non-detectable) – concentrations were less than the analytical Limit of Quantitation (LOQ) of 0.1 μg MDI/sample.
(4) Sample result is an estimate only – flow rate at end of sampling period was significantly less than flow rate at beginning.

PUBLIC COPY

TABLE 2
AIRBORNE POLYMERIC METHYLENE DIPHENYL DIISOCYANATE (PMDI) CONCENTRATIONS
Personal & Area Samples – Single Family Home
– December 19, 2007

Sample Number	Location/ Job Description	Sampling Period	Sample Volume (liters)	PMDI[1] (ug/m^3)	TWA[2] (ug/m^3)
PERSONAL SAMPLES					
23526-1	, Applicator	10:28-11:20	39.1	1228[4]	572
23526-2	(23526-2 is a short term sample)	11:24-11:39	15.4	672	
23526-3		11:40-13:20	81.0	216[4]	
23525-1	, Applicator Assistant	10:25-13:20	158.2	203	203
AREA SAMPLES – STATIONARY					
916-1	Truck Trailer	08:25-12:28	207.3	ND[3]	--
916-2		12:28-13:30	52.9	ND	--
19036-1	1st Floor	09:24-13:35	277.6	ND	--
19020-1	2nd Floor	09:25-13:35	190.0	ND	--
22780-1	3rd Floor	09:26-13:40	254.5	34	--
AREA SAMPLES – MOBILE					
22781-1	10 feet	10:35-13:35	190.4	76	-
19031-1	10 feet (short term sample)	11:18-11:33	15.4	224	-
23516-1	20 feet	10:35-13:35	134.1	12.3[4]	
23524-1	20 feet (short term sample)	11:38-11:56	18.6	ND	
18437-1	30 feet	10:35-13:35	194.4	ND	
23524-2	30 feet (short term sample)	12:10-12:25	15.3	ND	-
AREA SAMPLES – POST SPRAY					
19036-2	1st Floor	14:09-14:40	33.0	ND	-
19036-3		14:43-15:11	30.8	ND	-
19036-4		15:13-15:41	30.1	ND	-
19036-5		15:43-16:19	36.3	ND	-
19020-2	2nd Floor	14:00-14:32	32.4	ND	-
19020-3		14:35-15:07	30.9	ND	-
19020-4		15:09-15:35	26.6	ND	-
19020-5		15:37-16:13	36.0	ND	-
22780-2	3rd Floor	13:50-14:25	29.0	ND	-
22780-3		14:30-15:01	32.4	ND	-
22780-4		15:03-15:32	30.1	ND	-
22780-5		15:34-16:07	35.4	ND	

(1) Reported values are a combination of MDI found in the impinger solution and MDI found on the back-up 13mm filter.
(2) Time Weighted Average (TWA) based on the combined sampling times.
(3) ND (Non-detectable) – concentrations were less than the analytical Limit of Quantitation (LOQ) of 3 μg/sample .
(4) Sample result is an estimate only – flow rate at end of sampling period was significantly less than flow rate at beginning.

PUBLIC COPY

TABLE 3
AIRBORNE 1,1,1,3,3-PENTAFLUOROPROPANE (245FA) CONCENTRATIONS
Personal & Area Samples – Single Family Home
[redacted] · December 19, 2007

Sample Number	Location/ Job Description	Sampling Period	Sample Volume (liters)	245fa (ppm)	TWA[1] (ppm)
PERSONAL SAMPLES					
195-1	, Applicator	10:28-13:20	2.4	131	
193-1	, Applicator Assistant	10:25-13:20	2.5	109	
AREA SAMPLES – STATIONARY					
19904-1	Truck Trailer	08:25-12:27	5.8	31.3	--
19904-2		12:27-13:30	1.5	ND[2]	--
6017-1	1st Floor	09:24-13:35	3.1	21.3	--
6018-1	2nd Floor	09:25-13:35	4.1	48.7	--
6020-1	3rd Floor	09:26-13:40	3.9	83.8	--
AREA SAMPLES – MOBILE					
19901-1	10 feet	10:35-13:35	4.2	108	--
19902-1	20 feet	10:35-13:35	4.4	108	--
19903-1	30 feet	10:35-13:35	4.4	107	--
AREA SAMPLES – POST SPRAY[3]					
6017-2	1st Floor	14:09-14:40	0.4	ND	--
6017-3		14:43-15:11	0.3	ND	--
6017-4		15:13-15:41	0.3	ND	--
6017-5		15:43-16:19	0.4	ND	--

(1) Time Weighted Average (TWA) based on the combined sampling times.
(2) ND (Non-detectable) – concentrations were less than the analytical Limit of Quantitation (LOQ) of 100 ug/sample.
(3) Post spray samples for the 2nd and 3rd floors were invalid due to sampling pump problems.

PUBLIC COPY

TABLE 4
AIRBORNE AMINE CATALYST CONCENTRATIONS
Personal & Area Samples – Single Family Home
[illegible] – December 19, 2007

Sample Number	Location/ Job Description	Sampling Period	Sample Volume (liters)	[illegible] (ppb)	[illegible] (ppb)	[illegible] (ppb)
PERSONAL SAMPLES						
058-1	, Applicator	10:28-13:20	81.6	ND[1]	ND	ND
053-1	, Applicator Assistant	10:25-13:20	95.3	ND	ND	ND
AREA SAMPLES - STATIONARY						
2130-1	Truck Trailer	08:25-13:30	150.1	ND	ND	ND
949-1	1st Floor	09:24-13:35	140.3	ND	ND	ND
951-1	2nd Floor	09:25-13:35	171.4	ND	ND	ND
954-1	3rd Floor	09:26-13:40	135.0	ND	ND	ND
AREA SAMPLES - MOBILE						
955-1	10 feet	10:35-13:35	86.7	ND	ND	ND
985-1	20 feet	10:35-13:35	109.9	ND	19.4	ND
2129-1	30 feet	10:35-13:35	91.7	ND	27.4	ND
AREA SAMPLES - POST SPRAY						
949-2	1st Floor	14:05-14:40	37.5	ND	ND	ND
949-3		14:43-15:11	30.0	ND	ND	ND
949-4		15:13-15:41	30.0	ND	ND	ND
949-5		15:43-16:19	38.5	ND	ND	ND
2173-1	2nd Floor	14:02-14:32	30.2	ND	ND	ND
2173-2		14:35-15:07	32.2	ND	ND	ND
2173-3		15:09-15:35	26.2	ND	ND	ND
2173-4		15:37-16:13	36.3	ND	ND	ND
954-2	3rd Floor	13:50-14:25	36.3	ND	ND	ND
954-3		14:30-15:01	32.1	ND	ND	ND
954-4		15:03-15:32	30.1	ND	ND	ND
954-5		15:34-16:07	34.2	ND	ND	ND

(1) ND (Non-detectable) - concentration was less than the analytical Limit of Quantitation (LOQ) of 5 ug/sample for [illegible] 10 ug/sample fo[illegible] [illegible], and 8 ug/sample for [illegible]

PUBLIC COPY

Bayer MaterialScience

August 11, 2008

Mr.
President

Dear :

Please find enclosed the report of the industrial hygiene evaluation conducted by Bayer MaterialScience on July 7, 2008 at a single family home located at

The airborne levels of 2,4- and 4,4-diphenylmethane diisocyanate (MDI), polymeric MDI (PMDI), and two amine catalysts were measured during the installation of spray polyurethane foam insulation.

It was a pleasure being of service to you, and I'd like to express my appreciation for the cooperation that we received from your personnel. Please feel free to contact me if you have any questions.

Sincerely,

Enclosure

PUBLIC COPY

Bayer MaterialScience

An Evaluation of Airborne Methylene Diphenyl Diisocyanate (MDI), Polymeric MDI, and Amines

for

at

Conducted by:

Reported by:

Date of Evaluation: July 7, 2008
Date of Report: August 11, 2008

The testing and evaluation described in this report have been conducted as a customer service at no additional charge to the Customer. As such, any information contained in this Report has been obtained in accordance with industry standards and is, to the best of our knowledge, true and accurate, and is based only upon the conditions observed at the time of the evaluation. The test results, recommendations and/or suggestions contained in this Report are made only as a courtesy as part of our customer service and Bayer makes no warranty, either expressed or implied, with respect to any such test results, recommendations and/or suggestions.

PUBLIC COPY

TABLE OF CONTENTS

PAGE

SUMMARY 1

I. INTRODUCTION.....4

II. PROCESS OBSERVATIONS 4

III. CRITERIA.....6

IV. SAMPLING AND ANALYTICAL TECHNIQUES.....6

V. RESULTS AND DISCUSSION 8

VI. RECOMMENDATIONS.....13

TABLE 1 Airborne MDI Concentrations - Personal & Area Samples.....14

TABLE 2 Airborne PMDI Concentrations - Personal & Area Samples.....15

TABLE 3 Airborne Amine Catalyst Concentrations - Personal & Area Samples.....16

PUBLIC COPY

SUMMARY

On July 7, 2008 personal and area monitoring for methylene diphenyl diisocyanate (MDI), polymeric MDI, and two amine catalysts ( ) were conducted at a single-family home at , during the installation of spray polyurethane foam insulation by ,

Personal samples included full-shift samples for two employees and short-term samples for one employee. Area samples included stationary samples on the 1st – 3rd floors of the structure, mobile samples during spraying (to remain at approximately 10, 20, and 30 feet from the applicator), and multiple post-spray samples on the 1st – 3rd floors of the structure. Sample results are summarized in Tables 1-3.

Personal Samples

A full-face supplied air hood or half-face air purifying respirator with dual organic vapor/particulate cartridges was worn by both employees during spraying activities. Therefore, the actual airborne concentrations to which the workers were potentially exposed were likely less than the concentrations reported in Tables 1-3 and in the following paragraphs.

Airborne MDI was detected in all six of the long term samples collected in the breathing zones of two individuals. Airborne concentrations for one of the employees were 10.3, 208, and 3.58 ug/m^3, with a corresponding sampling period TWA concentration of 55 ug/m^3. Airborne concentrations for the second employee were 7.2, 20, and 194 ug/m^3 , with a corresponding sampling period TWA concentration of 88 ug/m^3. The airborne concentrations measured for both employees exceeded the ACGIH TLV-TWA of 51 ug/m^3. Airborne MDI was detected in the one short-term sample that was collected in the breathing zone of one of the employees during a time when he was spraying foam. The airborne concentration was 865 ug/m^3, which is greater than the OSHA PEL-C of 200 ug/m^3.

Airborne PMDI was detected in three of the six long term samples collected in the breathing zones of two individuals. Airborne concentrations for one employee were nondetect for two samples collected when not spraying, and 356 ug/m^3 when spraying, for a corresponding sampling period TWA concentration of 85.5 ug/m^3. Airborne concentrations for the second employee were nondetect, 33.6, and 332 ug/ m^3, for a corresponding sampling period TWA concentration of 147 ug/m^3. Airborne PMDI was detected in the one short-term sample collected in the breathing zone of one of the employees during a time that he was spraying foam. The airborne concentration was 1,691 ug/ m^3. While there is no OEL for PMDI, it should be viewed as similar to monomeric MDI as to precautions for handling and use. If the OELs for 4,4'-MDI are used as reference limits, the measured airborne levels of PMDI exceeded both the ACGIH TLV-TWA of 51 ug/m^3 and the OSHA PEL-C of 200 ug/m^3.

PUBLIC COPY

Airborne(was identified in all three long term samples collected in the breathing zones of two employees. The airborne oncentrations for one of the employees were 76 and 1,203 ppb, with a corresponding sampling period TWA concentration of 883 ppb. The airborne concentration for the second employee was 523 ppb.

Airborne( )was detected in the one short-term sample that was collected in the breathing zone of one of the employees during a time when he was spraying foam. The airborne concentration was 936 ppb,(

Airborne( )was identified in two of the three long term samples collected in the breathing zones of two employees. The airborne concentrations for one of the employees were nondetect and 136 ppb, with a corresponding sampling period TWA concentration of 105 ppb. The airborne concentration for the second employee was 187 ppb. There is no published OEL for(at this time.

Airborne( )was detected in the one short-term sample that was collected in the breathing zone of one of the employees during a time when he was spraying foam. The airborne concentration was 394 ppb. As previously stated, there is no published OEL for(

Stationary Area Samples

Airborne MDI was detected in one of the five long term samples collected from four locations. Airborne concentrations were nondetect in the trailer, and on the first and second floors. The airborne concentration on the third floor was 13 ug/m^3.

Airborne PMDI was detected in one of the five samples collected from four locations. Airborne concentrations were nondetect in the trailer, and on the first and second floors. The airborne concentration on the third floor was 20.1 ug/m^3.

Airborne( )was identified in three of the four samples collected from four locations. Airborne concentrations were nondetect in the truck trailer, and 3.4, 3.8, and 876 ppb on the first, second, and third floors, respectively.

Airborne was identified in one of the four samples collected from four locations. Airborne concentrations were nondetect in the truck trailer, first floor, and second floor, and 67 ppb on the third floor.

These results suggest that, with the exception of( ), these compounds did not migrate from the floor being sprayed to the floors below it.

PUBLIC COPY

Mobile Area Samples

Airborne MDI was identified at 28 ug/m^3 10 feet from the applicator, and 2.4 ug/m^3 30 feet from the applicator. In addition, short-term samples collected at 10, 20, and 30 feet from the applicator indicated airborne concentrations of 25 ug/m^3, nondetect, and nondetect, respectively.

Airborne PMDI was identified at 39.0 ug/m^3 10 feet from the applicator, but was not detected in the sample collected at 30 feet from the applicator. In addition, airborne PMDI was not detected in the short-term samples collected at 10, 20, and 30 feet.

Airborne was identified at 1034, 855, and 656 ppb at 10, 20, and 30 feet from the applicator, respectively. In addition, short-term samples collected at 10 feet from the applicator indicated airborne concentrations of 696 and 664 ppb. The short-term sample collected at 20 feet from the applicator indicated an airborne concentration of 805 ppb. The short-term samples collected at 30 feet from the applicator indicated airborne concentrations of 551 and 945 ppb.

Airborne was identified at 111, 90, and 81 ppb at 10, 20, and 30 feet from the applicator, respectively. However, the short-term samples collected at 10, 20, and 30 feet from the applicator were all nondetect.

Post Spray Samples

Neither airborne MDI nor PMDI was identified in any of the post spray samples.

While neither amine catalyst was identified in any of the samples collected on the first and second floors, both were identified in all of the samples collected on the third floor. Airborne was identified at 2113, 1980, 1137, and 1351 ppb, with each sample being collected approximately 30 minutes later than the previous. Airborne was identified at 251, 220, 151, and 244 ppb, again, with each sample being collected approximately 30 minutes later than the previous. These data suggest that, even at about 2.5 hours following the end of spraying, the use of respiratory protection would still have been needed on the third floor of the structure.

Recommendations based on results and observations at the time of the evaluation appear on Page 13.

PUBLIC COPY

I. INTRODUCTION

At the request of Bayer MaterialScience (BMS)/BaySystems, and with the cooperation of , the BMS Product Safety & Regulatory Affairs Department sampled for potential airborne MDI, polymeric MDI (PMDI), and two amine catalysts during the installation of 1/2 pound per cubic foot spray polyurethane foam insulation at a single family home located at . The home was in the process of being renovated at the time of the evaluation. Bayer supplies and to for the manufacture of spray polyurethane foam. contains approximately equal amounts of monomeric MDI and PMDI. For the purpose of this report, PMDI refers to molecules containing greater than two methylene-linked-phenyl rings, where each phenyl ring has an isocyanate group and methylene links to one or two other phenyl rings. , a polyol blend, contains numerous components; however, only the amine catalysts were of interest for this investigation.

II. PROCESS OBSERVATIONS

has a typical mobile spray polyurethane foam insulation system. Major components include a mobile truck trailer, diesel generator, drums of A-side ( ) and B-side ( ) material, pumps, preheaters, compressor, proportioner, several hundred feet of hoses (one for A-side, one for B-side, one for compressed air) and an air purge spray gun. The A and B hoses are equipped with heated jackets to maintain the desired temperature. Most of these components are housed in the truck trailer. The hoses are used to deliver A-side and B-side material from the proportioner to the spray gun, where the chemicals mix together just prior to being dispensed as a reacting foam into wall cavities and/or onto the underside of roof decking.

Various equipment and operating parameter details are presented in the following table.

Proportioner type	Gusmer H2000
Diaphragm pump type	Gusmer
Gun type	Graco P2/01
Preheater temperature for A-side	115 degrees Fahrenheit
Preheater temperature for B-side	115 degrees Fahrenheit
Hose heater temperature	Not recorded
Pressure	1100 PSI
# Foam passes	1 to 2
Foam thickness	Walls - 3 to 4 inches Underside of roof deck - 5 to 6 inches
Weather conditions	Mostly Sunny High temperature: 85 degrees F At 20:00 - 79 degrees F / 72% RH
Indoor temperature and relative humidity	At 15:00 - 84 degrees F / 61% RH

PUBLIC COPY

Ventilation	HVAC system not operating; First floor: front door and two windows open to outside; Third floor: one window fully open and one partially open to outside; Truck trailer: rear door and side door open to outside.

The single-family home consisted of four floors – a finished basement, first floor, second floor, and third floor/attic. Each floor was approximately 30 feet (in its longest dimension) by 40 feet (longest dimension). The height of the third floor was approximately 15 feet at its highest point, sloping downward to less than a foot where the sloping roof deck met the floor at the the perimeter. There were a few areas of vertical walls on the perimeter, and the height was approximately 7 feet at those locations. The perimeter wall systems consisted of two-inch by four-inch wood framing, with exterior walls constructed of two-inch by eight-inch lumber. The roof deck was constructed of two-inch by six-inch wood framing with two-inch by twelve-inch lumber decking. Only the framing for interior walls and ceiling was present, such that the third floor and attic were essentially one continuous room.

Prior to spraying, preparation activities included applying a one-component foam caulk/sealant (aerosol can) around windows, doors, and other cracks, moving hoses, gun, and other equipment into the home, adjusting controls and equipment in the truck trailer, and discharging a small amount of a residual foam system through the spray gun into a trash bag while outside.

Spray polyurethane foam was applied to the inside surfaces of the perimeter walls and the underside of the roof decking of the third floor/attic on the day of the evaluation. Spraying began at approximately 10:45 a.m. and finished at approximately 4:55 p.m. Spraying was not conducted from approximately 12:10 to 1:40 p.m.

Two employees were monitored during this investigation, an applicator and an applicator assistant. The applicator and applicator assistant swapped roles at mid-day, such that the applicator became the applicator assistant, and the applicator assistant became the applicator. The applicator used the spray gun to apply the foam. The applicator assistant used a manual scraper to remove foam drips from the floor and a manual saw to trim foam from wall surfaces, and for brief periods of time applied a one component foam around doors and windows. For the vast majority of the time during spraying, the assistant was on the same floor as the applicator.

The employees wore shoes, shorts, and sleeveless or short-sleeved shirts. While spraying, one employee wore a full face supplied air respirator, a Kimberly Clark Kleenguard® A20 long sleeve jacket, fabric head covering, and coated fabric gloves. While spraying, the second employee wore a Survivair half face air purifying respirator (APR) with organic vapor cartridges and particulate prefilters, Kimberly Clark Kleenguard® A20 full-body suit, fabric head covering, and safety glasses with side shields. While functioning as the applicator assistant, both employees

PUBLIC COPY

wore a Survivair half face air purifying respirator (APR) with organic vapor cartridges and particulate prefilters, and safety glasses with side shields.

III. CRITERIA

MDI/PMDI

The American Conference of Governmental Industrial Hygienists (ACGIH) has adopted a Threshold Limit Value - Time Weighted Average (TLV-TWA) for 4,4'-methylene bisphenyl isocyanate (MDI) of 0.005 parts per million (ppm) (i.e., 5 parts per billion, ppb) or 0.051 milligrams per cubic meter of air (mg/m^3). This is an airborne concentration for a normal 8-hour workday and a 40-hour workweek and represents conditions under which nearly all workers can be exposed without adverse effect. In addition, the federal Occupational Safety and Health Administration (OSHA) has established a Permissible Exposure Limit (PEL) for 4,4'-MDI of 0.02 ppm or 0.2 mg/m^3 as a Ceiling (C) limit. The Ceiling limit is a concentration that should not be exceeded during any part of the day.

At present, neither an ACGIH TLV nor a federal OSHA PEL has been established for 2,4'-MDI or polymeric MDI. However, Bayer MaterialScience recommends that the exposure limits for 4,4'-MDI be used for the 2,4'- MDI isomer. Further, the 4,4'-MDI OELs also should be considered as reference limits for PMDI.

AMINE CATALYSTS

IV. SAMPLING AND ANALYTICAL TECHNIQUES

Sampling Media

13-mm Impregnated Filter

Prior to any spraying activity, samples of airborne MDI/PMDI were collected using coated 13mm glass fiber filters, mounted in Swinnex holders and connected to SKC Airchek 52 air sampling pumps. The filters were either attached to the workers' lapels (i.e., personal samples) or placed in the surrounding work area (i.e., area samples). All pumps were calibrated before sample collection to a sampling rate of approximately 1 liter per minute (Lpm) using a Bios DryCal® DC-Lite Primary Air Flow Meter. The sampling rate was reconfirmed after the sampling event, with the average value used in the volume calculation. Prior to mounting the filter to the

PUBLIC COPY

Swinnex holder, each filter was coated with 2 mg of 1-(2-pyridyl)piperazine and diethyl phthalate. Immediately upon completion of sampling, the filters were removed from the Swinnex holders and desorbed in 2 ml of acetonitrile/dimethyl sulfoxide (90:10 v/v) solution. When airborne MDI/PMDI is drawn through the filter it is converted to a stable urea derivative, which is quantitatively analyzed by High Performance Liquid Chromatography (HPLC) using Bayer MaterialScience Method 1.7.7.

Impinger and 13-mm Impregnated Filter

During and following active spraying, samples of airborne MDI/PMDI were collected using glass impingers containing 15 milliliters of a solution of toluene and 1-(2-pyridyl)piperazine backed up by coated 13mm glass fiber filters, mounted in Swinnex holders and connected to Ametek P2500B or A.P. Buck Basic 5 air sampling pumps. The impinger/filter sampling trains were either attached to the workers' lapels (i.e., personal samples) or placed in the surrounding work area (i.e., area samples). All pumps were calibrated before sample collection to a sampling rate of approximately 1 Lpm, using a Bios DryCal® DC-Lite Primary Air Flow Meter. The sampling rate was reconfirmed after the sampling event, with the average value used in the volume calculation. Prior to mounting the filter to the Swinnex holder, each filter was coated with 2 mg of 1-(2-pyridyl)piperazine and diethyl phthalate. Immediately upon completion of sampling, the filters were removed from the Swinnex holders and desorbed in 2 ml of acetonitrile/dimethyl sulfoxide (90:10 v/v) solution. When airborne MDI/PMDI is drawn through the impinger solution it is converted to a stable urea derivative, which is quantitatively analyzed by HPLC using Bayer MaterialScience Method 1.20.1. The 13mm filters were analyzed according to Bayer MaterialScience Method 1.7.7.

XAD-2 Sorbent Tubes

Samples of amine catalysts were collected using XAD-2 sorbent tubes (8 mm diameter X 110 mm) connected to SKC Airchek 52 air sampling pumps. Sampling devices were either attached to the workers' lapels for breathing zone sampling or placed in fixed locations for area sampling. All pumps were calibrated before and after sample collection to approximately 0.5 Lpm (1.0 Lpm for short-term and post-spray samples), using a Bios DryCal® DC-Lite Primary Air Flow Meter. Each sample was quantitatively analyzed by Gas Chromatograph / Mass Spectrometer using BMS Industrial Hygiene Laboratory Method 2.10.3.

All samples collected were analyzed at the Bayer MaterialScience Industrial Hygiene Laboratory, which is accredited by the American Industrial Hygiene Association (AIHA).

Background Area Samples

Because and Bayer arrived at the site at about the same time, background samples were not collected.

PUBLIC COPY

Stationary Area Samples

With the exception of the basement, one sample was collected at approximately the center of each floor from just prior to the start of spraying until 15 minutes after the end of spraying for the day. The air sampling pumps and associated media were attached to stands such that the samples were drawn from a height of approximately 4 to 5 feet off of the floor.

In addition to these samples, samples were collected inside the truck trailer (at about the midpoint of the long wall above B-side drum) from a height of approximately 4 to 5 feet off of the floor.

Mobile Area Samples During Spraying

Samples were collected at distances of approximately 10, 20, and 30 feet from the applicator during spraying. The air sampling pumps and associated media were attached to stands such that the samples were drawn from a height of approximately 4 to 5 feet above the floor. The stands were moved periodically to achieve the desired distances from the applicator as the spraying progressed. Due to the near constant movement of the applicator, the 10-foot samples respresented a distance of about 10 to 15 feet, the 20-foot samples represented a distance of about 20 to 25 feet, and the 30-foot samples represented a distance of about 30 to 35 feet. The pumps were shut off over the lunch period.

Area Samples Following Spraying

With the exception of the basement, four samples were collected from the approximate center of each floor following the end of spraying. The air sampling pumps and associated media were attached to stands such that the samples were drawn from a height of approximately 4 to 5 feet off of the floor. The following table depicts the number of minutes following the end of spraying for the four samples at each location. Each sample ran for a duration of about 30 to 40 minutes.

Location	1st Sample (min.)	2nd Sample (min.)	3rd Sample (min.)	4th Sample (min.)
3rd Floor	22	57	94	127
2nd Floor	27	63	96	130
1st Floor	33	68	101	133

V. RESULTS AND DISCUSSION

The analytical results for this evaluation are presented in Tables 1-3. Tables 1 and 2 contain the results for MDI and PMDI, respectively. In both tables, the reported values are a combination of the MDI/PMDI found in the impinger solution and the MDI/PMDI found on the back-up 13mm filter. Table 3 contains the results for the amine catalysts. Each table contains the results of the personal and area samples.

PUBLIC COPY

Personal Samples

A supplied air hood or half face air purifying respirator was worn by both employees during spraying activities. Therefore, the airborne concentrations to which the employees were potentially exposed were likely less than the concentrations reported in Tables 1-3 and in the following paragraphs.

MDI

Airborne MDI was detected in all six of the long term samples collected in the breathing zones of two individuals. Airborne concentrations for one of the employees were 10.3, 208, and 3.58 ug/m^3, with a corresponding sampling period TWA concentration of 55 ug/m^3. Airborne concentrations for the second employee were 7.2, 20, and 194 ug/m^3 , with a corresponding sampling period TWA concentration of 88 ug/m^3. The airborne concentrations measured for both employees exceeded the ACGIH TLV-TWA of 51 ug/m^3.

Airborne MDI was detected in the one short-term sample that was collected in the breathing zone of one of the employees during a time when he was spraying foam. The airborne concentration was 865 ug/m^3, which is greater than the OSHA PEL-C of 200 ug/m^3.

In some cases, MDI was identified on the back-up 13mm filters, typically at very low levels compared to the amount found in the impinger solution.

PMDI

Airborne PMDI was detected in three of the six long term samples collected in the breathing zones of two individuals. Airborne concentrations for one employee were nondetect for two samples collected when not spraying, and 356 ug/m^3 when spraying, for a corresponding sampling period TWA concentration of 85.5 ug/m^3. Airborne concentrations for the second employee were nondetect , 33.6, and 332 ug/ m^3, for a corresponding sampling period TWA concentration of 147 ug/m^3.

Airborne PMDI was detected in the one short-term sample collected in the breathing zone of one of the employees during a time that he was spraying foam. The airborne concentration was 1,691 ug/ m^3.

While there is no OEL for PMDI, it should be viewed as similar to monomeric MDI as to precautions for handling and use. If the OELs for 4,4'-MDI are used as reference limits, the measured airborne levels of PMDI exceeded both the ACGIH TLV-TWA of 51 ug/m^3 and the OSHA PEL-C of 200 ug/m^3.

In one sample, PMDI was identified on the back-up 13mm filter, but at a much lower level than the amount found in the impinger solution.

PUBLIC COPY

Amine Catalysts

Airborne [redacted] was identified in the three long term samples collected in the breathing zones of two employees. The airborne [redacted] concentrations for one of the employees were 76 and 1,203 ppb, with a corresponding sampling period TWA concentration of 883 ppb. The airborne [redacted] concentration for the second employee was 523 ppb. [redacted]

Airborne [redacted] was detected in the one short-term sample that was collected in the breathing zone of one of the employees during a time when he was spraying foam. The airborne concentration was 936 ppb. [redacted]

Airborne [redacted] was identified in two of the three long term samples collected in the breathing zones of two employees. The airborne [redacted] concentrations for one of the employees were nondetect and 136 ppb, with a corresponding sampling period TWA concentration of 105 ppb. The airborne [redacted] concentration for the second employee was 187 ppb. There is no published OEL for [redacted] at this time.

Airborne [redacted] was detected in the one short-term sample that was collected in the breathing zone of one of the employees during a time when he was spraying foam. The airborne concentration was 394 ppb. As previously stated, there is no published OEL for [redacted]

Area Samples

Background Samples

Background samples were not collected during this investigation.

Stationary Samples

MDI

Airborne MDI was detected in one of the five long term samples collected from four locations. Airborne concentrations were nondetect in the trailer, and on the first and second floors. The airborne concentration on the third floor was 13 ug/m^3. These results suggest that airborne MDI did not migrate from the floor being sprayed to the floors below it.

In the sample in which MDI was identified, MDI was not detected on the back-up 13mm filters, suggesting that the impinger efficiently captured the airborne MDI.

PUBLIC COPY

PMDI

Airborne PMDI was detected in one of the five samples collected from four locations. Airborne concentrations were nondetect in the trailer, and on the first and second floors. The airborne concentration on the third floor was 20.1 ug/m^3. These results suggest that airborne PMDI did not migrate from the floor being sprayed to the floors below it.

In the one sample in which PMDI was identified, PMDI was not detected on the back-up 13mm filter, suggesting that the impinger efficiently captured the airborne PMDI.

Amine Catalysts

Airborne was identified in three of the four samples collected from four locations. Airborne concentrations were nondetect in the truck trailer, and 3.4, 3.8, and 876 ppb on the first, second, and third floors, respectively. These results may suggest a slight migration of from the floor being sprayed to the floors below it.

Airborne was identified in one of the four samples collected from four locations. Airborne concentrations were nondetect in the truck trailer, first floor, and second floor, and 67 ppb on the third floor. These results suggest that this compound did not migrate from the floor being sprayed.

Mobile Samples During Spraying

MDI

Airborne MDI was identified at 28 ug/m^3 10 feet from the applicator, and 2.4 ug/m^3 30 feet from the applicator. In addition, short-term samples collected at 10, 20, and 30 feet from the applicator indicated airborne concentrations of 25 ug/m^3, nondetect, and nondetect, respectively.

In all cases, MDI was not detected on the back-up 13mm filters, suggesting that the airborne MDI was efficiently captured by the impingers.

PMDI

Airborne PMDI was identified at 39.0 ug/m^3 10 feet from the applicator, but was not detected in the sample collected at 30 feet from the applicator. In addition, airborne PMDI was not detected in the short-term samples collected at 10, 20, and 30 feet.

Amine Catalysts

Airborne was identified at 1034, 855, and 656 ppb at 10, 20, and 30 feet from the applicator, respectively. In addition, short-term samples collected at 10 feet from the applicator

indicated airborne concentrations of 696 and 664 ppb. The short-term sample collected at 20 feet from the applicator indicated an airborne concentration of 805 ppb. The short-term samples collected at 30 feet from the applicator indicated airborne concentrations of 551 and 945 ppb.

Airborne [redacted] was identified at 111, 90, and 81 ppb at 10, 20, and 30 feet from the applicator, respectively. However, the short-term samples collected at 10, 20, and 30 feet from the applicator were all nondetect.

Post Spray Samples

Neither airborne MDI nor PMDI was identified in any of the post spray samples.

While neither amine catalyst was identified in any of the samples collected on the first and second floors, both were identified in all of the samples collected on the third floor. Airborne [redacted] was identified at 2113, 1980, 1137, and 1351 ppb, with each sample being collected approximately 30 minutes later than the previous. Airborne [redacted] was identified at 251, 220, 151, and 244 ppb, again, with each sample being collected approximately 30 minutes later than the previous. The period evaluated for the post-spray samples started at about 20 minutes post-spray (start of first sample), and ended at about 2 hours and 40 minutes post-spray (end of last sample).

These data suggest that, even at about 2.5 hours following the end of spraying, the use of respiratory protection would still have been needed on the third floor of the structure.

PUBLIC COPY

VI. RECOMMENDATIONS

The following recommendations are based on the sampling results and observations that occurred during the day of this evaluation.

1. During spraying, respiratory protection should continue to be worn by the applicator and all other employees who are working on the same floor as the applicator. However, the data from this investigation indicate that, rather than half mask air-purifying respirators, full-face or hood-type supplied air respirators operated in the positive pressure or continuous flow mode are needed, including during post-spray activities in the areas where foam was installed. This type of respiratory protection also has the advantage of protecting the eyes from vapors and aerosols.

2. During spraying, the applicator should wear a full-body disposable suit (e.g., Tyvek®, Kleenguard®), rather than solely a disposable jacket, as was worn by one of the employees. Furthermore, a disposable suit should be worn by helpers working on the same floor to reduce the likelihood of aerosol contact with skin and clothing. In addition, disposable boot/shoe covers (e.g., Tyvek®, Kleenguard®) are recommended for the applicator.

3. The partially-coated fabric gloves worn by the applicators during spraying should be substituted with gloves that have the coating on the back of the glove as well as the front. The recommended coating material is nitrile, neoprene, butyl, or PVC. This should reduce the likelihood of reacting foam penetrating to the skin, in the event of an accidental spray to the hand.

4. If weather and job site conditions permit, consider the use of ventilation during and after spraying, such as by opening windows and/or doors on opposite sides of the structure.

5. Employees were observed spraying the residual from a previously-applied foam system into a garbage bag without the use of respiratory protection. Respiratory protection should be worn during this type of activity.

PUBLIC COPY

TABLE 1
AIRBORNE METHYLENE DIPHENYL DIISOCYANATE (MDI) CONCENTRATIONS
Personal & Area Samples –
( ) – July 7, 2008

Sample Number	Location/ Job Description	Sampling Period	Sample Volume (liters)	2,4'-MDI (ug/m³)	4,4'-MDI (ug/m³)	Total MDI[1] (ug/m³)	TWA[2] (ug/m³)
PERSONAL SAMPLES – LONG TERM							
289-1	, Applicator (a.m.)	8:25-10:21	119.2	1.93	8.39	10.3	**55**
18437-1		10:25-12:05	97.0	27.9	180	208	
18437-2	Applicator Assistant (p.m.)	13:35-16:55	215.2	0.60	2.97	3.58	
277-1	, Applicator Assistant (a.m.)	8:22-10:19	116.8	1.54	5.65	7.2	**88**
19031-1		10:22-12:05[3]	83.5	3.23	16.8	20	
19031-2	Applicator (p.m.)	13:34-16:55[3]	159.4	25.5	168	194	
PERSONAL SAMPLES – SHORT TERM							
19020-1	, Applicator Sprays foam	11:45-12:00	13.9	115	750	**865**	--
AREA SAMPLES – STATIONARY							
393-1	Truck Trailer	8:44-13:33	305.2	ND[4]	ND	ND	--
393-2		13:33-16:58	216.5	ND	ND	ND	--
22781-1	1st Floor	10:30-17:10	391.6	ND	ND	ND	--
23525-1	2nd Floor	10:30-17:10	454.8	ND	ND	ND	--
23526-1	3rd Floor	10:30-17:10	392.0	2.3	11	13	--
AREA SAMPLES - MOBILE							
22780-1	10 feet	10:45-12:10 13:40-17:10	333.9	5.4	23	28	--
19036-1	10 feet (short term sample)	11:48-12:03	12.4	ND	25	25	--
535-1	20 feet	Sample is void – pump malfunction					
19020-2	20 feet (short term sample)	14:55-15:10	14.1	ND	ND	ND	
195-1	30 feet	10:45-12:10 13:40-17:10	314.8	0.57	1.8	2.4	--
19036-2	30 feet (short term sample)	15:00-15:15	15.8	ND	ND	ND	
AREA SAMPLES – POST SPRAY							
22781-2	1st Floor	17:28-18:01	35.4	ND	ND	ND	--
22781-3		18:03-18:35	34.2	ND	ND	ND	--
22781-4		18:36-19:07	33.1	ND	ND	ND	--
22781-5		Sample is void – pump malfunction					
23525-2	2nd Floor	Sample is void – pump malfunction					
535-2		17:58-18:30	32.8	ND	ND	ND	--
535-3		18:31-19:04	33.5	ND	ND	ND	--
535-4		19:05-19:32	29.7	ND	ND	ND	--
23526-2	3rd Floor	17:17-17:50	33.6	ND	ND	ND	--
23526-3		17:52-18:28	34.7	ND	ND	ND	--
23526-4		18:29-19:01	32.2	ND	ND	ND	--
23526-5		19:02-19:29	28.1	ND	ND	ND	--

1. Reported values are a combination of MDI found in the impinger solution and MDI found on the back-up 13mm filter.
2. Time Weighted Average (TWA) based on the combined sampling times.
3. Sample pump was removed from worker, turned off, and then shortly thereafter turned on and placed back on worker one or more times during this time period to accommodate worker.
4. ND (Non-detectable) – concentrations were less than the analytical Limit of Quantitation (LOQ) of 0.1 μg/sample.

** A supplied air hood or half face air purifying respirator was worn by both employees during spraying activities. Therefore, the airborne concentrations to which the employees were potentially exposed were likely less than the concentrations shown.

PUBLIC COPY

TABLE 2
AIRBORNE POLYMERIC METHYLENE DIPHENYL DIISOCYANATE (PMDI) CONCENTRATIONS
Personal & Area Samples –
– July 7, 2008

Sample Number	Location/ Job Description	Sampling Period	Sample Volume (liters)	PMDI[1] (ug/m^3)	TWA[2] (ug/m^3)
PERSONAL SAMPLES – LONG TERM					
289-1	, Applicator (a.m.)	8:25-10:21	119.2	ND	**85.5**
18437-1		10:25-12:05	97.0	356	
18437-2	Applicator Assistant (p.m.)	13:35-16:55	215.2	ND[4]	
277-1	, Applicator Assistant (a.m.)	8:22-10:19	116.8	ND	**147**
19031-1		10:22-12:05[3]	83.5	33.6	
19031-2	Applicator (p.m.)	13:34-16:55[3]	159.4	332	
PERSONAL SAMPLES – SHORT TERM					
19020-1	, Applicator Sprays foam	11:45-12:00	13.9	**1691**	--
AREA SAMPLES – STATIONARY					
393-1	Truck Trailer	8:44-13:33	305.2	ND	--
393-2		13:33-16:58	216.5	ND	--
22781-1	1st Floor	10:30-17:10	391.6	ND	--
23525-1	2nd Floor	10:30-17:10	454.8	ND	--
23526-1	3rd Floor	10:30-17:10	392.0	20.1	--
AREA SAMPLES – MOBILE					
22780-1	10 feet	10:45-12:10 13:40-17:10	333.9	39.0	--
19036-1	10 feet (short term sample)	11:48-12:03	12.4	ND	--
535-1	20 feet	Sample is void – pump malfunction			
19020-2	20 feet (short term sample)	14:55-15:10	14.1	ND	
195-1	30 feet	10:45-12:10 13:40-17:10	314.8	ND	--
19036-2	30 feet (short term sample)	15:00-15:15	15.8	ND	--
AREA SAMPLES – POST SPRAY					
22781-2	1st Floor	17:28-18:01	35.4	ND	--
22781-3		18:03-18:35	34.2	ND	--
22781-4		18:36-19:07	33.1	ND	--
22781-5		Sample is void – pump malfunction			
23525-2	2nd Floor	Sample is void – pump malfunction			
535-2		17:58-18:30	32.8	ND	--
535-3		18:31-19:04	33.5	ND	--
535-4		19:05-19:32	29.7	ND	--
23526-2	3rd Floor	17:17-17:50	33.6	ND	--
23526-3		17:52-18:28	34.7	ND	--
23526-4		18:29-19:01	32.2	ND	--
23526-5		19:02-19:29	28.1	ND	--

1. Reported values are a combination of PMDI found in the impinger solution and PMDI found on the back-up 13mm filter.
2. Time Weighted Average (TWA) based on the combined sampling times.
3. Sample pump was removed from worker, turned off, and then shortly thereafter turned on and placed back on worker one or more times during this time period to accommodate worker.
4. ND (Non-detectable) – concentrations were less than the analytical Limit of Quantitation (LOQ) of 3 μg/sample.

** A supplied air hood or half face air purifying respirator was worn by both employees during spraying activities. Therefore, the airborne concentrations to which the employees were potentially exposed were likely less than the concentrations shown.

PUBLIC COPY

TABLE 3
AIRBORNE AMINE CATALYST CONCENTRATIONS
Personal & Area Samples –
– July 7, 2008

Sample Number	Location/ Job Description	Sampling Period	Sample Volume (liters)	(ppb)	TWA[1] (ppb)	[illegible]	TWA[1] (ppb)
PERSONAL SAMPLES – LONG TERM							
058-1	, Applicator (a.m.), Applicator Assistant (p.m.)	10:21–12:05 13:34-16:55	157.4	523	**523**	187	187
053-1	, Set Up (a.m.)	8:22-10:19	66.5	76	**883**	ND[2]	105
053-2	, Applicator Assistant (a.m.) Applicator (p.m.)	10:19-12:05 13:34-16:55	152.2	1203		136	
PERSONAL SAMPLES – SHORT TERM							
442-1	, Applicator Sprays foam	11:45-12:00	16.3	**936**	-	394	-
AREA SAMPLES - STATIONARY							
348-1	Truck Trailer	8:44-16:58	269.7	ND	-	ND	-
951-1	1st Floor	10:30-17:10	268.4	3.4	-	ND	-
902-1	2nd Floor	10:30-17:10	242.4	3.8	-	ND	-
949-1	3rd Floor	10:30-17:10	245.2	**876**	-	67	-
AREA SAMPLES - MOBILE							
985-1	10 feet	10:45-12:10 13:40-17:10	162.3	**1034**	-	111	-
2129-1	10 feet (short term)	11:48-12:03	7.7	**696**	-	ND	-
442-3	10 feet (short term)	15:50-16:05	16.6	**664**	-	ND	-
962-1	20 feet	10:45-12:10 13:40-17:10	148.1	**855**	-	90	-
442-2	20 feet (short term)	14:55-15:10	16.3	**805**	-	ND	-
942-1	30 feet	10:45-12:10 13:40-17:10	169.7	**656**	-	81	-
2129-2	30 feet (short term)	14:56-15:10	7.2	**551**	-	ND	-
2326-1	30 feet (short term)	15:50-16:05	15.5	**945**	-	ND	-
AREA SAMPLES – POST SPRAY							
951-2	1st Floor	17:28-18:01	34.5	ND	-	ND	-
951-3		18:03-18:35	33.4	ND	-	ND	-
951-4		18:36-19:07	32.4	ND	-	ND	-
951-5		19:08-19:34	27.2	ND	-	ND	-
902-2	2nd Floor	17:22-17:53	32.4	ND	-	ND	-
902-3		17:58-18:30	33.4	ND	-	ND	-
902-4		18:31-19:04	34.4	ND	-	ND	-
902-5		19:05-19:32	28.2	ND	-	ND	-
949-2	3rd Floor	17:17-17:50	33.2	**2113**	-	251	-
949-3		17:52-18:28	36.2	**1980**	-	220	-
949-4		18:29-19:01	32.2	**1137**	-	151	-
949-5		19:02-19:29	27.1	**1351**	-	244	-

1. Time Weighted Average (TWA) based on the combined sampling times.

2. ND (Non-detectable) - concentrations were less than the analytical Limit of Quantitation (LOQ).

** A supplied air hood or half face air purifying respirator was worn by both employees during spraying activities. Therefore, the airborne concentrations to which the employees were potentially exposed were likely less than the concentrations shown.

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

Bayer MaterialScience Environmental Analytics Laboratory
Industrial Hygiene Laboratory
BMSEAL Method No: 1.7.7

Method Synopsis

Title

Determination of Airborne Methylene bis(phenylisocyanate) by Sampling on a 1-(2-pyridyl)piperazine/Diethylphthalate-Coated Glass-Fiber Filter and Analysis by High Performance Liquid Chromatography

Date

Original - March 8, 1991; Revision 6 - February 17, 2009

Synonyms

Methylene diphenylisocyanate(MDI); 4,4'-Diphenylmethane diisocyanate; 4,4'-MDI; Methylenediphenylmethane diisocyanate; 1,1'-Methylene bis(isocyanato benzene)

2,4'-Diphenylmethane diisocyanate; 2,4'-MDI

CAS

4,4'-MDI	101-68-8
2,4'-MDI	5873-54-1

PUBLIC COPY

Exposure Limits

Isocyanate	OSHA-PELs PPM	ACGIH-TLVs PPM	NIOSH-RELs PPM	Bayer MaterialScience PPM or mg/m^3
4,4'-MDI	0.02 C	0.005 TWA	0.005 TWA 0.02 C	None None
2,4'-MDI	None	None	None	None

OSHA-PEL = Occupational Safety and Health Administration Permissible Exposure Limit
ACGIH-TLV = American Conference of Governmental Industrial Hygienists Threshold Limit Value
NIOSH- REL = National Institute for Occupational Safety and Health Recommended Exposure Limit
TWA = Time Weighted Average
C = Ceiling

Sensitivity

The limit of quantitation routinely achievable with this method for MDI is 0.1 µg/sample. The recommended flow rate for sampling is 1 L/min. The minimum air concentration quantifiable at a 1 L/min flow rate and a 15-min sampling period is 0.007 mg/m^3 for MDI.

Storage Stability

- The samples are stable when stored in the dark at ambient laboratory temperatures for 1 week and in a freezer at -20 °C for 3 more weeks.
- The stock concentrated calibration standard solutions of the isocyanate-1-(2-pyridyl)piperazine derivatives (listed in this method) dissolved in dimethylsulfoxide (DMSO) or in 90/10 Acetonitrile/DMSO and stored at ambient laboratory temperature and pressure are stable for at least 2 months tested and the diluted working standards are stable for at least 1 week.

Special Requirements

- The 13-mm 1-(2-pyridyl)piperazine(PP)-coated filters are not commercially available; they have to be prepared in the laboratory.
- Minimize the exposure of the PP-coated filters to light. Direct exposure of PP filters to fluorescent light for 3 days at ambient temperatures degraded the PP reagent and enhanced the background in the HPLC chromatograms. This could cause some blank problems.

PUBLIC COPY

BMSEAL Method 1.7.7

Determination of Airborne Methylene Bis(phenyl-isocyanate) by Sampling on a 1-(2-pyridyl)piperazine/Diethylphthalate-Coated Glass-Fiber Filter and Analysis by High Performance Liquid Chromatography

Note: Throughout this method the generic term MDI will be used to indicate both 2,4'- and 4,4'-MDI.

1.0 Principle of the Method

1.1 A known volume of air is drawn through a 13-mm glass-fiber filter coated with 1-(2-pyridyl)piperazine (PP)/ diethylphthalate (DEP) and held in a SKC 13-mm filter cassette. The MDI reacts with the PP on the filter to form the corresponding urea.

1.2 The filter is extracted with 90/10 (Volume/Volume) acetonitrile/dimethylsulfoxide (ACN/DMSO) and analyzed by high performance liquid chromatography (HPLC) with an ultraviolet (UV) or a fluorescence detector.

2.0 Accuracy, Precision and Limit of Quantitation

2.1 This method was validated according to the Bayer MaterialScience Environmental Analytics Laboratory's (BMSEAL) minimum validation protocol (Reference 9.1).

2.2 The limit of quantitation (LOQ), accuracy and the precision of this method were determined as follows: 13-mm glass-fiber filters coated with PP and DEP were liquid spiked with 2,4'- or 4,4'-MDI-PP derivative solutions from LOQ to high concentrations. Air at 80% relative humidity (RH) was drawn through these filters at 1 L/min for four hours. After sampling, the cassettes with the PP-filters were stored for 1 week at room temperature, and then for 3 weeks in a freezer at -20 °C, and analyzed by this procedure. The following table summarizes the results of this validation.

PUBLIC

Summary of the Limit of Quantitation, the accuracy and the precision (Coefficient of Variation) for MDI Analysis by BMSEAL Method 1.7.7

Isocyanate	# of samples spiked	Accuracy/ % recovery	Coefficient of variation, %	LOQ µg/sample
2,4'-MDI	30	97.0	2.6	0.1
4,4'-MDI	30	98.0	3.2	0.1

Note: For additional details see the appendix and Reference 9.1.

2.3 The UV detector is linear from 0.25 to 20 µg/mL and the fluorescence detector is linear from 0.05 to 2.0 µg/mL for MDI using this method.

2.4 Each laboratory using this method should determine a reliable LOQ for the reagents, instruments, accessories and procedures it uses. The sensitivity needed to meet the current exposure limit is near the limit of the method; therefore, close attention must be paid to obtaining a representative blank. Sets of blanks with statistical averaging may be required to obtain the desired LOQ.

3.0 Apparatus and Reagents

3.1 Apparatus

3.1.1 Battery operated personal sampling pump capable of maintaining a flow rate of 1 L/min to within ±5% with the sampling device in line.

3.1.2 Two-piece SKC Filter Cassette for holding a 13-mm filter.

3.1.3 13-mm glass-fiber filter, type A/E binder free, SKC or similar.

3.1.4 Soap film or Bios dry flow calibrator or similar.

3.1.5 Tygon® tubing and miscellaneous sampling accessories.

3.1.6 HPLC with UV detector, automatic injector and a computerized data acquisition system.

3.1.7 HPLC column: The following 10-cm x 4.6-mm ID columns manufactured by Phenomenex and Supelco work well for this method. (1): Phenomenex Synergi 4µ Fusion – RP 80A or similar with Fusion RP 4 x 3.0 mm

PUBLIC COP

Security Guard cartridge in a Guard column and (2) Supelco Discovery® RP Amide C16 5μ.with Supelco's recommended guard column.

3.1.8 1-oz. wide-mouth glass vial (amber glass preferred) with Polyseal® or Teflon®-lined cap for desorption of the filter.

3.1.9 Fluoropore membrane filter, 0.45 μm pore size with Luer connector, Millipore Millex-SR or similar.

3.1.10 2.5-mL disposable syringe with male Luer slip end, B-D cat. no. 301112.

3.1.11 Whatman #4, qualitative filter, 15-cm diameter, Fisher Scientific.

3.1.12 Nickel-Chromium wire gauze 15 x 15 cm, Fisher Scientific.

3.1.13 Miscellaneous laboratory accessories, analytical balance (0.1 mg sensitivity), volumetric flasks, pipettes, laboratory shaker, etc.

3.2 Reagents

Caution: Read MSDSs before handling chemicals. Isocyanates must be handled only in a laboratory fume hood.

3.2.1 HPLC grade solvents: methylene chloride, hexane, acetonitrile, dimethylsulfoxide, toluene, acetone and water, Fisher Scientific.

3.2.2 1-(2-pyridyl)piperazine (99.5 + % pure), Aldrich, Milwaukee, WI.

3.2.3 4,4'- and 2,4'-MDI, Bayer MaterialScience.

3.2.4 Ammonium acetate, HPLC grade, Fisher Scientific.

3.2.5 Glacial acetic acid, reagent grade, Fisher Scientific.

3.2.6 Diethylphthalate, reagent grade, Fisher Scientific.

PUBLIC COPY

4.0 Sample Collection

4.1 Preparation of PP-coated glass-fiber filters

4.1.1 Weigh 200 mg of PP in a wide-mouth glass vial; add 0.5 mL of DEP and 9.5 mL of toluene. Mix well.

4.1.2 Place separately the required number of 13-mm glass-fiber filters on a nickel-wire gauze (in a hood). In dim light, using a 50 µL dispensing pipette with Teflon tips add 50 µL aliquot of the toluene PP/DEP solution onto each filter. Add another 50 µl aliquot to each filter after 2 minutes. Let the filters air dry for one hour in dark in a hood. Minimize exposure to light during drying. Alternatively, a number of filters can be placed in the coating solution and gently shaken to wet all the filters for ≈5 min. The filters are then air dried individually on a nickel wire gauze.

4.1.3 Load the dry coated filters into the 13-mm SKC filter cassette (See Figure 1). Store in a cool, dark place until use.

4.2 Sampling

4.2.1 Connect the loaded PP-filter cassette to the sampling pump with Tygon tubing. Calibrate the flow to 1.0 L/min. using the flow calibrator.

4.2.2 Clip the PP-filter cassette, facing down, to the worker's shirt lapel, for a personal breathing-zone sample and attach the battery-operated pump to the worker's waist belt.

4.2.3 Start the sampling pump and record the start time. After the desired sampling period, turn off the pump and record the stop time.

Note: **Do not sample for more than 4 hours or 240 liters. PP slowly evaporates from the filter, especially in hot and humid environments (90° F and 90% RH). The PP added to the filter will suffice for 4 hours sampling.**

4.2.4 After sampling, check the flow rate with the filter in line using the flow calibrator. The flow rate must be within ±20% of the pre-sampling flow rate. If the post-sampling flow rate is outside these limits, label the sample invalid.

4.2.5 Open the filter cassette in the field, carefully remove the filter with tweezers and place it in a 4-mL glass vial. Using a pipette, add exactly 2.0 mL of 90/10 ACN/DMSO to the bottle and shake well. Desorb a blank PP-filter sample for every ten samples collected. Treat the blank filter cassettes/sample(s) to exactly the same environmental conditions as the actual samples except do not draw air through the blank(s). Label the samples and the blank(s) vials appropriately, secure the vial caps with pressure tape and ship to the laboratory for analysis.

Note: **The BMSEAL validation of this method, with MDI solution spiked on PP filters, showed that the MDI-PP derivatives on the filter are stable when stored in the laboratory at ambient conditions for 1 week plus 3 weeks in a freezer at -20 °C before analysis. However, a recent study at a stranded-wood-manufacturing plant where airborne wood particles coated with MDI were sampled, the results of immediate desorption of the PP-filters in the field were compared to laboratory-desorption 1 or 2 days post collection (Reference 9.9). The study showed significant losses of MDI in the laboratory-desorbed samples. Based on this study, field desorption for <u>all MDI samples</u> is recommended because the industrial hygienist cannot, a priori, predict the physical state of MDI in an operation he/she is going to survey.**

5.0 Calibration

5.1 Synthesis of the MDI-PP urea derivative for the preparation of standards

Recrystallizing the MDI

5.1.1 Add ≈20 g of MDI to ≈100 mL of hexane and heat it slightly over a hot plate with constant stirring.

Note: **MDI dimerizes slowly on storage with time. The dimers are insoluble in hot hexane. The amount of MDI dissolving will depend upon the age and purity of MDI.**

5.1.2 Filter the hot slurry through a #4 Whatman filter and discard the undissolved residue in the proper chemical waste container. Cool the filtrate in a refrigerator overnight to precipitate MDI.

5.1.3 Filter the white MDI precipitate, wash with cold hexane, and dry under

vacuum. Place the recrystallized MDI in an amber bottle and store in a freezer.

5.1.4 Dissolve 0.5 g of the recrystallized MDI in 25 mL of methylene chloride.

5.1.5 Dissolve 0.7 g of PP in 50 mL of methylene chloride.

Note: PP slowly reacts with methylene chloride; therefore, prepare the PP solution fresh prior to use.

5.1.6 Mix the PP and the MDI solution slowly with continuous stirring. A white slurry of MDI-PP urea will form. Stir the slurry for 1 hour.

5.1.7 Add the slurry slowly to ≈300 mL of hexane to completely precipitate the MDI-PP derivative. Filter and redissolve the precipitate in a minimal volume of methylene chloride and reprecipitate again with hexane. Filter and wash the precipitate with hexane, and vacuum dry the precipitate.

5.1.8 Bottle, label, and date the product appropriately. Determine the purity of the MDI-PP derivative with nuclear magnetic resonance (NMR) spectroscopy. If the NMR shows the percent purity to be <95%, purify the product further or resynthesize the derivative using new MDI and PP.

5.2 Preparation of MDI standards

Note: The stock concentrated calibration standard solutions of the isocyanate-1-(2-pyridyl)piperazine derivatives (listed in this method) dissolved in dimethylsulfoxide (DMSO) or in 90/10 Acetonitrile/DMSO and stored at ambient laboratory temperature and pressure are stable for at least 2 months tested and the diluted working standards are stable for at least 1 week.

MDI standards for this method can be prepared by two procedures:

- Using the pre-synthesized MDI-PP derivatives and/or
- By reacting the MDI with an excess of the PP in solution.

5.2.1 Preparation of standards using the MDI-PP urea derivatives.

5.2.1.1 Prepare two independent stock solutions for each MDI isomer; one for quality control (QC) and the other for

PUBLIC COPY

preparing working standards.

5.2.1.2 Weigh approximately 0.10 g of the desired MDI-PP derivative in a 50-mL volumetric flask using an analytical balance with a sensitivity of 0.1 mg. Record the exact weight.

5.2.1.3 Dissolve the MDI-PP derivative in the flask and dilute to the mark with DMSO.

5.2.1.4 Calculate the concentration of the DMSO stock solution in mg/mL units of the MDI as shown below.

mg/mL as MDI = mg/mL (MDI-PP) x F

where

$$F = \frac{250.26\ (\text{MW MDI})}{576.71\ (\text{MW MDI-PP})} = 0.434$$

The F factor is the same for 2,4'- and 4,4'- MDI.

5.2.1.5 Add 1.0 mL of the MDI-PP stock solution in DMSO to a 10-mL volumetric flask and dilute to the mark with neat acetonitrile to obtain working standards in 90/10 (V/V) ACN/DMSO.

5.2.1.6 Prepare a series of standards (minimum 5) by appropriately diluting the working standard solution in 5.2.1.5 with 90/10 (V/V) ACN/DMSO solution for a range of isocyanate concentrations from 0.05 to 20 µg/mL.

5.2.1.7 Following the steps described in 5.2.1.2 to 5.2.1.6 prepare two QC standards of approximately 1 µg/mL and 50 µg/mL MDI using the QC stock solution for each isocyanate.

5.2.1.8 Place a PP filter in each of two separate 4-mL glass vials. Using the 1µg/mL QC standard, spike one filter with ≈0.05 µg MDI, and using the 50 µg/mL QC standard spike the other filter with ≈2.0 µg MDI.

5.2.1.9 Desorb the QC filters with 2.0 mL of 90/10 ACN/DMSO solution and analyze them along with the standards (section 5.3).

5.2.2 Preparation of standards using neat monomers

Note: Use fresh, recrystallized MDI (see section 5.1.1 to 5.1.3) for making standards.

5.2.2.1 Prepare a 1 mg/mL solution of PP in ACN/DMSO as described below.

5.2.2.2 Dissolve 200 mg of PP in 200 mL of ACN/DMSO.

5.2.2.3 Weigh ≈0.03 g of MDI in a 100-mL volumetric flask using the analytical balance. Record the exact weight.

5.2.2.4 Dissolve the MDI and dilute to the mark with the 1 mg/mL solution of PP in ACN/DMSO (concentration of the stock MDI standard is ≈0.3 mg/mL). Mix well and allow the solution to stand overnight to assure complete reaction of the isocyanate with PP.

5.2.2.5 Dilute the standard stock solution appropriately with ACN/DMSO to give a series of standards from 0.05 to 20 µg/mL concentration of MDI.

5.2.2.6 Prepare an independent MDI QC stock solution using the same procedure described in 5.2.2.1 to 5.2.2.6. Dilute the QC stock solution to prepare 50 and 1 µg/mL QC solutions.

5.2.2.7 Using the procedure described in 5.2.1.7 to 5.2.1.9, prepare two spiked QC filters and analyze them along with the standards (See section 5.3).

5.3 HPLC Analysis of Standards and QCs

Analyze the standards and the QCs in a batch at the same time using the following HPLC conditions:

Column: HPLC column: (1): 10 cm x 4.6 mm ID Phenomenex

PUBLIC COPY

	Synergi 4μ Fusion – RP 80A or similar with Fusion RP 4 x 3.0 mm Security Guard cartridge in a Guard column or 10 cm x 4.6 mm Supelco Discovery® RP Amide C16 5μ.with Supelco's recommended guard column.
Mobile Phase:	A = Acetonitrile and B = water buffered with 0.01 M ammonium acetate adjusted to pH 6.2 with acetic acid
Mobile phase Gradient:	30% A / 70% B from 0 to 4 minutes, 30% A/70% B to 50% A / 50% B in 8 minutes hold at 50% A/50% B for 2 minutes
Flow Rate:	2.0 mL/min
Injection Volume:	10-25 μL
Detector:	UV at 254 nm and FLD Excitation at 240 nm and Emission at 370 nm

See Figure 2 for a typical chromatogram of the 2,4'- and 4,4'-MDI-PP derivatives.

Note: At the BMSEAL the HPLC system used for isocyanate analysis has a UV and a FLD detector connected serially to the column exit line. Data from both UV and FLD detectors are collected by the data acquisition system.

5.4 Determine the linear regression equation.

5.4.1 Enter each MDI standard's concentration (X value) and its corresponding peak area (Y value) into the linear regression program of the data system or a programmable calculator.

5.4.2 Record the linear regression equation constants: slope, intercept, and correlation coefficient.

5.4.3 Examine the constants for deviations from linearity: correlation coefficient significantly less than unity; intercept significantly different from zero intercept? Recalibrate if necessary.

5.4.4 A typical calibration line for 4,4'-MDI analysis by this method is shown in Figure 3.

PUBLIC COPY

5.5 Check the calibration by analyzing quality control samples.

5.5.1 Calculate the µg of MDI in the QC samples by the analysis of the QC samples following the procedures described in section 7.0.

5.5.2 Divide the calculated µg of MDI by the true µg value spiked, to obtain the percent recovered.

5.5.3 Use the MDI validation data (Appendix A) to prepare quality control charts. Proceed with the sample analysis if the QC values are within the control limits; if not, investigate the reasons for the QC outliers.

6.0 Sample Preparation and Analysis

6.1 Inspect the 4-mL sample vials with the ACN/DMSO-desorbed-filter samples from the field for any visible damage or loss of solvent. Carefully remove the sealing tape from the vial caps and wipe the outside of the bottles clean.

6.2 Filter the extracts with 0.45-µm ACRO LC13 syringe filters into separate HPLC vials.

6.3 Analyze the samples along with the standards using the conditions described for the standards (section 5.3). Analyze a MDI calibration standard as a control after every five sample injections. Calculate the concentration of the control standard (section 8.0). The analysis of the control standard must be within ± 10% of its actual concentration. If not, investigate the reasons for the deviation and reanalyze the five samples before and all the samples after the out-of-control standard.

6.4 All samples must be bracketed by the standards. Dilute and rerun any samples outside the standards' concentration range.

7.0 Desorption Efficiency (DE) and Storage Stability/Retention Efficiency (SS*RE)

7.1 The DE and the SS*RE values, determined by the BMSEAL validation protocol, for 2,4'- and 4,4'-MDI analyzed by this method are given in the Appendix.

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

8.0 Calculation

8.1 Calculate the µg/sample for MDI from the calibration line as follows:

µg/sample MDI = $[\mu g/mL]_C \times V_c \times 1/(CF)$

where,

$[\mu g/mL]_C$ = The µg/mL of MDI calculated from the sample's MDI-PP derivative peak area in the regression equation.

V_c = The volume of ACN/DMSO used to desorb the sample in mL (V_c=2 for routine analysis).

(CF) = A correction factor obtained by multiplying the DE and the SS*RE values from the validation studies.

8.2 Calculate the airborne concentration of MDI in mg/m^3:

mg/m^3 of MDI = µg/sample of MDI x $1/V_L$

where

V_L = volume of air sampled in liters

8.3 Calculate the airborne concentration in ppm for MDI as follows:

ppm MDI = $mg/m^3 \times \frac{24.45}{250}$

where

24.45 = g-mole volume of an ideal gas in liters at 25°C and 1 atmospheric pressure.

250 = molecular weight of MDI. The molecular weight is same for 2,4'- and 4,4'-MDI.

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

9.0 References

9.2 Burright, D., Methylene bis(phenylisocyanate) (MDI), Method 47, Organic Methods Evaluation Branch, OSHA Analytical Laboratory, Salt Lake City, Utah, March 1983 (cited in the Appendix).

9.3 "Particle Size-Selective Sampling in the Workplace", A report of the American Conference of Governmental Industrial Hygienists on air Sampling Procedures, Cincinnati, Ohio, 1985 (cited in the Appendix).

9.4 Coyne, L. B., "Monitoring of MDI Vapors/Aerosols in the Workplace", A summary of several Dow Chemical Company's laboratory studies, International Isocyanate Institute, Reference 27123, April, 1989 (cited in the Appendix).

9.5 Burright, D., Methylene bis(phenylisocyanate) (MDI), Method 47, Organic Methods Evaluation Branch, OSHA Analytical Laboratory, Salt Lake City, Utah, March 1989 (cited in the Appendix).

9.9 Karoly, W., "Stability Studies of Diphenylmethane Diisocyanate (MDI) on Glass Fiber Filters", American Industrial Hygiene Association Journal, Vol 59, No. 9, pages 645-647, 1998.

Appendix A

Summary of Validation of BMSEAL Method 1.7.7 for MDI

The following summarizes the results obtained per the BMSEAL Standard Operating Procedures for minimum validation and determination of the limit of quantitation of a BMSEAL sampling and analysis method (Reference 9.1).

A.1.0 Determination of the desorption efficiency (DE)

A.1.1 Five sets of six 13-mm PP filters were liquid spiked with various quantities (LOQ to high concentrations) of 2,4'- or 4,4'-MDI, respectively. The samples were allowed to stand overnight and analyzed per this method. Three blanks were included.

A.1.2 The results of the DE determinations for 2,4'- or 4,4'-MDI are listed in Table A.1.2. The bottom row, N=30, is the average for the five spike levels.

Note: The results in the top two rows were obtained using fluorescence detector and the bottom 3 rows using UV detector.

TABLE A.1.2: DE Values for 2,4'-MDI

# of samples	Spike level, µg	DE ± 1 SD
6	0.05	0.92 ± 0.04
6	0..10	0.83 ± 0.03
6	0.51	0.94 ± 0.05
6	2.04	1.00 ± 0.02
6	15.0	1.09 ± 0.04
N=30	xxx	0.96 ± 0.097

TABLE A.1.2: DE Values for 4,4'-MDI

# of samples	Spike level, µg	DE ± 1 SD
6	0.050	0.89 ± 0.05
6	0.10	0.86 ± 0.02
6	0.50	0.91 ± 0.03
6	2.00	1.03 ± 0.02
6	15.9	0.98 ± 0.03
N=30	xxx	0.93 ± 0.069

A.2.0 Determination of the combined storage stability and retention efficiency (SS*RE)

A.2.1 Five sets of six 13-mm PP filters were liquid spiked with various quantities (LOQ to high concentrations) of 2,4'- and 4,4'-MDI, respectively. The filters were loaded into cassettes and attached to a manifold and air at 80% relative humidity was drawn at 1.0 L/min for 4 hours through each filter and three blank filters.

A.2.2 After drawing air, the PP-filter cassettes were removed from the manifold and stored at room temperature for 1 week and at -20 °C for 3 weeks.

A.2.3 After 1 month the PP filters were analyzed using this method.

A.2.4 The results of the SS*RE determinations for 2,4'- and 4,4'-MDI are listed in Table A.2.3. The bottom row, n = 30, is the average SS*RE for the 30 spiked samples. The results in the first two rows of the Table were based on fluorescence and the last three rows were based on UV detection.

TABLE A.2.3: SS*RE Values for 2,4'-MDI

# of samples	Spike level, µg	DE ± 1 SD
6	0.104	0.99 ± 0.06
6	0.203	0.94 ± 0.04
6	0.51	0.98 ± 0.03
6	2.02	0.99 ± 0.03
6	15.15	0.94 ± 0.04
N=30	Xxx	0.97 ± 0.026

TABLE A.2.3: SS*RE Values for 4,4'-MDI

# of samples	Spike level, µg	DE ± 1 SD
6	0.10	1.00 ± 0.06
6	0.20	0.96 ± 0.08
6	0.49	1.01 ± 0.06
6	1.96	0.98 ± 0.01
6	14.7	0.93 ± 0.06
N=30	xxx	0.98 ± 0.032

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

A.3.0 Determination of the limit of quantitation (LOQ)

A.3.1 The LOQ as defined by the Bayer MaterialScience SOP on method validation and LOQ determination, is the lowest mass for which acceptable DE or SS*RE values were obtained.

A.3.2 In Tables A.2.3, the LOQs for 2,4'- or 4,4'-MDI are, respectively, the first row of the spiked amount. The LOQs for 2,4'- and 4,4'-MDI are 0.1 µg/sample.

Appendix B

1. This method uses a 13-mm glass-fiber filter coated with PP/DEP in a SKC filter cassette, whereas OSHA Method 47 (.Reference 9.2) recommends using a 37-mm glass-fiber filter coated with 1.0 mg PP in an open-face cassette for sampling airborne MDI.

   The reason for the 13-mm PP/DEP coated filter is an increased face velocity at the sampling inlet for efficient aerosol collection. The American Conference of Governmental Industrial Hygienists (ACGIH) has shown that a sampling device with an inlet face velocity of ≈125 cm/sec closely simulates the capture velocity and deposition characteristics of human inhalation for an aerosol (Reference 9.3). The 37-mm filter with open-face sampling at 1.0 L/min has a calculated face velocity of 1.7 cm/sec compared to 125 cm/sec for the 13-mm filter cassette.

   DOW Chemical Corporation (Reference 9.4) claims that a 13-mm PP/DEP-coated filter collects MDI more efficiently than a 37-mm PP-coated filter. However, studies by the Bayer MaterialScience Environmental Analytics Laboratory demonstrated no significant difference between the 13- and the 37-mm PP filter (Reference 9.6). The particle-size distribution of the Bayer MaterialScience's test atmosphere was not characterized.

2. In a recent update of OSHA method 47 (Reference 9.5), OSHA claims that the 37-mm glass-fiber filter coated with 1.0 mg of PP can be used to sample air for 480 minutes at 1 L/min. However Bayer MaterialScience's experience has been that on hot and humid days as much as 67% of the PP can be lost from 37-mm PP filters in 2 hours sampling (Reference 9.7). Therefore, Bayer MaterialScience conservatively recommends no more than 4 hours of sampling at 1 L/min with a 13-mm filter coated with at least 2 mg of PP. The coating procedure used for the 13-mm filter deposits 2-3 mg PP on the filters.

3. PP filters were found to be stable for at least 2 weeks after preparation for sampling, and the MDI-PP derivatives were stable for at least 2 weeks after sampling when stored in the laboratory at ambient temperature and humidity conditions (Reference 9.8).

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

4. This method should not be used for sampling hot environments (>120°F). The PP on the filter will evaporate rapidly (Reference 9.7).

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

Bayer MaterialScience Environmental Analytics Laboratory
BMSEAL Method No: 1.7.7

Determination of Airborne Methylene bis(phenylisocyanate) by Sampling on a 1-(2-pyridyl)piperazine/Diethylphthalate-Coated Glass-Fiber Filter and Analysis by High Performance Liquid Chromatography

Written by: _____ Date

Approved by: _____ Date

_____ Date

Method Status _____x_____Interim, _____ Final

Revision: ___6_____ Supersedes: Revisions 3, 4, & 5

Disclaimer: While_Bayer MaterialScience believes that the data contained herein is factual, the data is not to be taken as a warranty or representation for which Bayer MaterialScience, LLC, assumes legal responsibility. It is offered solely for your consideration, investigation, and verification.

PUBLIC CO

Hardcopies are uncontrolled. Official copy is on-line.

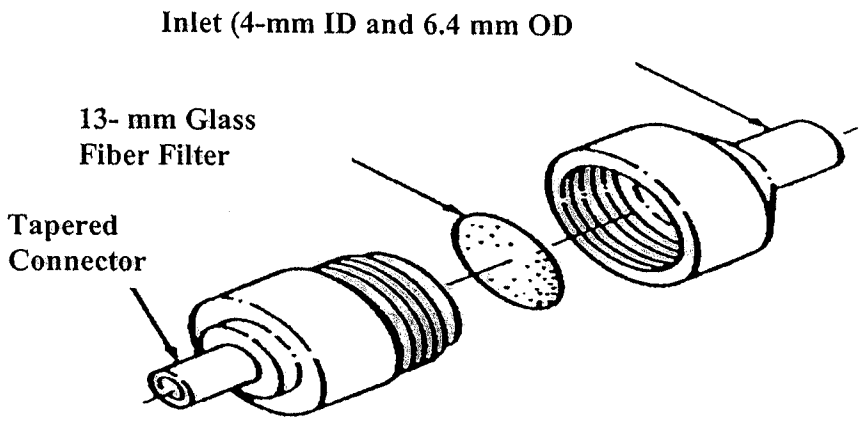


Figure 1: 13-mm SKC Filter Cassette

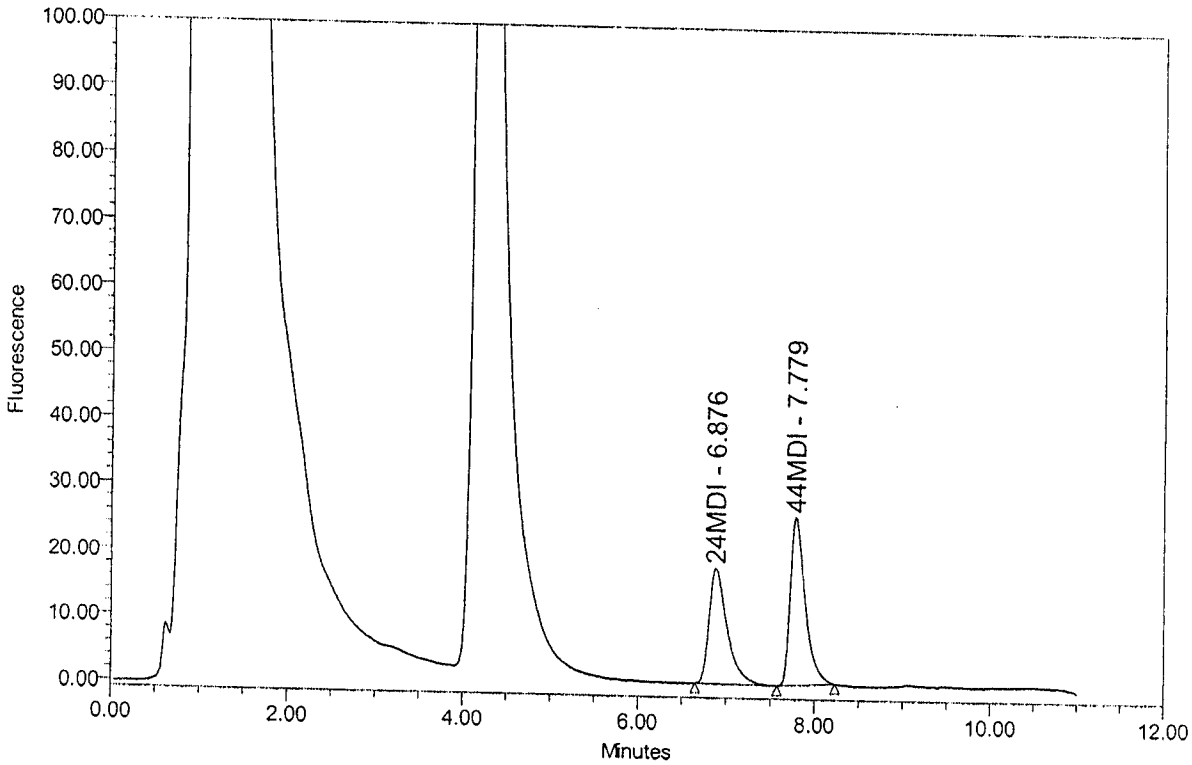


Figure 2: A typical chromatogram with 2,4- & 4,4'-MDI by this method

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

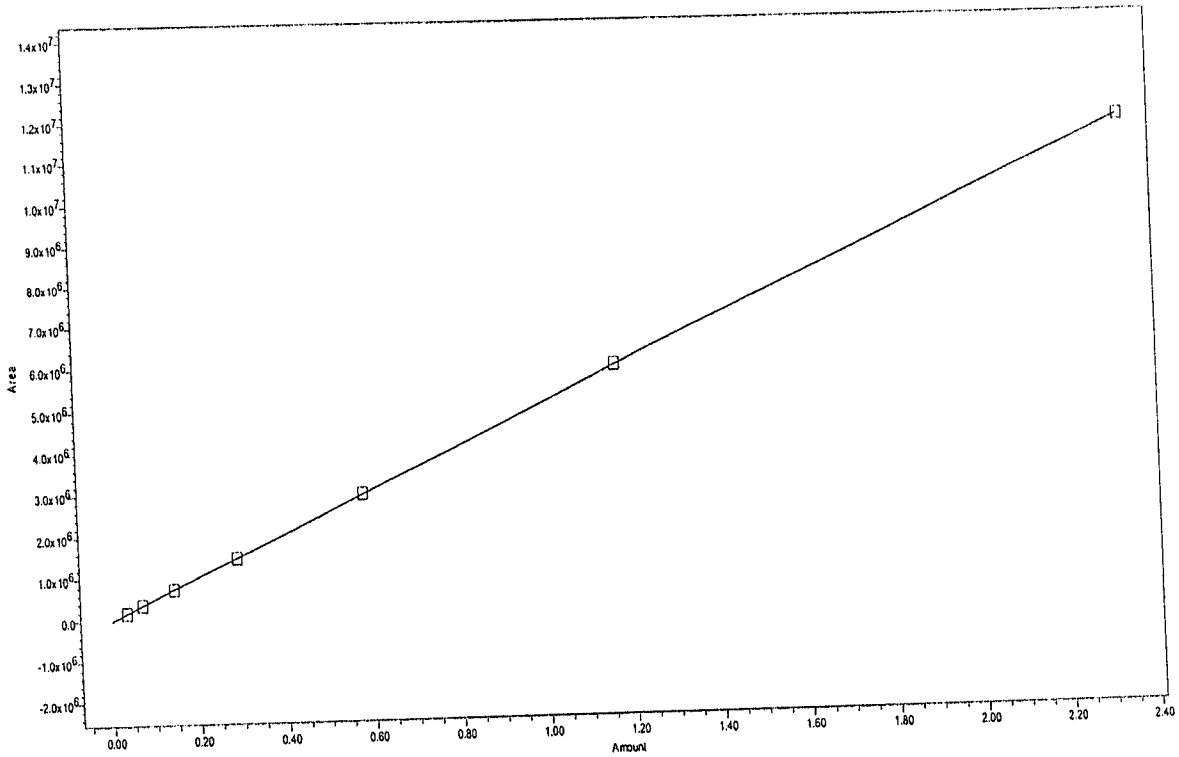


Figure 3: A typical calibration curve for 4,4'-MDI by this method

Supplement to CIHL 1.7.7 for sampling and analysis of polymeric MDI (pMDI) in air samples.

Written by: [redacted] 11/13/08

Date

The proposed experiment is to collect vapors of pMDI coming from cured foam using a glass-fiber filter coated with 1-(2-pyridyl)-piperazine (PP). The method, CIHL 1.7.7, is written for 4,4'- and 2,4'-MDI. No mention is made of pMDI, although it is used for sampling pMDI in spray applications where pMDI is aerosolized and most likely to match the raw product in composition.

BMS markets pMDI under a variety of product names. [redacted] the most common of these, is [redacted] The fraction called "pMDI" in the MSDS is composed of molecules containing greater than two methylene-linked-phenyl rings. Each phenyl ring has an isocyanate group and methylene link(s) to one or two other phenyl rings. The next largest peak after the 4,4'-MDI in the chromatogram (Fig. 1) is assumed to be due to the three-phenyl-ringed molecule. This is the peak selected for calibration with pMDI standards and quantitation of the mass of pMDI in air samples.

What is accomplished in the analytical procedure is the determination of the mass of the product found in the sample using the raw pMDI product as the reference standard. This is done by weighing a mass of the raw pMDI, derivatizing the free isocyanate groups (uv absorbing/fluorescent ureas formed) and preparing a set of working standards from this stock for analysis by high performance liquid chromatography. One peak is selected for calibration. The area of the same peak in a sample is used in the regression equation to calculate the mass of pMDI in the sample.

The 4,4'-MDI peak will be the largest peak in the chromatogram (Fig. 1). DO NOT USE THIS PEAK OR ONE OF THE OTHER MONOMERIC ISOMER PEAKS FOR CALIBRATION. Use the second largest peak, which is the three-phenyl-ringed component of pMDI for calibration and quantitation.

This procedure gives an estimation of the total pMDI in an air sample. Total pMDI means the combination of 4.4'- MDI, mixed MDI isomers and the 40 – 55% fraction referred to as pMDI in the MSDS. This estimation is accurate if the composition of raw pMDI material is preserved in the air sample. This is most likely to be the case in a spray application.

If 4,4'- MDI is quantitated separately, that is using pure 4,4'-MDI standard to prepare a calibration, then 4,4'- MDI gets reported again, since it is already part of the total mass of

PUBLIC COPY

the pMDI reported. One way around this is to subtract the mass of 4,4'-MDI, say 48% of the pMDI standard's weight, to obtain the weight of the true "pMDI" in the standard, and subsequently in the sample. Again, the accuracy of this approach depends on the sample's composition being the same as that in the raw product. If the sample's composition is different, then determining the concentration of each component using a standard of each component for a separate calibration is the only truly accurate way. This approach is stymied by the lack of standards for the pMDI components other than for 4,4'- and 2,4' - MDI. Preparative-scale gel-permeation chromatography would have to be used to separate and purify all the components in pMDI

If vapors effusing from a foam piece are sampled, the composition of chemicals in the vapor phase will be a function of the relative vapor pressures of each of the foam's components and therefore will not be the same on a percentage basis as is found in the raw pMDI. MDI likely will make up an even higher percentage of the total mass vaporizing from the foam (if it hasn't all polymerized) than exists in the raw pMDI just based on relative molecular weights. All are likely to be non-detectable, even 4,4'-MDI, because of extremely low vapor pressures. The MSDSs list the vapor pressure of 4,4'-MDI as < 0.00001 mm Hg @ 25 °C and that of pMDI as < 0.0001 mm Hg @ 25 °C. Do not take the order of magnitude difference as significant, since this difference is likely due to the experimental limits of separate determinations.

BASED ON PHYSICAL PROPERTIES ALONE, ONE CAN CONCLUDE THAT IF THERE IS NO 4,4'-MDI IN THE AIR ABOVE A FOAM SAMPLE MADE FROM pMDI, THEN THERE IS LIKELY NO OTHER pMDI COMPONENTS IN THE SAME AIR SAMPLE.

Reagents

1-(2-pyridyl)piperazine, ≥ 99.5%, Aldrich; FW = 163.22; EW = 163.22

Acetonitrile: HPLC grade

Water: HPLC grade

Dimethylsulfoxide: HPLC grade

pMDI: preferably a fresh sample from the same batch used in the process for which the air sampling was done.

Buffer: 0.01 M ammonium acetate in 95/5 (v/v) water/acetonitrile adjusted to pH 6.2 with acetic acid

Preparation of the pMDI calibration standards

PUBLIC COPY

The isocyanates in the pMDI are reacted with 1-(2-pyridyl)piperazine (PP) to make uv/absorbing/fluorescing urea derivatives. Therefore, there must be a molar excess (at least 10%) of PP over the equivalent molar isocyanate groups available in the pMDI added to the derivatizing solution.

The equivalent weight of the pMDI must be known in order to calculate the molar equivalents of PP needed to complete the derivatization. The equivalent weight, the mass of product per available NCO group, is available from product bulletins. The equivalent weights for a series of Bayer MaterialScience's ( )products listed in a recent product bulletin ranged from 130 to 134. Some vendors report percent NCO. The nominal atomic mass of NCO is 42 amu (Daltons Da). A product that is 32% NCO has an equivalent weight 42/0.32 = 131.

The derivatizing solution is 1 mg/mL PP in 90/10 (v/v) acetonitrile/dimethylsulfoxide (ACN/DMSO). The 1 mg/mL is the approximate concentration of PP in a sample following desorption of a filter sample, so the reagent composition of a standard matches that of a sample.

Following the procedure below for preparing standards, there will be a large excess of PP so as to leave the standard approximately 1 mg/mL after adding the pMDI.

Refer to standards preparation described immediately below:

3.0 mL of 1 mg/mL pMDI added to 22 ml of 1mg/mL PP: Total volume 25.0 mL

22.0 mL of 1 mg/mL PP contains:

(22.0 mL x 1 mg/mL)/(163.22 mg/meq) = 0.135 meq of PP
(meq = milliequivalent)

3.0 mL of 1mg/mL pMDI with an equivalent weight 131 mg/meq contains:

(3.0 mL x 1 mg/mL)/(131 mg/meq) = 0.023 meq of pMDI

There is 5.7 times the PP needed to fully react with the pMDI.

Derivatization of pMDI with 1-(2-pyridyl)-piperazine (PP)

Prepare a 1mg/mL solution of PP in 90/10 (v/v) ACN/DMSO by dissolving 100 mg of PP in 100 mL of 90/10 ACN/DMSO.

Weigh ≈50 mg of the pMDI in a 50-mL volumetric flask using an analytical balance. Record the weight to 0.1 mg.

Dissolve the isocyanate and dilute to the mark with ACN (the concentration of the

PUBLIC COPY

stock isocyanate standard should be ≈1 mg/mL).

Caution: The pMDI must be dissolved in ACN only. Do not dissolve pMDI in 90/10 ACN/DMSO. Isocyantes react slowly with DMSO. The reaction with PP is much faster, so when pMDI in acetonitrile is added to the 1 mg/mL PP in ACN/DMSO the reaction is with the PP. The DMSO is necessary to keep the ureas formed in solution. Also MDI dimerizes in ACN, so pMDI in ACN solutions in must be used fresh within 4 hours after preparation.

Depending on the desired final concentration, pipet 1.0, 2.0 or 3.0 mL of the pMDI stock solution into a 25-mL volumetric flask about half full of 1 mg/mL PP in 90/10 ACN/DMSO. Allow to stand for one hour, then dilute to the mark with the 1mg/mL PP. Mix well.

Prepare a range of working standards by diluting aliquots of the stock standard with 1 mg/mL PP 90/10 ACN/DMSO. Start at 0.2ug/mL.

Preparation of samples for analysis

Samples are desorbed in the field immediately after sampling. This procedure is described in CIHL 1.7.7.

Chromatography

HPLC: Waters Alliance 2695 or equivalent

Column: Phenomenex Synergi 4u Fusion-RP 80A

Detectors: Waters 2487 uv @ 254 nm

Waters 474 fld @ 240 nm excitation, 370 emission

Mobile Phase:

Solvent A:	Acetonitrile
Solvent B:	Buffer
Flow:	2.0 mL/min
Inj. Vol.	10 uL

Gradient:

Minute mark	%A	%B	
0	25	75	
4	25	75	
8	50	50	(Linear)

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

12	50	50	(End)

Calibration and quantitation

See Fig.1. Calibrate and quantitate using the area of the peak. This is the methylene linked three-phenyl-ringed triisocyanate that is indicative of pMDI.

Follow the calculations given in CIHL 1.7.7.

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

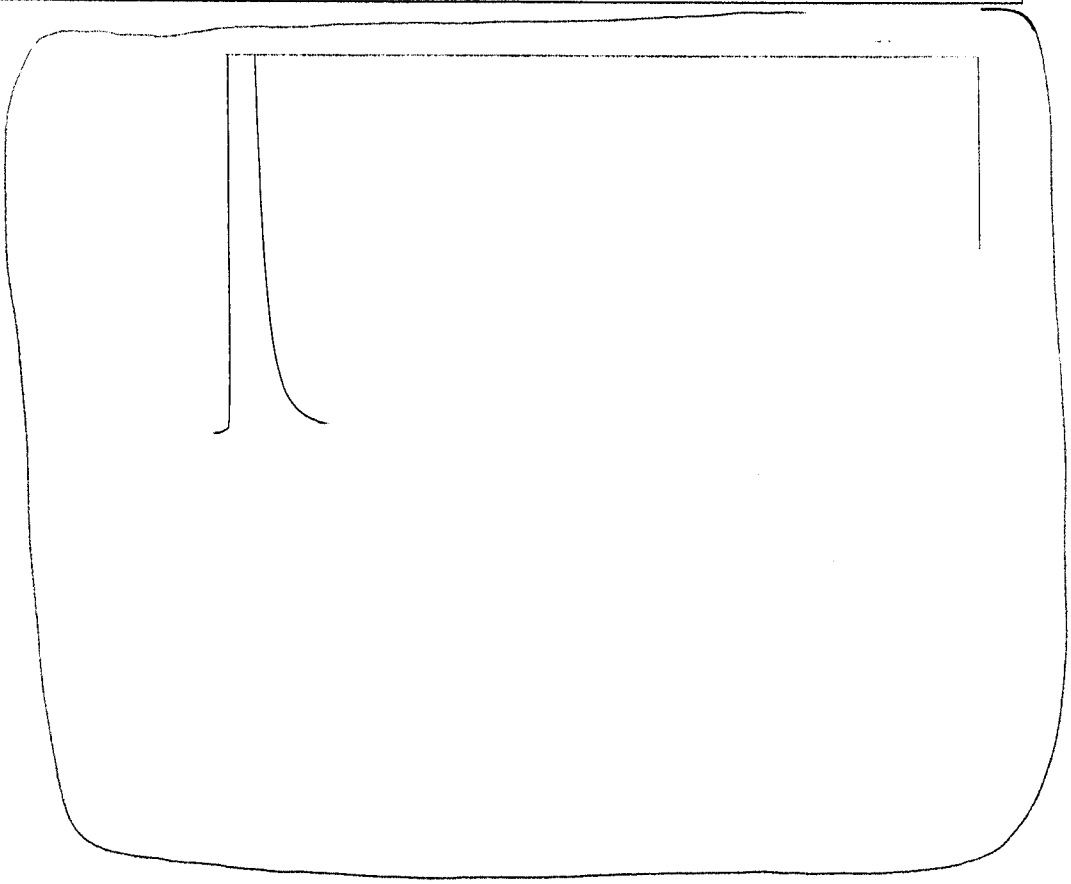
Figure 1

Individual Sample Report

Reported by User: Project Name: ISO_SEPT2008

SAMPLE INFORMATION

Sample Name:	8.69	Acquired By:	
Sample Type:	Standard	Date Acquired:	9/3/2008 4:44:35 PM EDT
Vial:	24	Acq. Method Set:	08 175 178 MDI
Injection #:	1	Date Processed:	11/5/2008 9:25:49 AM EST
Injection Volume:	10.00 ul	Processing Method:	08 178 MDI fld1
Run Time:	12.0 Minutes	Channel Name:	474 Ch1
Sample Set Name:	08 175 178	Proc. Chnl. Descr.:	fid



Report Method: LD CHROMATOGRAM - Printed 2:58:16 PM 11/13/2008

PUBLIC COPY

Bayer Polymers Americas Industrial Hygiene Laboratory

HSEQ Method No: 1.20.0.1

(Supplement to HSEQ Method 1.20.0)

Note: A supplement is added to a Bayer Corporate Industrial Hygiene (CIHL) method when a chemical is of the type listed in the parent method, uses the identical sampling medium, and is analyzed with minor modifications of the analytical procedure. **Only the modifications to each section are given in the supplement.**

Date: January 7, 2004

Chemical: 2,4-Toluenediisocyanate, 2,6-Toluenediisocyanate, 4,4'-Methylene bis (phenylisocyanate), 2,4'-Methylene bis (phenylisocyanate)

Synonyms: 2,4-TDI, 2,6-TDI, 4,4'-MDI, 2,4'-MDI

CAS No.:

2,4-TDI	584-84-9
2,6-TDI	91-08-7
4,4'-MDI	101-68-8
2,4'-MDI	26447-40-5

1.0 Principle

1.1 A known volume of air is drawn through an impinger containing 1-(2-pyridyl) piperazine (PP) in toluene. Isocyanates react with the PP reagent to form stable urea derivatives.

1.2 The urea derivatives are analyzed by high performance liquid chromatography (HPLC) with an ultraviolet (UV) or a fluorescence (Fld) detector.

2.0 Accuracy, Precision and Limit of Quantitation

2.1 This method was validated for 2,4-TDI, 2,6-TDI, 4,4'-MDI and 2,4'-MDI according to the Bayer Polymers Americas Industrial Hygiene Laboratory's (BPAIHL) minimum validation protocol

2.2 The accuracy, precision and the limit of quantitation (LOQ) of this method are summarized in the following table (for details see the Appendix).

PUBLIC COPY

Summary of the Limits of Quantitation and the Coefficients of Variation for Various Isocyanates by HSEQ Method 1.20.0.1

Isocyanate	No. of samples liquid spiked for validation	Accuracy / Percent Recovery	Coefficient of Variation, percent	LOQ, µg/sample
2,4-TDI	18	0.99	0.08	0.1
2,6-TDI	18	1.05	0.12	0.1
4,4'-MDI	18	1.03	0.03	0.1
2,4'-MDI	18	1.04	0.02	0.1

3.0 Apparatus and Reagents

3.1 2,4' & 4,4'-MDI Bayer Polymers or Aldrich, Milwaukee, WI

3.2 2,4 and 2,6-TDI, Bayer Polymers or Aldrich, Milwaukee, WI

4.0 Sample Collection

Same as Method 1.20.0

5.0 Calibration

Same as for HDI in Method 1.20.0

6.0 Sample Preparation and Analysis

Same as Method 1.20.0

7.0 Desorption Efficiency (DE) and Storage Stability/Retention Efficiency (SS*RE).

7.1 These values are given in Appendix.

8.0 Calculations

Same as Method 1.20.0

Appendix

Summary of Validation of HSEQ Method 1.20.0.1 for 2,4-TDI, 2,6-TDI, 4,4'-MDI and 2,4'-MDI

The following summarizes the results obtained per the Bayer Polymers Americas Standard Operating Procedures for minimum validation and determination of the limit of quantitation of a BPAIHL sampling and analysis method.

A.1 Determination of the desorption (recovery) efficiency (DE)

A.1.1 Three sets of six bottles, each containing a 15-mL aliquot of PP-absorber solution in toluene, were liquid spiked with isocyanates: one set at the LOQ, one set at a medium and the final set at a high concentration. The samples were allowed to stand overnight and analyzed per this method. Three blanks were included.

A.1.2 The results of the DE determinations for various isocyanates are listed in Table A.1.2. The bottom row, n=18, is the average for the three spike levels.

TABLE A.1.2: DE Values for 2,4-TDI*

# of samples	Spike level, µg	DE ± SD
n = 6	0.1	1.15 ± 0.06
n = 6	0.5	0.97 ± 0.02
n = 6	2.0	0.99 ± 0.02
n = 18	-	1.01 ± 0.08

* Analyzed with fluorescence detector

TABLE A.1.2: DE Values for 2,6-TDI*

# of samples	Spike level, µg	DE ± SD
n = 6	0.08	1.58 ± 0.17
n = 6	0.41	1.13 ± 0.03
n = 6	1.63	1.12 ± 0.02
n = 18	-	1.22 ± 0.20

* Analyzed with fluorescence detector

PUBLIC COPY

TABLE A.1.2: DE Values for 4,4'-MDI*

# of samples	Spike level, µg	DE ± SD
n = 6	0.09	1.05 ± 0.03
n = 6	0.46	1.00 ± 0.01
n = 6	1.82	1.03 ± 0.00
n = 18	-	1.03 ± 0.03

* Analyzed with fluorescence detector

TABLE A.1.2: DE Values for 2,4'-MDI*

# of samples	Spike level, µg	DE ± SD
n = 6	0.10	0.99 ± 0.02
n = 6	0.49	1.02 ± 0.03
n = 6	1.96	1.09 ± 0.02
n = 18	-	1.04 ± 0.05

* Analyzed with fluorescence detector

A.2 Determination of the combined storage stability and retention efficiency (SS*RE).

A.2.1 Three sets of six impingers, each containing 15 mL of PP-absorber solution, were liquid spiked with various quantities (LOQ, medium and high concentrations) of isocyanates respectively. The impingers were placed on a constant-temperature-humidity airflow manifold and air at 80% relative humidity was drawn at 1.0 L/min for 1 hour through each impinger and three blank impingers.

A.2.2 After drawing air, the impingers were removed from the manifold, and the contents were transferred to separate amber vials, capped, stored at room temperature for 6 days and then at -20 °C for 24 days.

A.2.3 After 30 days the PP reagent absorber solutions were analyzed using this method.

A.2.4 The results of the SS*RE determinations are listed in Table A.2.4. The bottom row, n = 18, is the average SS*RE for the 18 spiked samples.

PUBLIC COPY

TABLE A.2.4: SS*RE Values for 2,4-TDI

# of samples	Spike level, µg	SS/RE ± SD
n = 6	0.1	1.07 ± 0.10
n = 6	0.5	0.94 ± 0.01
n = 6	2.0	0.95 ± 0.00
n = 18	-	0.99 ± 0.08

TABLE A.2.4: SS*RE Values for 2,6-TDI

# of samples	Spike level, µg	SS/RE ± SD
n = 6	0.08	0.90 ± 0.07
n = 6	0.41	1.16 ± 0.03
n = 6	1.63	1.09 ± 0.02
n = 18	-	1.22 ± 0.20

TABLE A.2.4: SS*RE Values for 4,4'-MDI

# of samples	Spike level, µg	DE ± SD
n = 6	0.09	1.04 ± 0.01
n = 6	0.46	1.03 ± 0.03
n = 6	1.82	1.08 ± 0.02
n = 18	-	1.05 ± 0.02

TABLE A.2.4: SS*RE Values for 2,4'-MDI

# of samples	Spike level, µg	SS/RE ± SD
n = 6	0.10	1.02 ± 0.02
n = 6	0.49	1.06 ± 0.01
n = 6	1.96	1.06 ± 0.00
n = 18	-	1.04 ± 0.02

PUBLIC COPY

A.3 Determination of the limit of quantitation (LOQ).

A.3.1 The LOQ as defined by the Bayer Polymers SOP on method validation and LOQ determination is the lowest mass for which acceptable DE and SS*RE values were obtained.

A.3.2 In Table A.2.4, the LOQ for the various isocyanates is the first row of the spiked amount. For example the LOQ for MDI is 0.1 μg/sample.

PUBLIC COPY

Bayer Polymers Americas Industrial Hygiene Laboratory

HSEQ Method No: 1.20.0.1

(Supplement to HSEQ Method 1.20.0)

(PP-impinger Method for 2,4-TDI, 2,6-TDI, 4,4'-MDI and 2,4'-MDI)

Written by: 1/8/04

Date

Approved by 1/8/04

Date

Method status:_____ Interim; ____x____ Final

Revision:_____; Supersedes: _none_____

Disclaimer: While Bayer Polymers Americas believes that the data contained herein is factual, the data is not to be taken as a warranty or representation for which Bayer Polymers Americas assumes legal responsibility. It is offered solely for your consideration, investigation and verification.

PUBLIC COPY

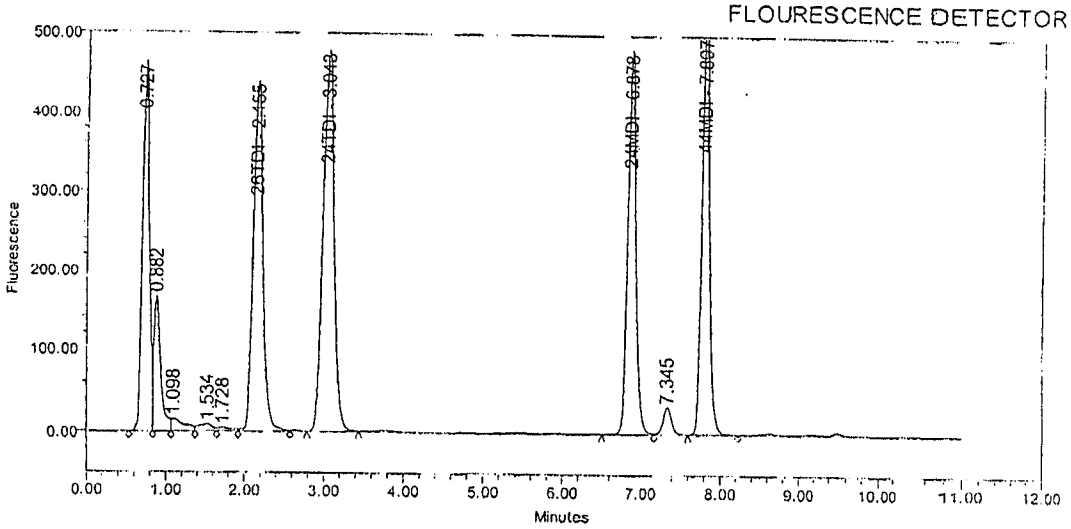


Figure 1: Typical Chromatogram of a Standard with 2,4 & 2,6-TDI and 4,4'- & 2,4'- MDI (all isocyanates ≅ 20 ng injected)

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

Bayer MaterialScience Environmental Analytics Laboratory
BMSEAL Method No: 1.20.1

Method Synopsis

Title

Determination of Isocyanates in Air by Sampling with an Impinger Containing 1-(2-pyridyl) piperazine in Toluene and Analysis by High Performance Liquid Chromatography

Date

Revision 1 – October 29, 2004; Original – August 8, 2003 ;

Chemical Names

This method has been evaluated per the Bayer MaterialScience's validation protocol for the following isocyanates:

- HDI; 1,6-Hexamethylenediisocyanate
- HDI based polyisocyanates; BayerMaterialScience's

Note: **The term polyisocyanate is used generically for all aromatic-, and aliphatic-isocyanate-based polyisocyanates, adducts, modified polyisocyanates, prepolymers and polymers.**

CAS

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

Exposure Limits

Isocyanate	OSHA-PELs PPM	ACGIH-TLVs PPM	NIOSH-RELs PPM	Bayer MaterialScience PPM or mg/m^3
HDI	None	0.005 TWA	0.005 TWA 0.02 C	0.02 C
Polyisocyanate	None	None	None	1 mg/m^3 STEL 0.5 mg/m^3 TWA

OSHA-PEL = Occupational Safety and Health Administration Permissible Exposure Limit
ACGIH-TLV = American Conference of Governmental Industrial Hygienists Threshold Limit Value
NIOSH- REL = National Institute for Occupational Safety and Health Recommended Exposure Limit
TWA = Time Weighted Average; **STEL** = Short Term Exposure Limit; **C** = Ceiling

Sensitivity

The limit of quantitation (LOQ) routinely achievable with this method is 0.1 µg for the monomer (HDI) and ≈ 1.0 µg/sample for the polyisocyanates (see appendix for the LOQ of specific polyisocyanates). At the recommended flow rate of 1.0 L/min, the minimum quantifiable air concentration for a 15-min sampling period is 0.006 mg/m^3 for the monomers and 0.067 mg/m^3 for polyisocyanates.

Storage Stability

The samples are stable for one week when stored in the dark at ambient laboratory temperatures, and for an additional 3 weeks in a freezer at -20 °C.

Special Requirements

- Exposure of the 1-(2-pyridyl)-piperazine impinger (PP-IMP) absorber solution to light must be kept to a minimum.

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

- The collection efficiency of a standard midget impinger is poor for airborne aerosols in ≈ 0.1 - 2 μm mass-median-aerodynamic diameter size range. Generally, in isocyanate-based paint spray atmospheres the amount of isocyanates present in this size range is <1% of the amount found in the spray mist by an impinger. However, in special applications, where airborne isocyanate aerosols in this size range are expected, the impinger must be backed up with a suitable reagent coated filter for the efficient collection of the isocyanates. BPAIHL Method 1.7.6 describes the filter method that must be used for backing up the impinger (see Reference 8.1).

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

Bayer MaterialScience Environmental Analytics Laboratory BMSEAL Method No: 1.20.1

Determination of Isocyanates in Air by Sampling with an Impinger containing 1-(2-pyridyl) piperazine in Toluene and Analysis by High Performance Liquid Chromatography

1.0 Principle

1.1 A known volume of air is drawn through an impinger containing 1-(2-pyridyl) piperazine (PP) in toluene. Isocyanates react with the PP reagent to form stable urea derivatives.

1.2 The urea derivatives are analyzed by high performance liquid chromatography (HPLC) with an ultraviolet (UV) or a fluorescence (Fld) detector.

2.0 Accuracy, Precision and Limit of Quantitation

2.1 This method was validated according to the Bayer MaterialScience Environmental Analytics Laboratory's (BMSEAL) minimum validation protocol for HDI, series of polyisocyanates (Reference 8.2)

2.2 The limit of quantitation (LOQ) and the precision of this method were determined as follows: impingers containing PP absorber solution were spiked with isocyanates at three levels: low (LOQ), medium and high concentrations. Air at 80% relative humidity (RH) was drawn through these impingers at 1.0 L/min for four hours. After sampling, the absorber solutions were stored for 6 days at room temperature, and then for 24 days in a freezer at -20 °C before being analyzed by this procedure. The following table summarizes the results of this validation.

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

Summary of the Limits of Quantitation and the Coefficients of Variation for Various Isocyanates by BPAIHL Method 1.20.0

Isocyanate	No. of samples liquid spiked for validation	Accuracy / Percent Recovery	Coefficient of Variation, percent	LOQ, µg/sample
1,6 HDI	18	107	19	.1
[illegible]	18	113	20	1
[illegible])	18	118	34	1

Note: For additional details see the appendix or Reference 8.2.

2.3 For most isocyanates the response of the UV detector is linear from 0.25 to 20 µg/mL for the monomers and from 1 to 75 µg/mL for the polyisocyanates using this method. The Fld detector responses are linear from 0.05 to 5 µg/mL for monomers and 0.5 to 5 µg/mL for polyisocyanates.

2.4 Concurrent sampling and analysis of paint-spray-mist environments with reagent-coated filter and impinger methods, similar to this method, has shown that impinger results were consistently higher than the filter method. However, the results of impinger and the filter sampling correlated well statistically for isocyanate-monomer vapors (see Reference 8.3).

3.0 Apparatus and Reagents

3.1 Apparatus

3.1.1 Battery operated personal sampling pump capable of maintaining a 1.0 L/min flow rate to within ±5% with the sampling medium in line.

3.1.2 Spill-proof, standard midget glass impinger and impinger holder.

3.1.3 Fluran fluoroelastomer tubing, 1/4" ID, Fisher Scientific

3.1.4 HPLC with UV and/or Fld detector, automatic injector (optional) and an integrating recorder or a computerized data acquisition system.

3.1.5 10-cm x 4.6 mm ID stainless steel HPLC column, Phenomenex C8, 5 µm, or similar. Supelco Discovery Amide C16 column is recommended for

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

optimum separation of multiple isocyanate monomers.

3.1.6 Glass vials, 4, 15 and 40-mL sizes with Polyseal® or Teflon®-lined caps.

3.1.7 1-oz. amber bottles with Polyseal® caps.

3.1.8 2.5-mL disposable syringes with male Luer slip end, BD cat. No. 301112.

3.1.9 10-mL glass syringe and stainless steel canula.

3.1.10 A 0.45-µm pore-size fluoropore membrane filter cartridge with connector for disposable syringe, Gelman ACRO LC13 or similar.

3.1.11 Airflow calibrator, Bios dry or Gilian soap film calibrator or similar.

3.1.12 Vacuum oven, model 5831, National Appliance Company or similar.

3.1.13 Hot plate for heat-evaporating solvents from bottles under a nitrogen atmosphere.

3.1.14 Miscellaneous laboratory accessories, analytical balance (0.1 mg sensitivity), pH meter, Whatman filters, volumetric flasks, pipettes, laboratory shaker, pressure tape, etc.

3.2 Reagents

Caution: **Read the MSDSs before handling chemicals. Isocyanates must be handled only in a laboratory fume hood.**

3.2.1 HPLC grade toluene, acetonitrile, dimethylsulfoxide, hexane, methylene chloride and water, Fisher Scientific.

3.2.2 HPLC grade glacial acetic acid and anhydrous ammonium acetate, Fisher Scientific

3.2.3 1-(2-pyridyl) piperazine, 99.5+% pure, Aldrich, Milwaukee, WI

Caution: **Do not use the 98% pure 1-(2-pyridyl) piperazine available from the same supplier. The 2% impurities will cause problems in the analysis.**

PUBLIC COPY

3.2.4 HDI-based polyisocyanates [redacted] Bayer MaterialScience, Pittsburgh, PA.

3.2.5 HDI, Aldrich, Milwaukee, WI.

4.0 Sample Collection

4.1 Preparation of PP-impinger absorber solution.

4.1.1 Weigh 50 mg of PP in a 500-mL volumetric flask. Add ≈100 mL of toluene to the flask and swirl the solvent to dissolve PP completely and dilute to mark with toluene. The concentration of the absorber solution will be 0.1 mg/mL PP in toluene.

Caution: **The PP reagent degrades slowly with time and the decomposition is accelerated by exposure to light and heat. The number and concentration of the decomposition products produced depend upon several factors such as the purity, age, lot number of PP and also on the storage history of the reagent and that of the PP-impinger before and after sampling. Under certain analysis conditions (maybe due to the HPLC column, its age and use history, gradient used and ACN and buffer concentrations) the decomposition products can elute at the same retention time as an isocyanate and cause severe blank problems (See Reference 8.4). The following precautions are recommended to minimize or eliminate the interfering peaks and restore a smooth baseline to the chromatogram during analysis:**

- **Use a reagent lot of 99.5% or greater purity, which is less than 1 year old and stored in the freezer at -20 °C.**
- **Ideally, prepare fresh PP-absorber solution and use the absorber right away for sampling. If the PP-absorber solution has to be stored before sampling store it in a freezer at -20 °C. Do not use PP-absorber solution older than 4 weeks.**
- **The absorber solution can be prepared, shipped and used for sampling at ambient temperatures. However, minimize exposure to light and high temperatures during these processes and store it in the freezer as soon as you receive it.**

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

4.2 Sampling

4.2.1 Calibrate the sampling pump with an impinger containing 15 mL of the 0.1-mg/mL PP-reagent-absorber solution in line to a flow rate of 1.0 L/min using the airflow calibrator.

Caution: **During sampling, toluene condenses in the connecting tubing and may roll back into the impinger. Plasticizers from tubing such as PVC or silicone rubber are extracted and are interferents in the HPLC analysis. Using only the Fluran fluoroelastomer tubing eliminates this problem. If Fluran is not readily available, make a loop in the tubing to prevent roll back or place an empty impinger in line (Reference 8.5).**

Do not use other plastic containers to store or transfer PP reagent because these also can add plasticizers to the PP reagent.

4.2.2 Attach the outlet of an impinger with 15 mL of the 0.1-mg/mL PP absorber solution to the sampling pump using the Fluran tubing. Connect the impinger to the worker's shirt lapel with the impinger-holder for a personal breathing-zone sample. Attach the pump to the worker's waist-belt.

4.2.3 Start the pump and record the time. Periodically check the toluene-PP reagent level in the impinger and replenish the impinger with the PP reagent absorber solution when the level falls below ≈5 mL.

4.2.4 Stop the pump after the desired period of sampling and record the stop time. Do not exceed 2 hours sampling time.

4.2.5 Detach the impinger and transfer the absorbing solution to an amber glass vial using the glass syringe and canula. Rinse the impinger with ≈2 mL of toluene and transfer the rinse to the amber vial. Cap the vial securely, fasten with pressure tape and ship it to the laboratory. For every ten samples collected, transfer a 15-mL aliquot of the PP reagent absorber solution to an amber vial in the field, cap, fasten with pressure tape and ship it along with the samples as a blank.

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

Caution: **PP reagent is light sensitive. In direct sunlight and to a certain extent in fluorescent light it tends to decompose. The decomposition products can interfere in the analysis. Therefore, keep exposure to light to the minimum necessary. Use amber bottles and store in the dark.**

4.2.6 Check the sampling flow rate immediately after sampling with a toluene-PP reagent impinger in line. The post-sampling flow rate must be within ±10% of the pre-sampling flow rate. If the post-sampling flow rate is outside these limits, label the sample invalid.

5.0 Calibration

5.1 Synthesis of HDI-PP derivatives for the preparation of standards.

5.1.1 Dissolve 3.5 g of HDI in ≈25 mL of methylene chloride in a 100-mL glass beaker.

5.1.2 Dissolve 8.0 g of PP in ≈100 mL of methylene chloride in a 400-mL glass beaker.

5.1.3 Gradually add the HDI solution to the PP solution with constant stirring.

5.1.4 Evaporate the excess methylene chloride solvent by gently heating the solution for ≈10 minutes at 35°C. The HDI-PP derivative may start precipitating at this stage.

5.1.5 Add ≈50 mL of hexane slowly to this solution to complete precipitation of the HDI-PP.

5.1.6 Filter the slurry through a Whatman #4 qualitative filter and redissolve the HDI-PP precipitate in a minimum volume of methylene chloride and re-precipitate with hexane.

5.1.7 Filter and wash the precipitate with hexane and dry the precipitate in a vacuum oven.

5.1.8 Bottle, label, and date the product appropriately.

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

5.2 Preparation of Standards

Isocyanate standards for this method can be prepared by two procedures:

- Using the pre-synthesized HDI-PP derivatives or
- By reacting the isocyanate with an excess of PP in solution.

5.2.1 Preparation of standards using the isocyanate-urea derivatives.

5.2.1.1 Prepare two independent stock solutions for each isocyanate analysis; one for quality control (QC) and the other for preparing working standards.

5.2.1.2 Weigh ≈35 mg of the desired isocyanate-PP derivative in a 25-mL volumetric flask using an analytical balance with a sensitivity of 0.1 mg. Record the exact weight.

5.2.1.3 Dissolve the isocyanate-PP derivative in the flask and dilute to the mark with DMSO.

5.2.1.4 Calculate the concentration of the DMSO stock solution in mg/mL units of the isocyanate as shown below:

For HDI

mg/mL (HDI-PP) x F = mg/mL as HDI

where

$$F = \frac{168\ (\text{MW HDI})}{494\ (\text{MW HDI-PP})} = 0.34$$

5.2.1.5 Add 2.5 mL of the isocyanate-PP stock solution in DMSO to a 25-mL volumetric flask and dilute to the mark with acetonitrile to obtain working standards in 90/10 (V/V) ACN/DMSO.

5.2.1.6 Prepare a series of standards (minimum 4) by appropriately diluting the working standard solution in 5.2.1.5 with 90/10 (V/V) ACN/DMSO solution for a range of isocyanate

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

concentrations from 0.05 to 25 µg/mL.

5.2.1.7 Following the steps described in 5.2.1.2-5.2.1.6 prepare a QC standard of ≈ 100 µg/mL isocyanate concentration using the QC stock solution for each isocyanate.

5.2.1.8 Place 15 mL of PP-absorber solution in two separate 1-oz glass bottles. Spike the two solutions at ≈ 10 µg level using the QC solution (100 µL spikes).

5.2.1.9 Process the two QC absorber solutions exactly like the samples and analyze them along with the standards (section 5.3)

5.2.2 Preparation of standards using neat isocyanates (monomer or polyisocyanates)

Note: Use fresh isocyanates for making standards.

5.2.2.1 Prepare a 1-mg/mL solution of PP in 90/10 ACN/DMSO by dissolving 100 mg of PP in 100 mL of 90/10 ACN/DMSO.

5.2.2.2 Weigh ≈50 mg of the monomer or polyisocyanate in a 50-mL volumetric flask using the analytical balance. Record the exact weight.

5.2.2.3 Dissolve the isocyanate and dilute to the mark with ACN (the concentration of the stock isocyanate standard is ≈1 mg/mL).

Caution: The isocyanate solution in ACN is not very stable. It should be made fresh and used within 4 hours after it is made.

5.2.2.4 Pipet 1 to 3 mL of the isocyanate monomer or polyisocyanate stock solution into a 25-mL volumetric flask and dilute to the mark with the 1 mg/mL PP in 90/10 ACN/DMSO. Mix well and allow the solution to stand overnight to assure complete reaction of the isocyanate with PP.

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

Caution: **Follow the above procedure strictly; do not use more than 3 mL of the 1 mg/mL isocyanate solution to assure stoichiometric excess of PP.**

5.2.2.5 Dilute the standard stock solution appropriately with 90/10 ACN/DMSO to give a series of standards from 0.05 to 25 µg/mL.

5.2.2.6 Prepare an independent QC stock solution using the same procedure described in 5.2.2.1 to 5.2.2.5 and dilute the QC stock solution to prepare 100 µg/mL QC solution.

5.2.2.7 Using the procedure described in 5.2.1.7 to 5.2.1.9 prepare two spiked QC PP-absorber solutions and analyze them along with the standards (See section 5.3)

5.3 HPLC Conditions:

Analyze the standards and the QCs in a batch at the same time by the following HPLC conditions:

Column:	10-cm x 4.6-mm ID stainless steel column, Phenomenex C8, 5 µm or similar.
Mobile Phase:	A = Acetonitrile and B = water buffered with 0.01 M ammonium acetate adjusted to pH 6.2 with acetic acid.
Mobile phase gradient:	25% A / 75% B from 0-2 min, to 50% A/50% B linear in 3 min, hold 50% A/50% B till 8 min, back to 25% A/75% B at 8.1 min, with a run time of 11 min.
Flow Rate:	2.0 mL/min.
Injection Volume:	10-25 µL
Detector:	UV at 254 nm wavelength; Fld excitation 240 nm and emission 370 nm

PUBLIC COPY

See Figures 1 (A & B) and 2 for typical chromatograms of isocyanates and PP-impinger blank respectively, analyzed by this method.

5.4 Determine the linear regression equation.

5.4.1 Enter each standard's concentration (X value) and its corresponding peak area (Y value) into the linear regression program of the data system or a programmable calculator.

5.4.2 Record the linear regression equation constants: slope, intercept, and correlation coefficient. Print a hard copy of the linear regression line if this capability is available.

5.4.3 Examine the constants for deviations from linearity: correlation coefficient significantly less than unity; intercept significantly different from zero intercept. Examine the regression line for points significantly out of line. Recalibrate if necessary.

Note: **Fluorescence calibration for isocyanate concentrations <2 µg/mL and use UV calibration for > 2 µg/mL.**

5.4.4 Calibration lines for isocyanates analyzed by this method are shown in Figure 3.

5.5 Check the calibration by analyzing quality control samples.

5.5.1 Determine the µg of isocyanate in the QC samples by the analysis of the QC samples following the procedures described in section 7.0

5.5.2 Divide the calculated µg isocyanate by the true µg value spiked, to obtain the percent recovered.

5.5.3 Use the validation data (Appendix A) to prepare quality control charts. Proceed with the sample analysis if the QC values are within the control limits; if not, investigate the reasons for the QC outliers.

Note: **Determination of monomeric isocyanates by this method is relatively simple and straightforward. Usually the monomers are commercially available with 98+% purity for the preparation of standards. However, the commercially available HDI-based polyisocyanates are**

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

complex yet reproducible mixtures of HDI oligomers. Typically, the monomer content in polyisocyanates is <2%. Depending upon the isocyanate formulation, the chromatograms can have several peaks with and without the monomer peaks. The exact structures of the higher molecular weight species have not been elucidated and they are not available commercially as pure compounds for the preparation of standards. The BPAIHL prepares a series of standards from commercial polyisocyanate, and uses the major peak as a fingerprint. The area under the major peak is used for the calibration standards and the samples in order to quantify the polyisocyanate in the samples.

6.0 Sample Preparation and Analysis

6.1 Evaporate the toluene in the samples by either 6.1.1 or 6.1.2

6.1.1 Open the sample bottles and place in a water bath (watch out for labels) or hot plate maintained at 65 °C. Turn on the nitrogen over the sample headspace. Take to dryness under nitrogen.

6.1.2 Place the sample bottles inside a vacuum oven at ≈65 °C. Evacuate the oven, and maintain the vacuum until all the toluene has evaporated.

Caution: **(1) Use a cold trap of dry ice/isopropanol between the vacuum oven and the pump to prevent toluene vapors from entering the pump and the atmosphere.**

(2) If toluene is left in the sample, it can interfere chromatographically with some isocyanates; therefore, make sure the evaporation is complete. Use new caps to cap the sample bottles after evaporation to prevent toluene contamination from the old caps.

6.2 Remove the samples from the oven or the hot plate and cool them to room temperature.

6.3 Add 2.0 mL of 90/10 ACN/DMSO to each bottle, cap (use new caps to avoid toluene contamination), and shake the samples for 30 minutes. Filter the samples through 0.45-µm pore-size fluoropore filters into HPLC vials.

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

6.4 Analyze the samples using the conditions described for the standards (section 5.3). Analyze a control standard after every five sample injections. Calculate the concentration of the control standard (section 7.0). The analysis of the control standard must be within ± 15% of its actual concentration. If not, investigate the reasons for the deviation and reanalyze the five samples before and all the samples after the out-of-control standard.

6.5 All samples must be bracketed by the standards. Dilute and rerun any samples outside the standards' concentration range.

7.0 Calculations

Note: **BPAIHL uses two correction factors on all analytical results in order to arrive at a final mass of analyte in the samples. These correction factors are derived from the validation data. The first factor is for recovery of the analyte from the sampling medium and is called the desorption efficiency (DE) even if the medium is an impinger solution. The second factor (SS*RE) is for the combination of losses occurring as a result of storage (SS) and less than perfect retention (RE) during sampling.**

7.1 Calculation of HDI air concentration:

7.1.1 Calculate the µg/sample for HDI from the calibration line as follows:

$$\mu g/\text{sample HDI} = [\mu g/mL]_C \times V_c \times 1/(CF)$$

where,

$[\mu g/mL]_C$ = The µg/mL of HDI calculated from a sample's HDI-PP peak area using the regression equation.

V_c = The volume of ACN/DMSO used to desorb the sample in mL (V_c=2 for routine analysis).

CF = A correction factor obtained by multiplying the DE, and SS*RE factors from the validation studies, listed in Appendix A.

Note: **The QC samples are corrected only for DE.**

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

7.1.2 Calculate the airborne concentration of HDI in mg/m^3.

$$\text{HDI } mg/m^3 = \mu g/\text{sample} \times 1/V_L$$

where

V_L = volume of air sampled in liters

7.1.3 Calculate the airborne concentration in ppm for HDI which is a vapor at room temperature as follows:

$$\text{ppm HDI} = mg/m^3 \times \frac{24.45}{168}$$

where

24.45 = g-mole volume of an ideal gas in liters at 25°C and 1 atmospheric pressure.

168 = molecular weight of HDI.

7.2 Calculation of a polyisocyanate air concentration

7.2.1 Calculate the µg/sample for the polyisocyanate from the calibration line as follows:

$$\mu g/\text{sample polyisocyanate} = [\mu g/mL]_C \times V_e \times 1/(CF)$$

where

$[\mu g/mL]_C$ = The µg/mL of the polyisocyanate calculated from the sum of the samples' polyisocyanate-urea derivative peak area using the regression equation.

V_e = The volume of ACN used to desorb the sample in mL (V_e=2 for routine analysis).

CF = A correction factor obtained by multiplying the DE, and SS*RE factors from the validation studies,

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

listed in Appendix A.

Note: The QC samples are corrected only for DE.

7.2.2 Calculate the airborne concentration of the polyisocyanate in mg/m^3 as follows:

$$mg/m^3 \text{ polyisocyanate} = \mu g/\text{sample} \times 1/V_L$$

where

V_L = volume of air sampled in liters

8.0 References

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

Appendix A

Summary of Validation of BMSEAL Method 1.20.0 for Isocyanates

The following summarizes the results obtained per the Bayer MaterialScience Standard Operating Procedures for minimum validation and determination of the limit of quantitation of a BMSEAL sampling and analysis method.

A.1 Determination of the desorption (recovery) efficiency (DE)

A.1.1 Three sets of six bottles, each containing a 15-mL aliquot of PP-absorber solution in toluene, were liquid spiked with isocyanates: one set at the LOQ, one set at a medium and the final set at a high concentration. The samples were allowed to stand overnight and analyzed per this method. Three blanks were included.

A.1.2 The results of the DE determinations for various isocyanates are listed in Table A.1.2. The bottom row, n=18, is the average for the three spike levels.

TABLE A.1.2: DE Values for HDI

# of samples	Spike level, µg	DE ± SD
n = 6	.09 *	0.90 ± 0.06
n = 6	2.2*	0.95 ± 0.02
n = 6	35.3**	0.95 ± 0.01
n = 18	-	0.94 ± 0.04

* Analyzed with fluorescence detector
** Analyzed with UV detector

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

TABLE A.1.2: DE Values for

# of samples	Spike level, µg	DE ± SD
n = 6	0.14*	0.87 ± 0.09
n = 6	1.8*	0.89 ± 0.03
n = 6	28.8**	1.00 ± 0.01
n = 18	-	0.92 ± 0.08

* Analyzed with fluorescence detector
** Analyzed with UV detector

TABLE A.1.2: DE Values for

# of samples	Spike level, µg	DE ± SD
n = 6	0.18 *	0.76 ± 0.03
n = 6	2.2*	0.94 ± 0.01
n = 6	35.2**	0.94 ± 0.01
n = 18	-	0.88 ± 0.09

* Analyzed with fluorescence detector
** Analyzed with UV detector

A.2 Determination of the combined storage stability and retention efficiency (SS*RE).

A.2.1 Three sets of six impingers, each containing 15 mL of PP-absorber solution, were liquid spiked with various quantities (LOQ, medium and high concentrations) of isocyanates respectively. The impingers were placed on a constant-temperature-humidity airflow manifold and air at 80% relative humidity was drawn at 1.0 L/min for 1 hour through each impinger and three blank impingers.

A.2.2 After drawing air, the impingers were removed from the manifold, and the contents were transferred to separate amber vials, capped, stored at room temperature for 6 days and then at -20 °C for 24 days.

A.2.3 After 30 days the PP reagent absorber solutions were analyzed using this method.

A.2.4 The results of the SS*RE determinations are listed in Table A.2.4. The bottom row, n = 18, is the average SS*RE for the 18 spiked samples.

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

TABLE A.2.4: SS*RE Values for HDI

# of samples	Spike level, µg	SS*RE ± SD
n = 6	0.17*	0.91 ± 0.16
n = 6	1.7*	1.13 ± 0.21
n = 6	17.0**	1.17 ± 0.01
n = 18	-	1.07 ± 0.19

* Analyzed with fluorescence detector
** Analyzed with UV detector

TABLE A.2.4: SS*RE Values for

# of samples	Spike level, µg	SS*RE ± SD
n = 6	0.29*	1.10 ± 0.36
n = 6	2.9**	1.14 ± 0.02
n = 6	14.3**	1.16 ± 0.03
n = 18	-	1.13 ± 0.20

* Analyzed with fluorescence detector
** Analyzed with UV detector

TABLE A.2.4: SS*RE Values for

# of samples	Spike level, µg	SS*RE ± SD
n = 6	0.35*	1.63 ± 0.14
n = 6	3.5**	0.95 ± 0.02
n = 6	35**	0.94 ± 0.02
n = 18	-	1.18 ± 0.34

* Analyzed with fluorescence detector
** Analyzed with UV detector

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

A.3 Determination of the limit of quantitation (LOQ).

A.3.1 The LOQ as defined by the Bayer MaterialScience SOP on method validation and LOQ determination is the lowest mass for which acceptable DE and SS*RE values were obtained.

A.3.2 In Table A.2.4, the LOQ for the various isocyanates is the first row of the spiked amount. For example the LOQ for HDI is 0.1 µg/sample.

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

Bayer MaterialScience Environmental Analytics Laboratory
BPAIHL Method No 1.20.0

Determination of Isocyanates in Air by Sampling with an Impinger containing 1-(2-pyridyl) piperazine in Toluene and Analysis by High Performance Liquid Chromatography

Written by: Date

Approved by: Date

Date

Method Status: _X_ Interim ___ Final

Revisions: 1 Supersedes: 1.20.0

Note: Minor revisions were made to the method BPAIHL Method 1.20.0

Disclaimer: While Bayer MaterialScience believes that the data contained herein is factual, the data is not to be taken as a warranty or representation for which Bayer MaterialScience assumes legal responsibility. It is offered solely for your consideration, investigation and verification.

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

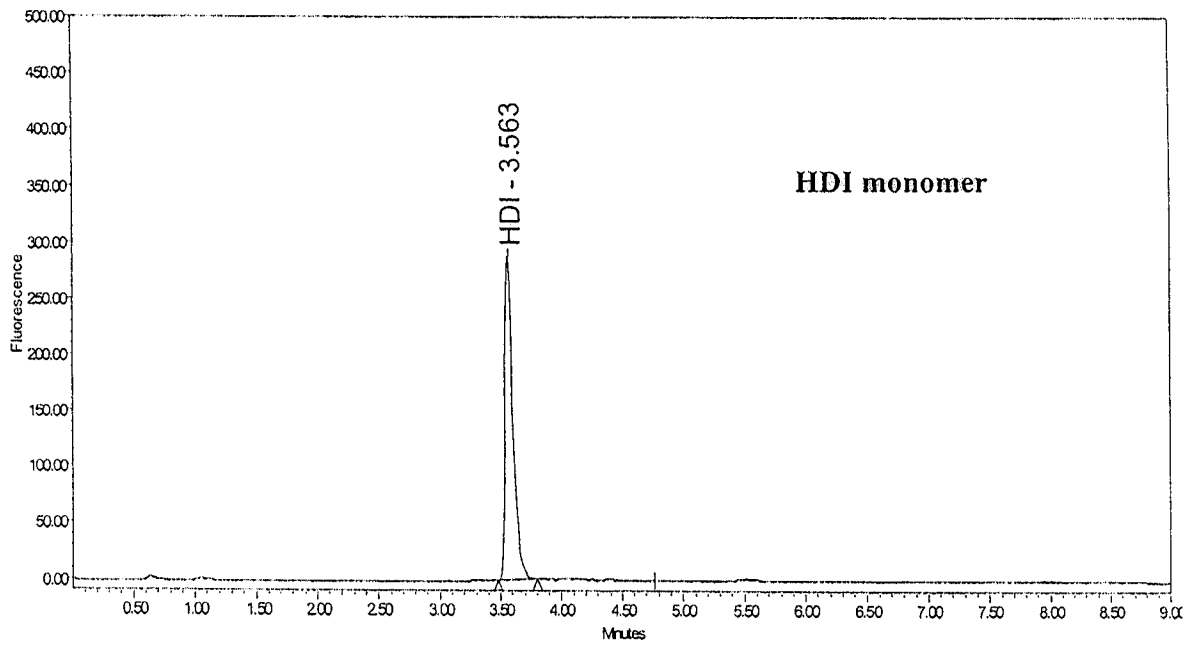


Figure 1A: A typical fluorescence chromatogram of HDI monomer

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

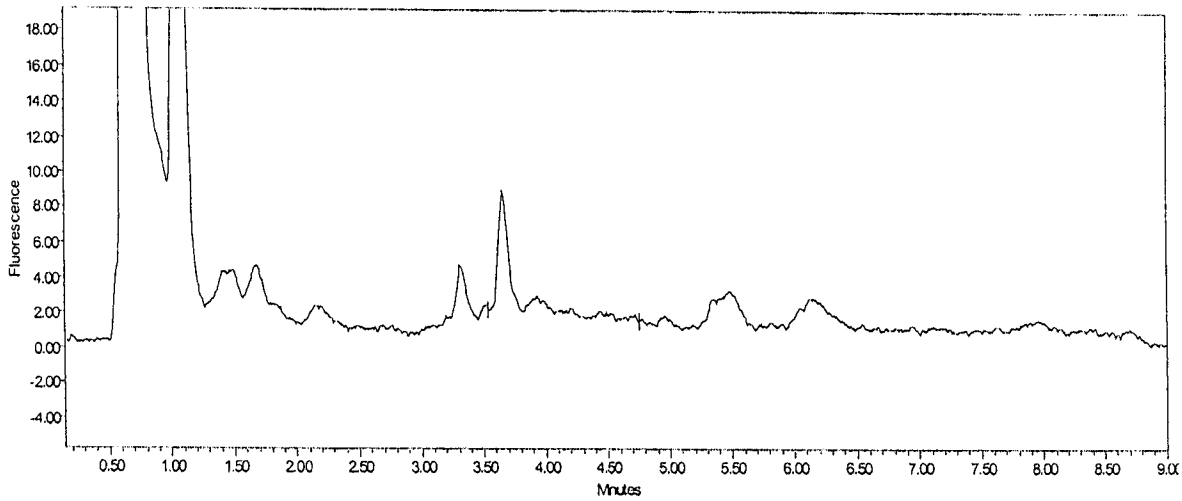
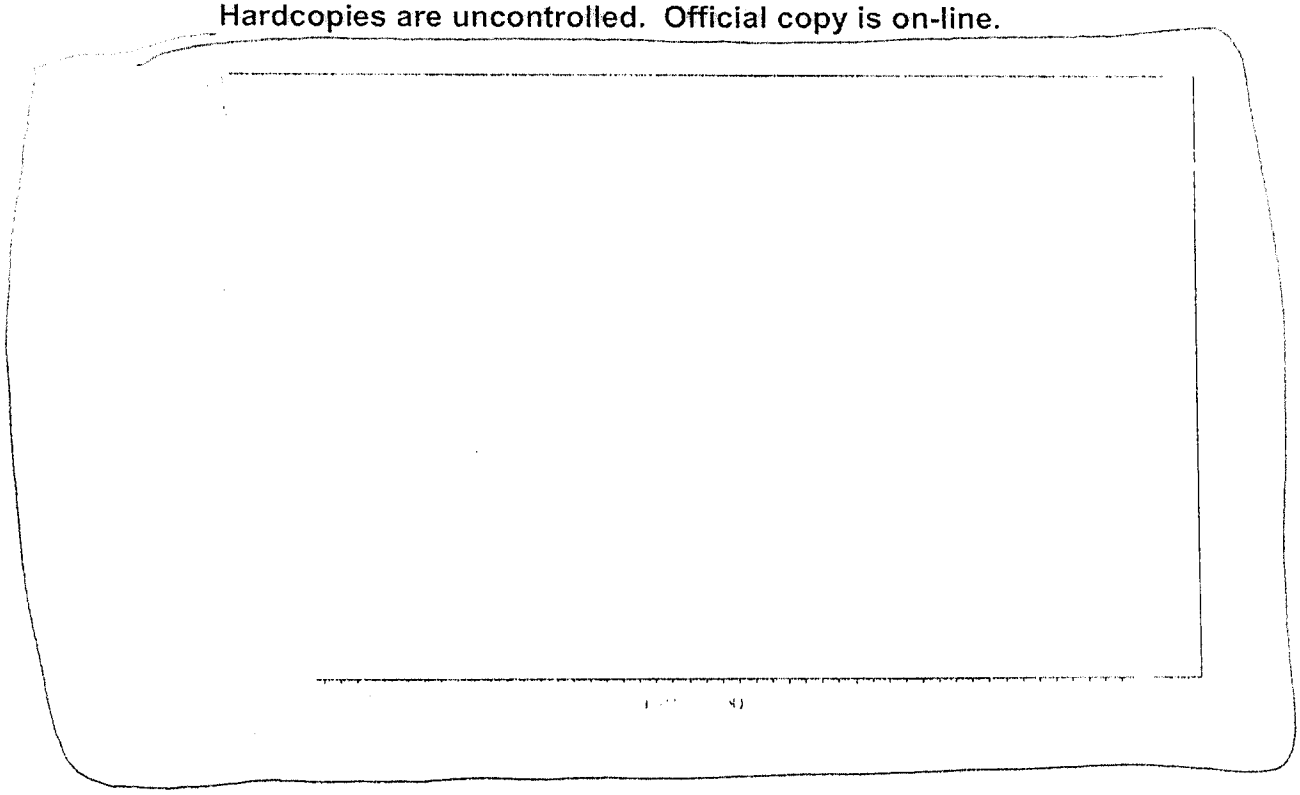


Figure 2: A typical chromatogram of a PP-impinger blank

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.



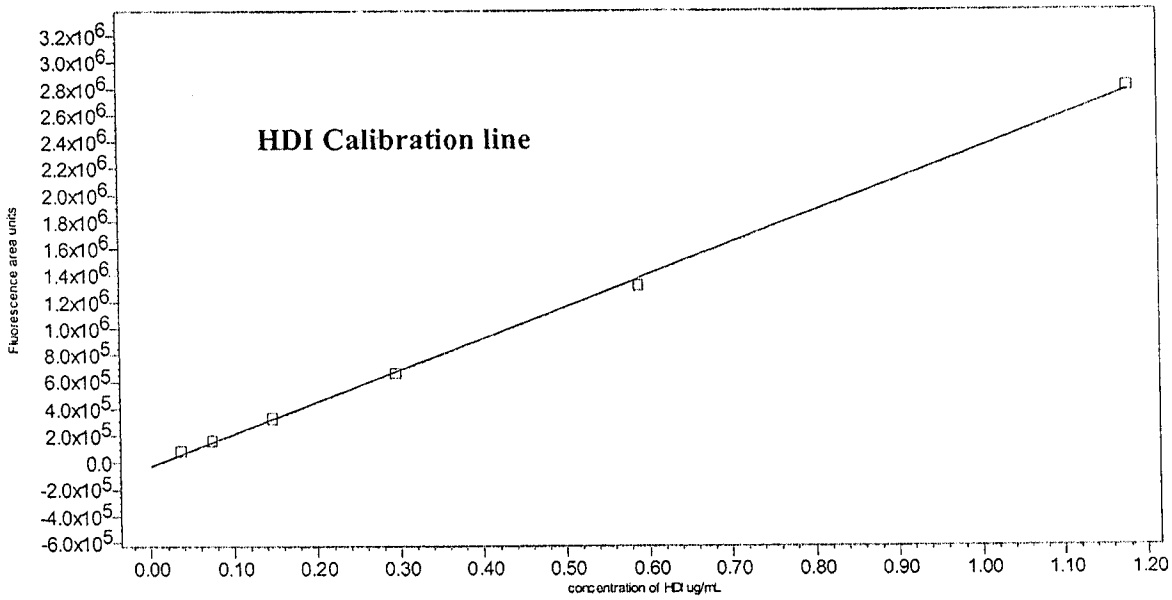


Figure 3: Typical calibration line for N-3300 & HDI

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

BAYER MATERIALSCIENCE ENVIRONMENTAL ANALYTICS LABORATORY
(BMSEAL)
METHOD 2.10.3

Title

Determination of Aliphatic Amine Catalysts in Air by Sampling with a XAD-2 Sorbent Tube and Analysis by Capillary Gas Chromatography

Date: April 2, 2008

Chemicals covered by this method

Chemical Names — The following list gives the trade name of the amine catalysts in bold opposite the chemical names of the catalysts. The acronyms in parentheses will be used to refer to the respective amines throughout this method.

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

Exposure Limits

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

BAYER CORPORATE INDUSTRIAL HYGIENE LABORATORY (BMSEAL) METHOD 2.10.3

Determination of Aliphatic Amine Catalysts in Air by Sampling with a XAD-2 Sorbent Tube and Analysis by Capillary Gas Chromatography

WARNING!

Read the MSDSs before handling the chemicals in this method. The hazards associated with these chemicals have not been fully investigated. Use only procedures for handling highly toxic compounds when handling these compounds. MSDSs can be obtained by calling (412) 777-2042.

1.0 Principle of the method

1.1 A known volume of air is drawn through a two section XAD-2 sorbent tube to trap the airborne amines.

1.2 The sections are desorbed separately, each with 2.0 mL of acetone, and analyzed by gas chromatography with nitrogen-selective detection.

1.3 The peak area of an amine from injection of a desorbate sample is compared to the peak areas of standards to calculate the amount (ug) of the amine collected by the sorbent tube.

1.4 The concentration of an amine in the air sample is calculated from the amount of the amine found in the sorbent tube and the volume of air sampled.

2.0 Validated Sampling Parameters, Accuracy, Precision and Limit of Quantitation

2.1 This method was validated following the Bayer standard operating procedure (**SOP**) on minimum validation and determination of the limit of quantitation (**LOQ**) for a Bayer industrial hygiene sampling and analysis method. Table 2.1 lists the validated sampling parameters and **LOQs**.

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

Table 2.1: Validated Sampling Parameters and LOQs

Amine	MxSR: mL/min	MxSV:Liters	LOQ: ug/sample
[redacted]	400	168	8
[redacted]	400	168	18
[redacted]	400	168	8
[redacted]	400	168	8
[redacted]	400	168	8

MxSR: Maximum validated sampling rate.

MxSV: Maximum validated sampling volume.

2.2 This method is 100% accurate for the amounts collected after correction for desorption efficiency (**DE**) and storage stability/retention efficiency (**SS*RE**). Table 2.2 lists these factors and the relative standard deviation (**RSD**) expected for each analyte in a typical analysis (see the Appendix for the determination of these factors).

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

Table 2.2: DE and Storage/Retention (SS*RE) Factors

Chemical	DE	SS*RE	RSD
	0.98	0.93	0.13
	0.92	0.83	0.08
	0.84	1.0	0.18
	0.82	1.0	0.18
	0.97	0.87	0.16

2.3 The precision for an analyte is the relative standard (**RSD**) over its validated range for **SS*RE** determination. Table 2.2 lists the **RSD**s. Also, see the appendix.

3.0 Apparatus and Reagents

3.1 Apparatus

3.1.1 Two-section, 75/150 mg XAD-2 sorbent sample tubes; SKC 226-30-05 Note: Earlier versions (2.10.1) called for a 200/400 mg tube, SKC 226-30-06. Validation has shown the performance of the two sorbent tubes to be equivalent.

3.1.2 Tube holders for 8 mm OD x 100 mm long sorbent tube; SKC 222-3L-1

3.1.3 Tygon tubing, 3/8-in OD x ¼-in ID, 30 in required per sampler.

3.1.4 Battery operated personal sampling pumps each capable of maintaining a flow rate of 400 mL/min within ± 15% for an 8 hr sampling period with the sampler in line. Gillian Model LFS or equivalent.

3.1.5 Flow calibrator, Buck M5 or similar.

3.1.6 Capillary gas chromatograph (GC) with temperature-gradient oven, fast auto-injector, split/splitless injector and nitrogen phosphorous detector

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

(NPD). HP 6890 or equivalent.

3.1.7 Data system: computerized data collection and processing system, or a digital recorder and a programmable calculator with linear-regression functions.

3.1.8 Capillary GC column:

Type:	Restek RTX-5 Amine (Crossbond 5% diphenyl - 95% dimethyl polysiloxane)
Dimensions:	30 m x 0.25 mm id, 1.0 um df

3.1.9 4-mL vials with PTFE-lined caps

3.1.10 Auto-injector vials with PTFE-lined caps

3.1.11 3-cc plastic syringes; BD 301112 or similar

3.1.12 0.45-um pore syringe filters, Gelman GHP Acrodisc 13 or similar

3.1.13 Sample labels

3.1.14 Volumetric flasks, pipettes

3.1.15 Glass tube-scoring tool

3.1.16 Tool to extract the glass wool plugs from a sorbent tube.

3.2 Reagents

PUBLIC COPY

3.2.6 Acetone: HPLC grade, Fisher Scientific

3.2.7 Propionitrile: Aldrich cat # 18,559, 99% purity, optional if internal standard is needed.

4.0 Sample Collection

4.1 Break the front and back tips off a sampling tube. A small wire cutter provides a convenient way to break these tips. At this point and hereafter caution must be exercised in handling the sampling tubes because of exposure to broken glass tips.

4.2 Calibrate a sampling pump for a flow rate of 400 mL/min or less using the flow calibrator.

Note: The total volumes and flow rate for sampling must not exceed the values given in Table 2.1.

4.3 Number the sampler with a sample label.

4.4 Clip the assembled sampler to a worker's lapel and a pump to the worker's belt. Connect the sampler to the pump with Tygon tubing.

4.5 Start the pump. Record the start time, the pump number and flow rate and the person's name and/or identification number along with the sorbent tube number. Also record any pertinent information that may affect sample collection.

4.6 After sampling is completed, stop the pump and record the stop time. Check the pump flow with the flow calibrator. Record this value. If the post-sampling flow rate is outside ± 20% of the pre-sampling flow rate, label the sample invalid.

5.0 Calibration

5.1 Standards

5.1.1 Prepare a stock standard by weighing approximately 25 mg of an amine in a 25 mL volumetric flask to the nearest 0.1 mg. Dilute to the mark with acetone.

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

5.1.2 Prepare working standards by dilutions of the stock standards with acetone to cover the range from one-half the **LOQ** to no more than 50 ug/mL. Amines may be combined at this stage as long as the retention times are known. Prepare at least five working standards to cover the range.

5.1.3 Since 2.0 m L of acetone is used to desorb a sample, ug/mL of a standard must be multiplied by 2.0 to obtain the equivalent ug/sample. Adjust the amine concentrations of one standard so that the concentrations are equivalent to one-half the **LOQ**s per sample. See table 2.1 for the **LOQ**s.

5.1.4 If the injector port and/or column are not inert toward amines, loss of sensitivity and departure from linearity, especially at low concentrations may occur. If these problems are observed, then use of an internal standard, such as propionitrile, is recommended.

5.2 Analyze the working standards using the following chromatography conditions:

5.2.1 Column: See 3.1.8.

Flow rate: He @ 3.0 mL /min, constant flow

Oven : Initial: 100° C for 1.0 min; to 180° C, linear @ 25°C/min; hold at 180° C for 10 min.

5.2.2 GC gases:

Carrier gas: He: high purity

Detector Gases: H_2: Whatman model 75-34 Hydrogen Generator

Air: compressed air, passed through a Whatman model 75-83-na Zero Air Generator

5.2 3 Injector: (deactivated for amines)

Mode: Splitless

Purge off: 0.5 min

PUBLIC COPY

Purge flow:	50 mL/min
Temperature:	200° C
Injection volume:	1.0 uL

5.2.4 Detector:

Type:	NPD
Temperature:	320° C
Gases:	H_2 @ 2.0 mL/min, air @ 60 mL/min.

5.2.5 Data collection:

5.2.5.1 Set the data system's sampling rate per the manufacturer's recommendations for the peak width of the lowest standard.

5.2.5.2 Run the full set of standards (and later the QCs and samples) without altering the sampling-rate parameters.

5.2.6. Figure 1 is the chromatogram of a 1 uL injection of a standard of all five amines at concentrations equal to aproximately one-half their respective LOQs.

5.3 Determine the y (area response) on x (concentration) regression line.

5.3.1 Set the noise and peak-area thresholds for data-system-peak-area integration by measuring the noise on a solvent-blank run with the data system.

5.3.2 Calculate the best-fit line, y (area response) on x (concentration) using the method of least squares in the data system's calibration programs.

5.3.3 Print a copy of the calibration line with calibration points and the regression equation.

PUBLIC COPY

5.4 Check the calibration by analyzing quality control (QC) samples.

5.4.1 Prepare at least two QC samples by spiking sampling tubes on the front section with a stock standard prepared just for this purpose. Prepare at least two QC samples, one of which should be spiked at the **LOQ** of each amine under analysis.

5.4.2 Analyze the QC samples the same as the field samples described in section 6.0.

5.4.3 Calculate the ug of each amine recovered following the equations in 7.1.2, **except** correct QC samples only for **DE**, not **DE x (SS*RE).**

5.4.4 Calculate the percent recovered for each QC. Compare the recoveries with those expected from control charts. If the recoveries are within the acceptable limits, then proceed with sample analysis.

6.0 Sample Preparation and Analysis

6.1 Desorption of the XAD-2

6.1.1 Score the sampling tube above the glass-wool plug of the front glass-wool section using a scoring tool

6.1.2 Use the glass-wool puller tool to extract the front-section glass wool and place it in a labeled 4 mL vial. Pour the front section XAD-2 beads into the same vial. Tap the tube with a pencil to jar the clinging beads from the tube.

6.1.3 Repeat 6.1.2 for the middle glass-wool plug and the back-up section of XAD-2 into a separate labeled vial. It is not necessary to remove the back glass-wool section.

6.1.4 Add 2.0 m L acetone, cap and shake each sample with a mechanical shaker for one hour.

6.1.5 Filter each sample using the syringe and filter described in 3.1.11 and 3.1.12, respectively. Filter into a GC vial and cap.

Hardcopies are uncontrolled. Official copy is on-line.

6.2 Analysis of the samples

6.2.1 Run the samples using the same conditions used for the standards.

6.2.2 The range of the standards must bracket the peak areas of all the samples run. Dilute and rerun any samples outside the standards' ranges.

7.0 Calculations

7.1 Calculation of the ug of an amine collected on a sorbent tube .

7.1.1 For each sample section, use each analyte's peak area in its respective regression equation (5.3) to calculate the **ug/mL** of analyte in the sample-section's desorbate

7.1.2 Convert the **ug/mL** to **ug/section** using the following equation:

$$\textbf{ug/section} = \frac{\{(\text{ug/mL}) \times 2.0\ \text{mL} \times \text{DF}\} - (\text{BL} \times 2.0\ \text{mL})}{\text{DE} \times (\text{SS*RE})}$$

where,

2.0 mL is the desorbate volume.

DF is the correction factor for any additional dilutions made to bring the analyte's peak area within the calibration range.

BL is the field blank result in **ug/mL**. Any peak area in a blank at the retention time of the analyte is calculated as **ug/mL** and subtracted, even if the result is below the **LOQ**. If more than one blank is run, use the average for the blanks.

DE and **SS*RE** are the recovery correction-factors given in Table 2.2 for each amine. The determinations of the recovery correction-factors are given in the Appendix.

7.1.3 The ug/sample is the sum of the front and back sections

$$\textbf{ug/sample} = (\textbf{ug/section})_{\text{front}} + (\textbf{ug/section})_{\text{back}}$$

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

7.2 Calculation of an amines's concentration in the air sample

7.2.1 The mg/m^3 in an air sample is:

$$\mathbf{mg/m^3 = ug/sample \times 1/V_L}$$

where,

V_L = volume of air sampled in liters.

7.2.2 In ppm:

$$\mathbf{ppm = mg/m^3 \times 24.45/MW}$$

where MW is the molecular weight of the amine.

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

APPENDIX

SUMMARY OF THE VALIDATION OF BAYER BMSEAL METHOD 2.10.3

This Appendix summarizes the results obtained per the Bayer SOP Minimum Validation and the Determination of the Limit of Quantitation (**LOQ**) of a Bayer BMSEAL Sampling and Analysis Method.

A.1.0 Determination of the desorption efficiencies (**DE**)

A.1.1 Preparation of spiked XAD-2 sorbent

Standards of approximately 1 mg/mL of each amine were prepared in acetone. To prepare a spiked sample, the front section (150 mg) of an XAD sorbent tube together with the front-glass wool plug was emptied into a four-mL vial. The XAD-2 sorbent in the vial was spiked with an amine standard using a uL syringe. Each amine was spiked onto separate XAD-2 samples. After allowing the sample to stand overnight with the cap off, 2.0 m L of acetone were added, the vial capped and then shaken for one hour. The sample was then analyzed as described in section 6.0 of this method.

A.1.2 The results of the **DE** determinations are listed in Tables **A.1.2.a -e**. Each **DE** is the fraction: **amount recovered/spike**. The last row (n = 18) is the average **DE** for the three levels and is used in the calculations of section 7.1.2.

Table A.1.2.a:

# SAMPLES	SPIKE (ug)	**DE**	±SD
n = 6	7.95	1.12	0.06
n = 6	42.4	0.93	0.05
n = 6	84.7	0.90	0.01
n = 18	xxx	0.98	0.11

Hardcopies are uncontrolled. Official copy is on-line.

Table A.1.2.b:

# SAMPLES	SPIKE (ug)	**DE**	±SD
n = 5	7.79	0.95	0.06
n = 6	42.9	0.89	0.05
n = 6	85.7	0.91	0.03
n = 18	xxx	0.92	0.05

Table A.1.2.c:

# SAMPLES	SPIKE (ug)	**DE**	±SD
n = 5	7.78	0.89	0.06
n = 6	38.6	0.83	0.08
n = 6	77.1	0.81	0.06
n = 18	xxx	0.84	0.07

Table A.1.2.d:

# SAMPLES	SPIKE (ug)	**DE**	±SD
n = 5	7.88	0.77	0.06
n = 6	39.6	0.86	0.07
n = 6	79.2	0.82	0.07
n = 18	xxx	0.82	0.07

PUBLIC COPY

Table A.1.2.e:

# SAMPLES	SPIKE (ug)	**DE**	±SD
n = 5	7.65	1.11	0.05
n = 6	39.2	0.93	0.07
n = 6	78.4	0.87	0.01
n = 18	xxx	0.97	0.11

A.2.0 Determination of the combined storage stability/ retention efficiency (**SS*RE**).

A.2.1 Preparation of the spiked XAD-2 sorbent tubes

Standards of approximately 1 mg/mL in acetone were prepared. An amine standard was spiked directly onto the front section of the XAD-2 in a tube with a uL syringe. Each amine was spiked onto a separate set of tubes. Spiked tubes were allowed to stand overnight uncapped.

A.2.2 Exposure of the spiked XAD-2 sorbent tubes

Eighteen spiked sorbent tubes and three blanks were attached to a manifold delivering air at 80% relative humidity (RH). This air was pulled through each sampler at 400 mL/min for 7 hrs. At the end of sampling, the sorbent tubes were capped and stored at ambient temperature for four days after which they were placed in a freezer at -30° C for an additional 26 days.

After completion of the storage period, the samples were analyzed as described in section 6.0. The amounts recovered were corrected for **DE** only in equation 7.1.2.

A.2.3 The results of the recoveries for each spike level are listed in Tables **A.2.3.a - e**. **SS*RE** is the fraction: **amount recovered/ spike**. The last row (n = 18) is the average **SS*RE** for the three levels and is used in the calculations of section 7.1.2.

Hardcopies are uncontrolled. Official copy is on-line.

Table A.2.3.a:

# Samples	Spike (ug)	SS*RE	±SD
n = 6	8.38	1.07	0.12
n = 6	42.4	0.84	0.03
n = 6	77.7	0.87	0.07
n = 18	xxx	0.93	0.13

Table A.2.3.b:

# Samples	Spike (ug)	SS*RE	±SD
n = 6	18.2	0.76	0.09
n = 6	45.3	0.85	0.05
n = 6	90.5	0.87	0.06
n = 18	xxx	0.83	0.08

Table A.2.3.c:

# Samples	Spike (ug)	SS*RE	±SD
n = 6	7.78	1.16	0.09
n = 6	38.6	0.96	0.18
n = 6	77.1	1.16	0.18
n = 18	xxx	1.09	0.18

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

Table A.2.3.d:

# Samples	Spike (ug)	**SS*RE**	±SD
n = 6	7.88	0.93	0.13
n = 6	39.6	0.95	0.17
n = 6	79.2	1.14	0.18
n = 18	xxx	1.00	0.18

Table A.2.3.e:

# Samples	Spike (ug)	**SS*RE**	±SD
n = 6	8.38	1.02	0.06
n = 6	38.8	0.70	0.12
n = 6	77.7	0.84	0.09
n = 18	xxx	0.85	0.16

A.4.0 Determination of a **LOQ.**

A.4.1 The **LOQ** as defined by the Bayer SOP on method validation and LOQ determination is the lowest mass for which acceptable **DE** and **SS*RE** values are obtained.

A.4.2 The **LOQs** for the five amines are listed in Table 2.1.

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

BAYER MATERIALSCIENCE ENVIRONMENTAL ANALYTICS LABORATORY
METHOD 2.10.3

Determination of Aliphatic Amine Catalysts in Air by Sampling with a XAD-2 Sorbent Tube and Analysis by Capillary Gas Chromatography

Written by:

Approved: 4/2/08
Date

4/2/08
Date

Method status: X Interim _____ Final

Revisions: Revision 1 Editorial only 4/2/08; Supersedes: 2.10.2

Disclaimer: While Bayer Corp. believes that the data contained herein is factual, the data is not to be taken as a warranty or representation for which Bayer Corp. assumes legal responsibility. It is offered solely for your consideration, investigation and verification.

PUBLIC COPY

Figure 1: Sample Chromatogram

Using conditions described in Section 5.2

Injected amounts (1 uL injection)

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

Bayer MaterialScience Industrial Hygiene Laboratory (BMSIHL) Method 3.53.0

METHOD SYNOPSIS

Title

Determination of Airborne 1,1,1,3,3-Pentafluoropropane by Sampling with Charcoal Tubes and Analysis by Capillary Gas Chromatography

Date

May 14, 2009

Chemical Names

Pentafluoropropane (PFP)
1,1,1,3,3-pentafluoropropane
HFC-245fa
Enovate 3000

CAS #

460-73-1

Exposure Limits

300 ppm TWA – 8 hrs: American Industrial Hygiene Association (AIHA) Workplace Environmental Exposure Level

See Honeywell MSDS number ENVT-002, Nov 2001 for additional information on hazards of PFP.

Validated sampling rate, maximum sample volume and reporting limit

This method was validated per the Bayer MaterialScience Industrial Hygiene Laboratory (BMSIHL) minimum validation protocol.

- The maximum validated sampling volume and flow rate are 10 L and 50 mL/min, respectively.

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

- The reporting limit (**RL**) is 100 ug/sample

PUBLIC COPY

WARNING!

Read the MSDSs before handling the chemicals in this method. MSDSs are available from the vendors.

1.0 Principle of the method

1.1 A known volume of air is drawn through two 37-mm charcoal tubes in series, each containing 600 mg of charcoal.

1.2 After sampling, the tubes are separated, capped and shipped on ice to the laboratory for analysis.

1.3 The charcoal from each tube is desorbed in 5.0 mL of methylene chloride (MECL). The amount of PFP desorbed from each charcoal section (tube) is determined by capillary gas chromatography with flame ionization detection (GC/FID).

1.4 The concentration (mg/m^3) of PFP in the air sample is equal to the sum of the amounts (ug) determined for the front and back tubes divided by the volume (L) of air sampled.

2.0 Accuracy, Precision and Reporting limit

2.1 This method was validated following the BMSIHL Standard Operating Procedure (**SOP**) on minimum validation and determination of the reporting limit (**RL**).

2.2 After correction for desorption efficiency (**DE**) and storage stability/retention efficiency (**SS*RE**) the method is 100% accurate for the amount collected.

2.3 The method precision for the amount collected is ±15%, which is the pooled relative standard deviation (RSD) over the 136 to 15000 ug spike/recovery tests for **RE.**

2.4 The validated **RL** of this method is 100 ug/sample, which is equivalent to 1 mg/m^3 in 100 L, the maximum allowable air-sample volume.

3.0 Apparatus and Reagents

3.1 Apparatus

3.1.1 SKC 226-09 coconut-shell-charcoal tubes. These tubes contain two sections of charcoal, 400 mg front and 200 mg back, for a total of 600 mg. Two tubes are used in series: one tube for the front and one tube for the backup.

3.1.2 Battery operated personal sampling pumps, each capable of maintaining a flow rate of 50 L/min within ± 10% for a 4 hr sampling period with two SKC 226-09 charcoal tubes in series.

3.1.3 Tube holders, SKC 222-3L-1, for 7 or 8 mm OD x 110 mm length tubes

3.1.4 Flow calibrator, Buck M5 or similar

3.1.5 Tubing: 3/8-inch OD x 1/4-inch ID Tygon®, 30 inches required per sampler; 5/16-inch OD x 3/16-inch ID rubber tubing, six inches needed per sampler.

3.1.6 Capillary gas chromatograph with flame ionization detector (GC/FID) and autoinjector, Agilent 6890 or similar

3.1.7 Capillary GC column:

J&W DB-VRX, 60 meter, 0.250 mm ID, 1.40 um film,
Part # 122-1564; Available from Agilent Technologies

3.1.8 Data system: computerized data collection and processing system. Waters Empower Chromatography Data System or other.

3.1.9 Hamilton microliter syringes, point style 2; various sizes – 10, 25, 50, 100, 250, and 500 uL.

3.1.10 40 and 20 mL borosilicate glass vials with open-top PTFE backed silicone septa; I-Chem Economy or similar.

3.1.11 Auto injector GC vials, 1mL, with PTFE lined septa

3.1.12 Glass volumetric pipets, 1.00, 2.00, 5.00, 10.0 and 20.0 mL

3.1.13 Pasteur pipets, 5.75 in

3.1.14 A tray for holding 20 mL I-Chem vials

3.1.15 A shaker for slow agitation of the vials during desorption

3.1.16 Sample labels.

3.1.17 A four place analytical balance

3.1.18 Tube breaker/capper, SKC 222-3-51 for 8-mm tubes

3.1.19 Tubing scorer

3.2 Reagents

3.2.1 1,1,1,3,3-pentfluoropropane, Honeywell Enovate 3000

3.2.2 Methylene Chloride, grade suitable for high resolution GC analysis

3.2.3 GC/FID grade He, H_2, and air

4.0 Sample Collection

4.1 Setting up the sampling train

Using the tube breaker/capper, break the tips off two charcoal tubes. Caution: the broken ends will be jagged and pose a cutting hazard. Place one tube in the tube holder, inserting the tube so the large charcoal section is at the tube-holder air inlet.

4.2 The outlet (back section) of the tube holder is connected to the back-up sampler tube with a short piece of the 5/16 inch OD x 3/16 inch ID rubber tubing. The flexible rubber tubing is needed here to adapt the outlet of the tube holder to the larger diameter sampling tube. Connect Tygon® tubing to the outlet of the back-up tube sufficient in length to reach the sampling pump on the worker's belt.

4.3 Calibrate the sampling pumps for a flow rate of ≈50 mL/min using the flow

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

calibrator. Record the flow rate.

4.4 Number the samplers.

4.5 Clip the assembled sampling train to the worker's collar. Clip a sampling pump to the worker's belt. Connect the sampling train to the pump. Because of the tenuous connection of the back-up tube to the tube holder and the pump line, be sure to make a final check on all connections.

4.6 Start the pump. Record the start time, the pump number and flow rate, and the person's name and/or identification number along with the sampler number. Also record any pertinent information that may affect sample collection.

Note: The total volume sampled must not exceed 10 L.

4.7 After sampling is completed, stop the pump and record the stop time. Check the pump flow with the flow calibrator. Record this value. If the post-sampling flow rate is outside ± 20% of the pre-sampling flow rate, label the sample invalid.

4.8 Remove the back-up tube from the sampling train and cap the ends. Be sure to add "B" for back-section to the tube's sample number. Remove the front tube from the tube holder and cap. Add "F" for front section to the front tube's label.

4.9 Refrigerate the samples as soon as possible, preferably in a freezer until shipping. Ship on ice overnight to the lab. Place in freezer immediately upon arrival.

5.0 Calibration

5.1 Stock standard

PFP boils at 59.5° F (15° C) and must be kept in the freezer. Before opening the PFP vial, make sure the vial has been in the freezer at least four hours. Keep a 500 uL syringe in a freezer-lock plastic bag in the freezer with the PFP. The syringe for drawing and dispensing the PFP must be kept cold, otherwise you will be unable to draw PFP into the syringe.

Add 10.0 mL of MECL using a glass volumetric pipette to a 20 mL I-Chem vial and cap. Tare the vial with the MECL.

Put on nitrile gloves and take the tared vial to the freezer. Place on a tray on a shelf in the freezer. Do not allow the tared vial to stand in the freezer any more

PUBLIC COPY

time than is required to make the PFP addition. Take the 500 uL syringe from the freezer bag and with as little handling as possible draw between 100 and 200 uL of PFP. Handle the syringe as deftly as possible to minimize hand contact and time. Moisture will condense on the outside of the syringe so do not over handle attempting to measure the volume accurately. Work as quickly as possible. Inject the PFP through the septum into the MECL in the vial. Immediately weigh and record the weight of the PFP. Immediately after weighing replace the punctured septum with a fresh septum. Calculate the concentration in ug/mL. Place PFP and syringe back into the freezer.

5.2 Working standards

Samples containing as high as 12 mg PFP were obtained using PFP in foaming applications. To calibrate for these high concentrations as well as covering down to the Reporting Limit, high (300 to 2000 ug/mL) and low (20 to 300 ug/mL) sets of working standards are recommended. The stock standard could likely serve as the top working standard. Since 5.0 mL are used to desorb the samples, a 2000 ug/mL standard is equivalent to 10 mg/sample.

Pipette 10.0 mL of MECL into each of five 20 mL-I-Chem vials using a 10.0-mL glass volumetric pipette. Cap immediately. Add an aliquot, using glass volumetric pipettes, of the stock standard to each of the five vials to cover the high range standards. Remove the cap and place the tip of the pipette slightly below the MECL meniscus while dispensing the stock solution. Cap immediately.

Standards are stable for two weeks when prepared and stored this way.

For the low range standards dilute the high range standards in the same way used to prepare the high range set.

When transferring to GC vials do it carefully. Draw a standard with a Pasteur pipette and discard the contents at least once. Immediately draw an aliquot and transfer to a GC vial with care avoiding making air bubbles through the solution as much as possible. Cap with a PTFE lined cap.

5.3 Analyze the working standards

5.3.1 Chromatography conditions:

Column: See 3.1.7

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

Oven:

Initial column oven temperature: 70° C

Final column oven temperature: 100° C

Oven temperature ramp: 25.0° C/min

No hold time

Carrier gas: He @ 2 mL/min constant flow

Injector: Split/splitless EPC

Temperature: 200° C

Mode: split

Split ratio/flow: 15/30 mL/min

Injection vol: 5.0 uL

Detector: FID

Temperature: 250° C

Fuel flow: H_2 @ 45 mL/MIN

Oxidizer flow: 300 mL/min

Makeup/combo flow: Constant @ 35 mL/min

5.3.2 Data collection:

5.3.2.1 Set up the chromatography data system to collect data for capillary GC runs.

5.3.3 Sample chromatogramS

Figure 1: Chromatogram of a 15 ug/mL (75 ng) injection of PFP

USER COPY

The RL requires a 100 ng injection sensitivity

Figure 2: Chromatogram of a 235 ug/mL (~ 1 ug) injection of PFP

5.4 Determine the y (area response) on x (concentration) regression line.

5.4.1 Integrate the peaks using to data system's programs.

5.4.2 Calculate the best-fit straight line, y (area response) on x (concentration) using the method of least squares from the data system's calibration programs.

5.4.3 Print a copy of the calibration line with calibration points and the regression equation. The calibration line is in units of peak area vs ug/mL.

5.5 Check the calibration by analyzing quality control (QC) samples.

5.5.1 Follow BMSIHL SOP Quality Control for Routine Industrial Hygiene Analysis to prepare and analyze QC samples.

5.5.2 QC results shall be acceptable before proceeding with the analysis of field samples.

6.0 Sample Preparation and Analysis

6.1 Condition samples and desorbing solvent in vials to -30° C

6.1.1 Label a 20-mL I-Chem vial for each of the samples, front and back-up tubes.

6.1.2 Add 5.0 mL of MECL to each vial using a 5.00 mL glass volumetric pipette and cap immediately.

6.1.3 Place the vials in a tray and put in a freezer at -30° C for at least four hours prior to use. The samples should already be in the freezer.

6.2 Desorption of the charcoal samples

6.2.1 Remove the front and back-up tube of a sample from the freezer. Likewise remove the corresponding MECL vials from the freezer. Remove only one

PUBLIC COPY

front/back set at a time. Do not remove the next set until step 6.2.2 is completed. If a set sits out more than ten minutes prior to desorption, return the set to the freezer and recondition.

6.2.2 Score and break the front tube just ahead of the front glass wool. Discard the glass wool and slowly pour the front charcoal section into the front tube's MECL vial. Remove and discard the foam separator, and slowly empty the back charcoal section into the same vial. Repeat for the back-up tube emptying its charcoal sections into the MECL vial for the back-up sample.

6.2.3 After all the charcoal tubes are transferred to MECL vials, place the vials on the shaker and desorb with gentle shaking for one hour.

7.0 Calculations

7.1 Calculation of the ug of PFP collected

7.1.1 For each sample and blank, use the PFP peak area in the regression equation (5.4) to calculate the **ug/mL** of the analyte in the sample's desorbate.

7.1.2 Convert **ug/mL** to **ug/tube** using the following equation:

$$\textbf{ug/tube} = \frac{\{(\textbf{ug/mL}) \times \textbf{DV} \times \textbf{DF}\} - (\textbf{BL} \times \textbf{DV})}{\textbf{CF}}$$

where,

BL is the blank in ug/mL. Any peak area in the blank at the retention time of PFP is calculated as ug/mL PFP, even if the area is below the **RL**. If more than one blank is run, **BL** is the average of the blanks.

DV is the desorption volume, which is 5.0 mL

DF is the factor for any additional dilutions required to bring the sample's peak area within the calibration range.

CF is the correction factor for the combined desorption efficiency (**DE**),

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

storage stability (**SS**) and retention efficiency (**RE**). The equation for calculating **CF** is:

$$\mathbf{CF = DE \times SS \times RE = (1.15 \times 1.06 \times 0.84) = 1.02}$$

See the Appendix for the determinations and values of **DE, SS** and **RE**.

7.2 The **ug/sample** is:

$$\mathbf{ug/sample = ug/tube_F + ug/tube_B}$$

where:

$\mathbf{ug/tube_F}$ is the amount of PFP collected on the front tube

$\mathbf{ug/tube_B}$ is the amount of PFP collected on the back tube

7.2 PFP concentration in an air sample

7.2.1 The mg/m^3 PFP in the air sample is:

$$\mathbf{mg/m^3 = ug/sample \times 1/V_L}$$

where,

V_L = volume of air sampled in liters.

7.2.2 The ppm PFP in the air sample is;

$$\mathbf{ppm = (mg/m^3) \times (24.45/MW)}$$

The molecular weight (**MW**) of PFP is 134.

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

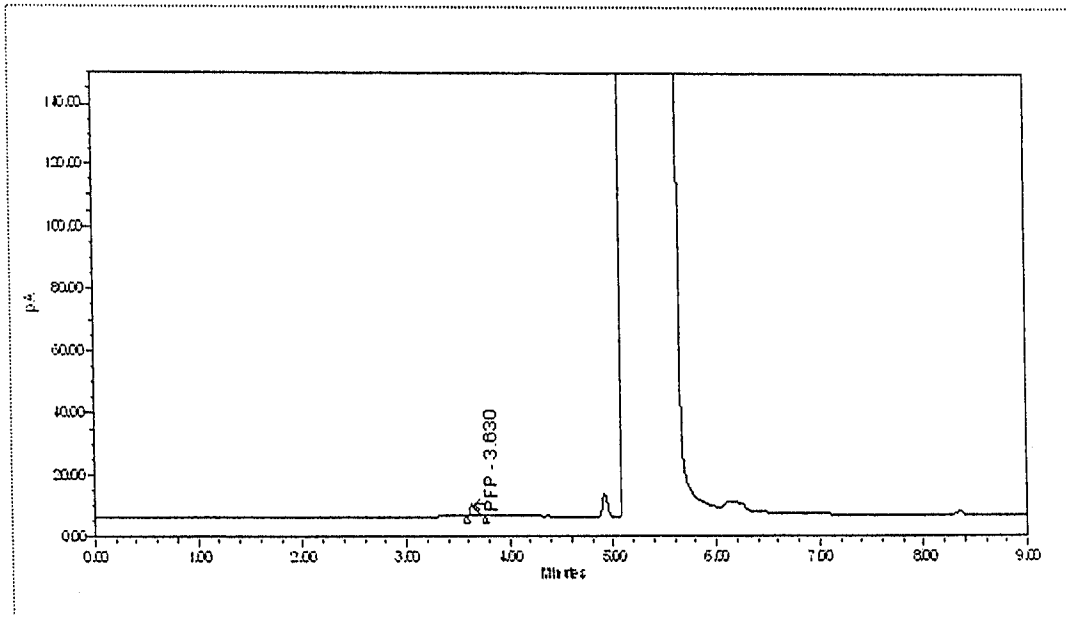


Figure 1: 15 ug/mL PFP standard; 75 ng injected

PUBLIC COPY

Hardcopies are uncontrolled. Official copy is on-line.

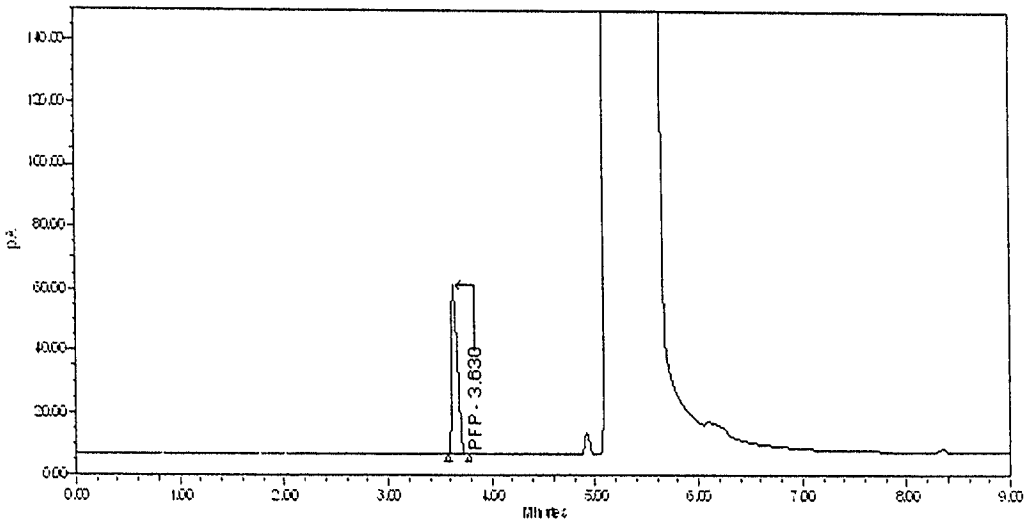


Figure 2: 235 ug/mL PFP standard; ~ 1 ug injected

PUBLIC COPY

APPENDIX A: Validation of BMSIHL 3.35.0

This Appendix summarizes the results obtained per the SOP, "Minimum Validation and the Determination of the Reporting limit (RL) of a BMSIHL Industrial Hygiene Sampling and Analysis Method."

A.1.0 Desorption efficiency (**DE**)

A.1.1 Preparation of PFP spiked charcoal

The two sections of SKC 226-09 were combined in an eight-mL vial. The front glass wool and middle and back foam plugs were disposed of. Each vial contained 600 mg of charcoal. Three charcoal samples at each of six levels were spiked. Three blanks were included in the set. All vials were capped within five minutes of spiking and then placed in the freezer at -30° C until analyzed according to the procedures described in this method.

A.1.2 The results of the **DE** determinations are listed in Table A.1.2. The **DE** of each of the first 6 rows is the average fraction, amount recovered/spike, for the three spikes at the respective level. The last row (n = 18) is the average of the six levels and is used for the **DE** in the calculations of section and 7.1.2. SD is the standard deviation for the **DE**s of the three samples per spike level. For the n = 18 row, SD is the pooled SD.

TABLE A.1.2: DE for PFP

# SAMPLES	SPIKE (ug)	**DE**	±SD
n = 3	124	1.58	0.06
n = 3	310	1.30	0.06
n = 3	830	1.04	0.03
n = 3	1660	1.0	0.02
n = 3	5450	0.93	0.03
n = 3	10900	1.04	0.08
n = 18	xxx	1.15	0.23

Actual DE used in method is 1.0.

A.2.0 Storage stability (**SS**)

A.2.1 Preparation of PFP spiked charcoal tubes

The tips were clipped off SKC 226-09 charcoal tubes and a solution of PFP in MECL2 was spiked onto the front charcoal section of each tube. Three tubes at each of five levels were spiked. The tubes were immediately capped, allowed to stand at ambient temperature for 48 hrs and then stored in a freezer at -30 C for 72 days, after which the samples were analyzed per this method.

A.2.2 The recoveries are given in Table A.2.2

Table A.2.2: SS for PFP on Charcoal

# Samples	Spike (ug)	SS	±SD
n = 3	310	1.32	0.01
n = 3	915	1.09	0.03
n = 3	1363	1.03	0.02
n = 3	5450	0.96	0.01
n = 3	10900	0.91	0.05
n = 15	xxx	1.06	0.15

A.3.0 Retention efficiency (**RE**)

A.3.1 Preparation of spiked SKC 226-09 charcoal tubes

SKC 226-09 charcoal tubes were spiked as described in A.2.1, except for the two highest levels listed in Table A.3.3. For these two sets, neat PFP was spiked onto the charcoal and the amount of the spike measured gravimetrically by taring the charcoal tube and weighing after spiking.

A.3.2 Exposure of the PFP spiked charcoal tubes

Each spiked tube was connected to a manifold with each port set to draw 50 room

air at 50 mL/min. A total volume of 10 L was drawn through each tube. The room air was at 50% RH. After completion, the tubes were capped at both ends and place in the freezer at -30° C until analyzed per this method.

A.3.3 The results of the recoveries for each spike level are listed in Tables A.3.3.

Table A.3.3: RE for PFP on Charcoal

# Samples	Spike (ug)	**RE**	±SD
n = 3	136	1.34	0.25
n = 3	333	1.15	0.08
n = 3	665	0.70	0.05
n = 3	1510	1.01	0.02
n = 3	7000	1.01	0.02
n = 3	15100	1.05	0. 02
n = 18	xxx	0.84	0.147

A.3.0 Reporting Limit (**RL**)

A.3.1 The **RL** as defined by the BMSIHL SOP on method validation and **RL** determination is the lowest mass for which acceptable **DE, SS** and **RE** values are obtained.

A.3.2 Based on the data from the above tables, the **RL** for PFP is rounded to100 ug/sample.

Hardcopies are uncontrolled. Official copy is on-line.

BMSIHL 3.53.0

Determination of Airborne Pentafluoropropane by Sampling on Charcoal tube and Analysis by Capillary gas chromatogaphy with FID Detection

Written by: _____ 6/1/09 Date

Reviewed By: _____ 6/1/09 Date

Method status: _X_ Interim _____ Final

Revision: Original Supersedes: None

Disclaimer: While Bayer MaterialScience believes that the data contained herein is factual, the data is not to be taken as a warranty or representation for which Bayer Corp. assumes legal responsibility. It is offered solely for your consideration, investigation and verification.

PUBLIC COPY