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A Thesis

by

JOHN LEE BELL, JR.

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 1994

Major Subject: Industrial Hygiene

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May 1994

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ABSTRACT

Evaluation of the OSHA 42 and NIOSH 5521 Methods in
Determining the Free Isocyanate Concentration in Aerosols
and Vapor Phases During Application of Two Component
1,6-Hexamethylene Diisocyanate Paints. (May 1994)

John Lee Bell, Jr., B.S., Southern Illinois University
Chair of Advisory Committee: Dr. James C. Rock

When sampling for isocyanates, the two currently recommended methods (OSHA 42 and NIOSH 5521) have limitations that cause under estimation of the isocyanate concentration reported.

During spray painting operations, isocyanate is present in both aerosol and vapor forms. When the NIOSH method is used the midget impinger inlet and outlet nozzles tend to plug as paint particles collect there during sampling. As the outlet nozzle opening becomes smaller, the velocity of the sampling stream increases causing particles to pass through the derivatizing agent without capture. Both phenomena result in underestimation of aerosol content of the sampled air. In the OSHA method,

particles adhere to the surface of the glass fiber filter as seen in Scanning Electron Microscope photographs. The presence of these particles reduce the effectiveness of solid sampling media such as glass fiber filters in sampling for aerosol isocyanates since only limited contact between the derivatizing agent and the aerosol particles collected on the filter surface occurs. Once the outer surface of the isocyanate particle is polymerized, the derivatizing agent cannot break the bonds in order to form urea.

When sampling for vapors, the OSHA and NIOSH methods are equally effective. Using a Fourier Transform Infrared Spectrometer reaction rates between isocyanates and the derivatizing agent for the OSHA method were studied. Although usually considered instantaneous, this study showed that these reactions took as long as several hours to go to completion. During this time isocyanate evaporation into the air flow is occurring. In both methods, as much as five percent of the isocyanates are lost due to slow reactions and/or sampling media break through.

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This thesis reflects the culmination of over twelve months of studying, writing, investigating, collecting, and learning. Through it all, one professor has consistently been there as my mentor, even before I had asked him to be. Dr. James C. Rock deserves my sincere thanks since he is also a retired Colonel from the same career field as mine in the Air Force, he has been able to help me on my career options also. I also wish to thank my other committee members and advisor, Dr. W. Wilson Pitt, Jr., Dr. Dwight C. Conway, and Dr. Walter E. Rudzinski for their insightful assistance and advice.

One very special individual who I would especially like to recognize is my beautiful and unselfish wife, Sherrie. For without her continued strength, determination, and encouragement I could not have finished this thesis ahead of time. There are many more organizations and individuals which contributed to this thesis, however none is more important than the good Lord above. They all deserve my thanks and gratitude.

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INTRODUCTION

Isocyanates are increasingly used as the base ingredient for many polyurethane plastics such as foams, coatings, adhesives, rubber and fibers[1]. Toluene -2,4-diisocyanate (TDI) CAS number 584-84-9, 1,6-hexamethylene diisocyanate (HDI) CAS number 28182-81-2, as well as 4,4' diphenylmethane diisocyanate (MDI) CAS number 101-68-8, are all currently used as key ingredients in polyurethane manufacturing. Because of the excellent physical characteristics that isocyanates provide, they and other polymers will be around for a long time to come. Even though isocyanates have been used since 1937, there are physical properties and health concerns which still need to be addressed. For this thesis project, only HDI was studied.

Isocyanates are chemicals containing -NCO functional groups. Mono, di, and poly are terms used to describe the chemical shape of the isocyanate molecule. The -NCO portion of the isocyanate molecule is the hazardous portion of the chemical. A monomer is the basic building block

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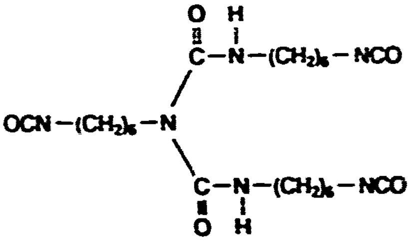
Style and format from <u>American Industrial Hygiene Association.</u>

building block of the HDI molecule and a trimer is three monomers tied together. Biuret of HDI is three molecules of HDI linked in such a way that the molecule has three active (-NCO) groups. The following are two of the different HDI molecules used.

Biuret of HDI:



HDI: $OCN\text{-}(CH_2)_6\text{-}NCO$

The electronic structure of the isocyanate group clearly shows the electrophilic character of the central carbon atom. By initiating an attack on the carbon atom, isocyanates are formed. The three main reactions used in isocyanate analysis are based on acid hydrolysis to an amine, addition of primary or secondary amines to form ureas and addition of alcohols to form urethanes.[2] The rates of reaction depend largely on the carbon atom and the density of the active hydrogen-containing element. During this reaction, any unreacted -NCO group is known as free isocyanate. After complete polymerization, the resulting polymers are no longer reactive and considered safe.

The current Threshold Limit Value for HDI, set by the American Conference of Governmental Industrial Hygienist is 0.005 parts per million (ppm) or 0.034 milligrams per meter cubed (mg/m^3).[3] The National Institute for Occupational Safety and Health (NIOSH) has a general recommendation of 0.005 ppm, time weighted average (TWA) and a ceiling of 0.02 ppm for all diisocyanates.

Numerous studies indicate that up to 5 percent of the population are sensitive to diisocyanates and react to exposure levels much lower than currently recommended.(2) In several studies, it has been noted that after being sensitized to one isocyanate, a person might be sensitive to other isocyanates without previous exposure to that chemical.

As reported in 1985 by Purnell and Walker, it is widely accepted that isocyanates present a health hazard.(2) However, there is still discussion as to what levels constitute safe working levels for isocyanates. Some believe that any reactive isocyanate reacts with molecules in the lungs once deposited. However, considerable controversy continues over what causes the sensitization. Both allergenic (immunological) and pharmacological mechanisms have been suggested.

Reported research has found aerosol particles for MDI and TDI in laboratory settings generally ranged from 0.01 to 2.0 microns in size. About 80% of the particles of MDI foam in a static atmosphere were between 0.34 and 1.9 microns.[4] However, Dharmarajan found particle mass median aerodynamic diameter (MMAD) of 11.0 microns in an MDI foam spray operation.[4] Rudzinski theorized that the key parameter in determining the amount of free isocyanate found in air could be the time between mixing the two part polyurethane components and spray painting application.[5] Because of the wide range of aerosol diameters reported and the inability to accurately sample for aerosols, many companies which apply polyurethane by spraying have required their workers to wear in-line respirators instead of filter respirators to ensure their health and safety.

According to Williamson and Munn, toluene diisocyanate (TDI) and 1,6-hexamethylene diisocyanate (HDI) were the most widely used isocyanates during the early stages of development.[6,7] Potential health problems with isocyanates were documented as early as 1941 with respiratory problems appearing during animal studies. Gross and Hellrung, as reported by Friebel and Lunchtrach, investigated the toxicity of TDI in dogs, cats, rabbits and guinea pigs.[8] At lower concentrations, irritation of the respiratory tract occurred and at higher concentrations, bronchitis, pneumonia and pulmonary edema have all been documented. The most severe problem with isocyanates is that some individuals are, or become extremely sensitive to very small amounts and suffer life threatening asthma-like symptoms upon repeat exposures.

A primary industrial hygiene question remains, are we accurately estimating the levels of isocyanates in the air or are we underestimating them? Are we underestimating isocyanates because of sampling or because the reactions between the derivatizing agent and the isocyanates are too slow to effectively collect all of the isocyanates passing through the sampling media? Wu, Stoyanoff and Gaind reported that the relative reaction rate for 1-(2-pyridyl) -piperazine was 49 and 100 for 1-(2-methoxyphenyl) -piperazine.[9]

The main purpose of this thesis was to evaluate the current OSHA 42 and NIOSH 5521 methods in order to determine their limitations and to determine if there were differences in the amount of free isocyanate concentration measured for vapor phases of 1,6-hexamethylene diisocyanates. I also wanted to try and shed some light on limitations on both methods which depend on whether you are sampling vapors or aerosols. Operations at an Air Force Base which uses polyurethane paints result in both aerosol and vapor exposures. Thus, both aerosol sampling from spray paint operations and vapor phase sampling from mixing and clean up operations were conducted under typical controlled industrial exposure conditions in a spray paint booth at Kelly Air Force Base (AFB) in San Antonio, Texas. Reaction rates for the polyurethane and urea reactions were determined using a Fourier Transform Infrared Spectrometer (FTIR) in the Chemistry Department at Texas A&M University. Also, a study was conducted at Kelly AFB, TX in order to determine the mass median aerodynamic diameter (MMAD) in a typical spray paint application. This research sheds new light on the two current methods, suggesting reasons why solid filter collection methods underestimate aerosol concentrations, mass median aerodynamic diameter and reaction rate comparisons using the FTIR.

METHODS

Aerosol and Vapor Sampling

The current NIOSH recommended method for the sampling of HDI isocyanate aerosols and vapors is NIOSH Method 5521 which uses a midget impinger and 1-(2-methoxyphenyl) -piperazine in toluene as the derivatizing agent.[10] The concentration of 1-(2-methoxyphenyl)-piperazine in toluene is 43 milligrams per liter (mg/L). Using a personal sampling pump with the midget impinger in line, the flow is calibrated for 1.0 liter per minute (lpm). Fifteen milliliters (ml) of the sampling medium are transferred into the impinger. After sampling for 15 minutes, the contents were transferred to a 40 ml glass vial for shipment. The impinger parts were rinsed using 2 ml of toluene and added to the sample. The samples were prepared for analysis by adding 25 microliters (ul) acetic anhydride to the sample. The sample is then evaporated to dryness under a stream of nitrogen while warming the sample to 60° C on a hot plate. The residue is then redissolved in 5.0 ml of methanol and agitated in an ultrasonic water bath for 15 minutes. The sample is then analyzed for the isocyanate derivative (urea) using High Performance Liquid

Chromatography (HPLC). This method utilizes both ultraviolet and electrochemical detectors to determine the concentration of isocyanate derivative (urea). The HPLC is set up for operation using the detailed procedures in Appendix A. The HPLC configurations for the NIOSH method are detailed in Appendix B. A calibration curve is used in order to determine the concentration of HDI present in the sample. See Figure 1 for this curve.

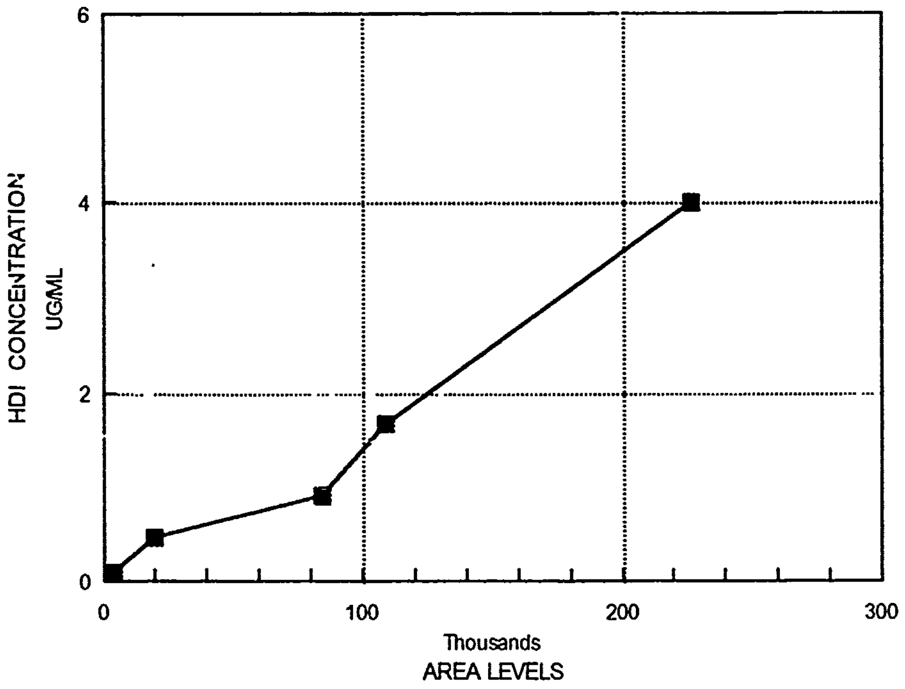


Figure 1: Calibration Curve for the NIOSH Method.

The OSHA Method 42 uses a glass fiber filter coated with 0.1 mg of 1-(2-pyridyl)-piperazine (1-2PP).[11] The filters were coated by preparing a solution of 0.2 mg/ml of 1-2PP in methylene chloride and applying 0.5 ml of the solution to the glass fiber filters. The filters were then allowed to dry (desorb) for 30 minutes in order to remove any residual methylene chloride and then placed into three piece cassettes with a backup pad. Samples were taken using a personal sampling pump with a calibrated flow rate of 1 lpm for 15 minutes in the open face condition. After sampling, the filters were placed into glass vials. Two ml of 90/10 acetonitrile and DMSO solution was added to each sample and then capped. The vial was shaken to ensure complete mixing and to remove air bubbles. After one hour the solutions were filtered and placed in two ml sampler vials. The sample is then analyzed for the isocyanate derivative (urea) using High Performance Liquid Chromatography (HPLC). This method utilizes only the ultraviolet detector to determine the concentration of isocyanate derivative (urea). The HPLC is set up for operation using the detailed procedures in Appendix A. The HPLC configurations for the OSHA method are detailed in

Appendix C. A calibration curve is used in order to determine the concentration of HDI present in the sample. See Figure 2 for this curve.

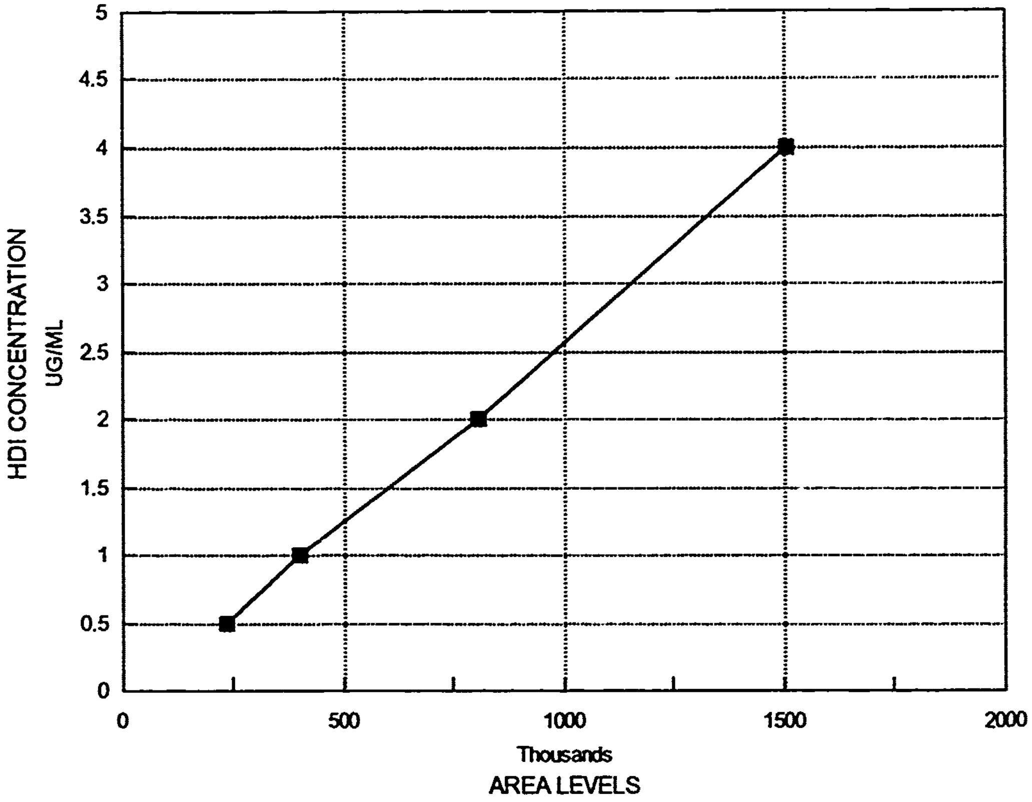


Figure 2: Calibration Curve for the OSHA Method.

Side-by-side air samples for both the NIOSH and OSHA methods were taken during static spray painting operations. A high volume - low pressure Sato Jet sprayer was used with a 10 NK sprayer nozzle attached and 20 pounds air pressure applied. Camouflage polyurethane paint from Deft, Inc. was used during this sampling. Both the OSHA and NIOSH samplers were set approximately two feet from the sprayer and 20 degrees from the center of the over-spray area. No part was being painted during the sampling process. The sampling pumps were set at 1 liter per minute and sampling lasted for 15 minutes. During this sampling, the samplers and sprayer were set up in one spot and not moved. The results of this sampling showed that the OSHA method reported "None Detected", which is < 1.0 ug HDI/ml, while the NIOSH method showed a level of 4.64 ug HDI/ml.

Since the OSHA method was unable to give me any data to compare, I further analyzed the process by which particulates are collected on a glass fiber filter. I wanted to determine why the aerosol particulates did not react to completion once they were collected on the filter.

NIOSH Method 5521 And Aerosol Collection

Next, I looked at the NIOSH method 5521 to see why it might underestimate the isocyanate levels when sampling aerosol particles. For this study, I used Spill-Proof Midget Impingers, manufactured by the Gilian Instruments

Corporation. The sampling flow rate was again set for 1.0 liter per minute and the total sampling time was 15 minutes. Two personal air samples were taken while white polyurethane paint was being sprayed. The total sampling time for the two samples was 30 minutes. Photographs were taken of the midget impinger in order to identify areas were polyurethane paints may have polymerized instead of being derivatized by the solution. These photographs can be seen in figures 3a through 3d.

OSHA Method 42 And Aerosol Collection

To do this study, I used a Amray 1820 Scanning Electron Microscope (SEM) which is located at Brooks AFB, Texas. This microscope has the ability to look at very small particles after they are collected on the filter. Also, used during this study was a Tracor Northern Elemental Analyzer called the Series II X-Ray Analyzer. This instrument has the ability to analyze individual particles under view in the Scanning Electron Microscope. See table 1 for the percent by weight of the elements detected.

The OSHA 42 method was used to prepare the glass fiber filters. An SKC sampling pump was calibrated for 1.0 lpm. To ensure individual particles could be seen, the sampling flow rate was reduced to 1.0 lpm and the sampling time was set for only two minutes. Again, the same sprayer was used with the same angle and distance as in the previous air sampling. Once the sampling was completed, the filters were desiccated using silica gel for 24 hours. This was done to remove any remaining vapors and volatile liquid which may have been on the filters after sampling. Volatile vapors could damage the lenses used in the SEM. Next, a small section of the filter was removed and mounted on a stud. Finally, the stud and sample are gold platted with 10 nanometers of gold using a Anatech LTD Hummer VI Sputtering System. The stud and sample are then inserted into the SEM and a vacuum is applied. The resulting photographs are shown in figures 5a through 5d.

Untreated Filter Collection Of Aerosols

Next, I wanted to verify that what I saw in the above photographs was from the polymerization of the isocyanates and not the reaction between the 1-(2-pyridyl)-piperazine.

This was accomplished by collecting aerosol particles on untreated glass fiber filters. The same sampling pump, sampling flow rate and sampling time of two minutes was again used. In Figures 6a through 6d you will observe polyurethane paint aerosols which were collected on untreated glass fiber filters and pictures were taken using the Scanning Electron Microscope.

Vapor Sampling Using OSHA 42 And NIOSH 5521

The next part of my thesis looked at both the NIOSH 5521 and OSHA 42 methods to see if there was in fact a significant difference in the amount of free isocyanate concentrations reported while sampling vapor. The sampling rates were again set at 1 liter per minute for a sampling time of 15 minutes. Side-by-side samples were taken from the head space of a one gallon isocyanate paint hardener can and analyzed using HPLC as listed for the aerosol sampling. The same hardener can was used each time with only two minutes allowed time between samples. A total of seven samples for each method were taken. The total volume of air drawn through the headspace of the hardener can was 30 liters for each set of samples. The samplers were taped into place to ensure the same sampler location each time. The can lid was partially installed while the samples were taken. This would ensure large air currents coming into the spray paint booth would not bias the measurements. Table 2 Shows the results of these side-by-side sampling measurements.

Dual OSHA 42 Glass Fiber Filters In-Line For Vapors

After concluding that the OSHA 42 method was as effective as the NIOSH 5521 method I wanted to determine if all of the isocyanate vapor was being captured in the glass fiber filter. For this I calibrated a sampling flow pump for 2 liters per minute with two glass fiber filters placed in line. After assembling the sampling train so that two treated glass fiber filters were in line I sampled the head space of an isocyanate paint hardener can. The sampling time was 30 minutes and the can lid was again placed on top while the sampling was in process. Air was still able to be freely be drawn into the can at a flow rate of 1 liter per minute through the half inch gap created by the sample tube.

Polyurethane Paint Reaction Rates

For this portion of my thesis, I looked at the reaction rates of polyurethane paints derivatizing to urea. Using an Fourier Transform Infrared Spectrometer (FTIR) I was able to view the transmittance through the chemical droplets and make comparisons for several days.

In viewing the Stadler Index for spectra of isocyanates, I discovered that isocyanates have an absorbance peak between 2000 to 2500 frequency $(cm)^{-1}$. In order to view such a highly reactive substance as polyurethane, I needed a material which did not absorb light in this region of the spectrum. After some searching I discovered that polyethylene sheeting did not absorb in this region and would be acceptable for this study.

Particle Size Distribution

The final area of my thesis addressed part of a question posed in the paper by Dr Dharmarajan et al, that is to determine the particle size distribution of a typical spray operation in the field. For this investigation, I used a Grasby-Andersen 8 stage cascade impactor with teflon filters. All of the filters were preweighted each morning prior to use. The impactor was attached to a sampling pump and calibrated for a flow of 2 liters per minute. The sampling times were for 15 and 21 minutes. The samplers were worn by the same individual during two different spraying operations of an airplane. See Table 3 for the Series 290 Impactor cut-points at 2 lpm.

RESULTS AND DISCUSSION

To determine why the NIOSH method may underestimate the isocyanate concentrations, photographs of a midget impinger taken after sampling were evaluated. Figure 3a shows the complete assembled midget impinger. This photo gives a good idea of the location of various parts identified in later photos. In the photograph of the inlet portion of the midget impinger, Figure 3b, visible evidence of polyurethane paint deposits are shown. The reason for the distinct line which was formed by the paint is unknown. A photo of the discharge outlet of the midget impinger is shown in Figure 3c. Again, visible signs of paint are present. The outlet diameter showed signs of closing. Finally, Figure 3d shows two distinct locations where the outlet air flow from the discharge tube struck the side of the midget impinger and polymerized there. The location of these paint spots are below the surface of the derivatizing agent. The polyurethane paints should not have polymerized on the glass if they had been derivatized by the solution.

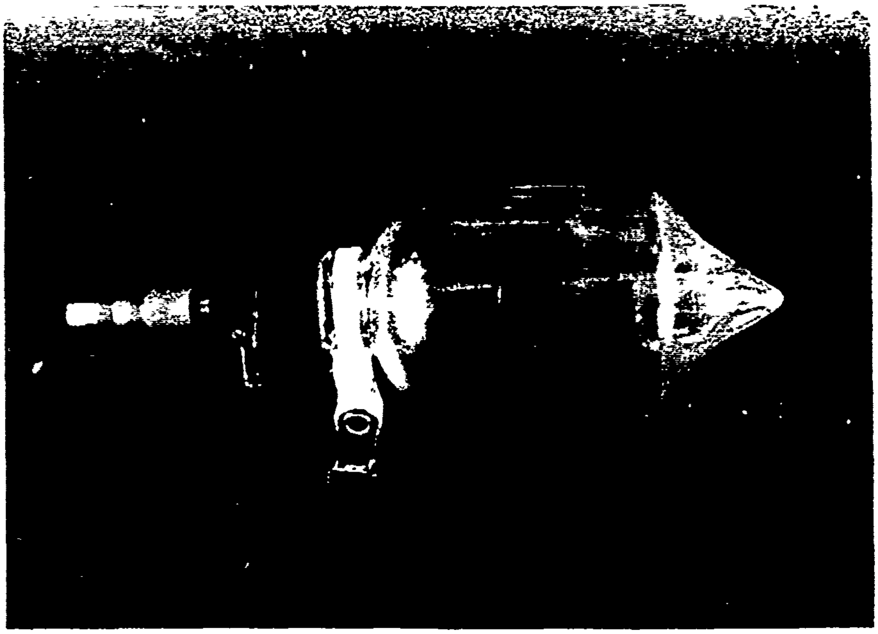


Figure 3a: Photograph of Midget Impinger. Midget impinger used in sampling aerosol particles for the NIOSH method.

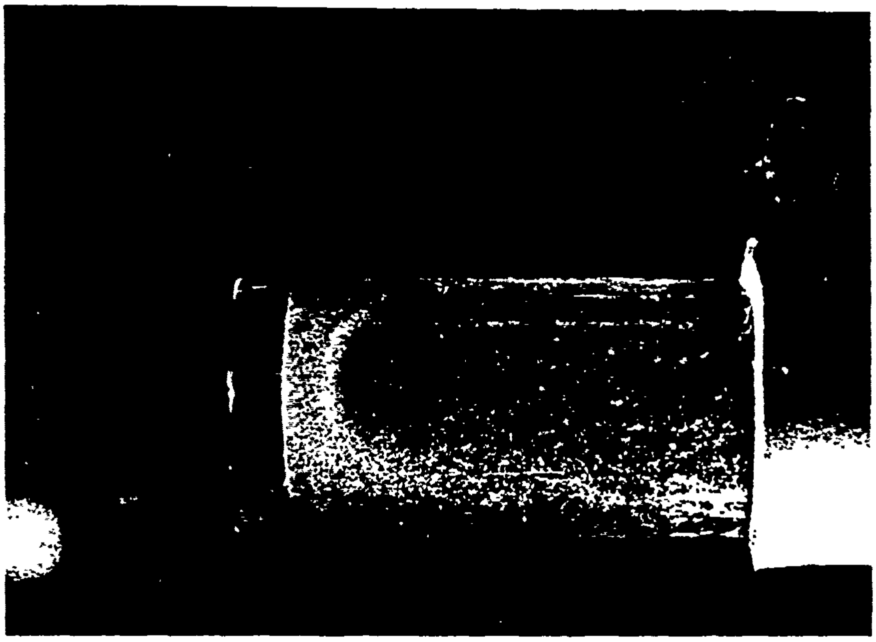


Figure 3b: Photograph of Midget Impinger Inlet Nozzle. Midget impinger inlet nozzle with visible signs of polyurethane paint deposits.

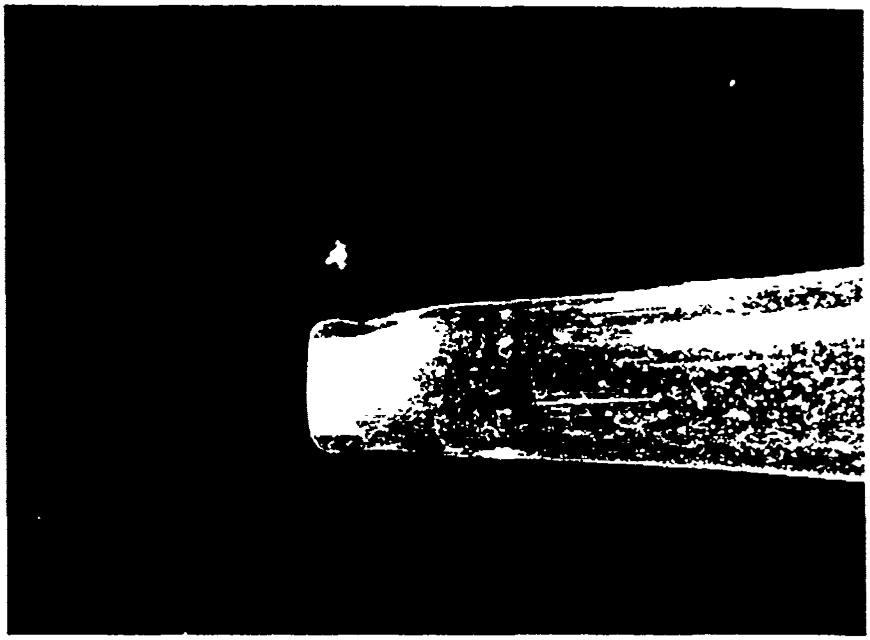


Figure 3c: Photograph of Midget Impinger Outlet Nozzle. Midget impinger outlet nozzle with visible signs of polyurethane paint deposits which reduce the opening and accelerate the air flow.

Figure 3d: Photograph of the Bottom of the Midget Impinger. Bottom portion of midget impinger where the aerosols strike polymerize after exiting the outlet nozzle.

Since it appeared that polymerization was continuing while the aerosol particles were in the solution, I decided to look for one of these particles and view it with the Scanning Electron Microscope. I sampled a polyurethane spray painting operation for 15 minutes using the protocol called for in the NIOSH 5521 method. The sampler was again calibrated at 1.0 liters per minute. After collecting the sample the solution was filtered using a 0.5 micron glass fiber filter and funnel. The filter was then desiccated for 24 hours using a silica gel desiccator. A piece from the center of the filter was mounted on a sampling stud and coated with gold as described earlier.

Upon viewing the sample, only a few particles could be seen. The texture and shape of the particle was visibly altered. Figure 4 is a picture of one of these particles. By using the Series II X-Ray Analyzer attached to the microscope I was able to determine that this was indeed a polyurethane particle. Apparently, once the outside of a polyurethane particle has polymerized, the derivatizing agent has very little effect in stopping or changing the reaction.

Figure 4: Particle Collected in Midget Impinger. Polyurethane particle, >10 micron, collected in the midget impinger derivatizing agent and filtered on an untreated glass fiber filter and viewed by SEM at 3120 power.

With the Amray 1820 Scanning Electron Microscope, I was able to observe the following results from the photographs. The surface of the treated glass fiber filter is shown at 133X in Figure 5a. Some of the particles appear to be spheres, while in other cases large masses of particles are agglomerated. Many of the agglomerates are larger than 100 microns in size. Figure 5b shows a 4.9 micron particle collected on a treated glass fiber filter. As you can see only a small portion of the particle is actually in contact with any of the fibers which were treated with 1-(2-pyridyl)-piperazine. I feel that this limited contact with the treated fibers is the reason why the filter methods have failed in the past to be effective in sampling aerosol particles. One observation made during this portion of my study was that I never saw any particles, even ones less than 1 micron, within the body of the filter. If smaller particles were in the matrix then better contact with the derivatizing agent would reflect higher concentrations of isocyanates. A cross-section of this same filter was viewed with the SEM (Fig. 5c). In this photo I could not find any particles in the body of the filter. Although the entire cross section was scanned, not a single particle below the outer surface of the filter was found. One interesting particle was noted while viewing this filter. In Figure 5d you can see a close up of a 11.2 micron aerosol particle. The interesting parts of this photo are the bubbles which are apparent on the outer surface. As polyurethane paints react and polymerize, carbon dioxide is given off during the reaction. The polymerization occurs from the outside inward. So, even though outside is polymerized, the inside can actually still be reacting. I feel this is the actual curing process as viewed in an individual particle. The small white specks on the surface of this particle is from the gold platting process described earlier.

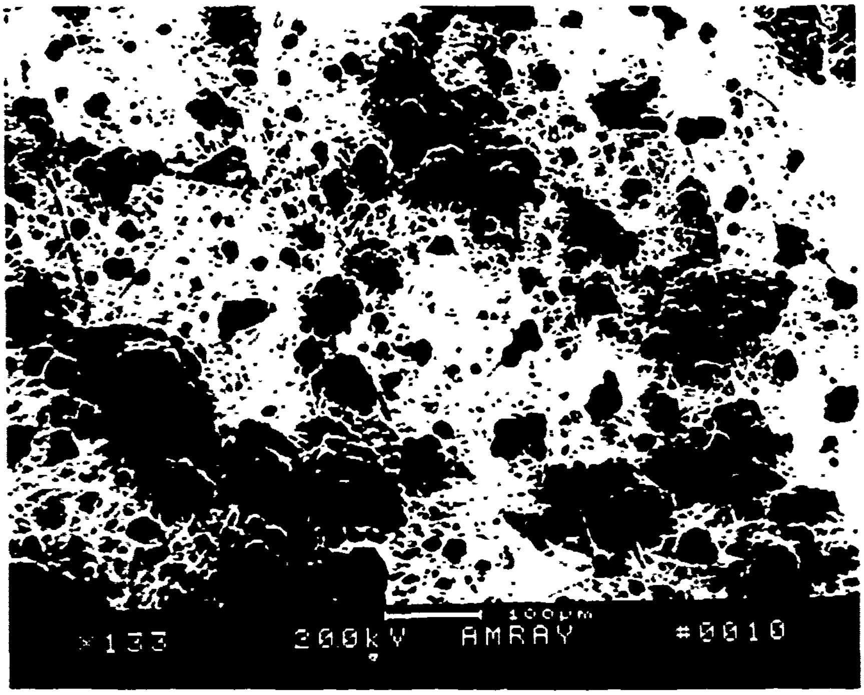


Figure 5a: Polyurethane Particles on Treated Filter. This photograph was taken using a Scanning Electron Microscope at 133 power.

Figure 5b: Polyurethane Particle (4.9 micron) on Treated Glass Fiber Filter.

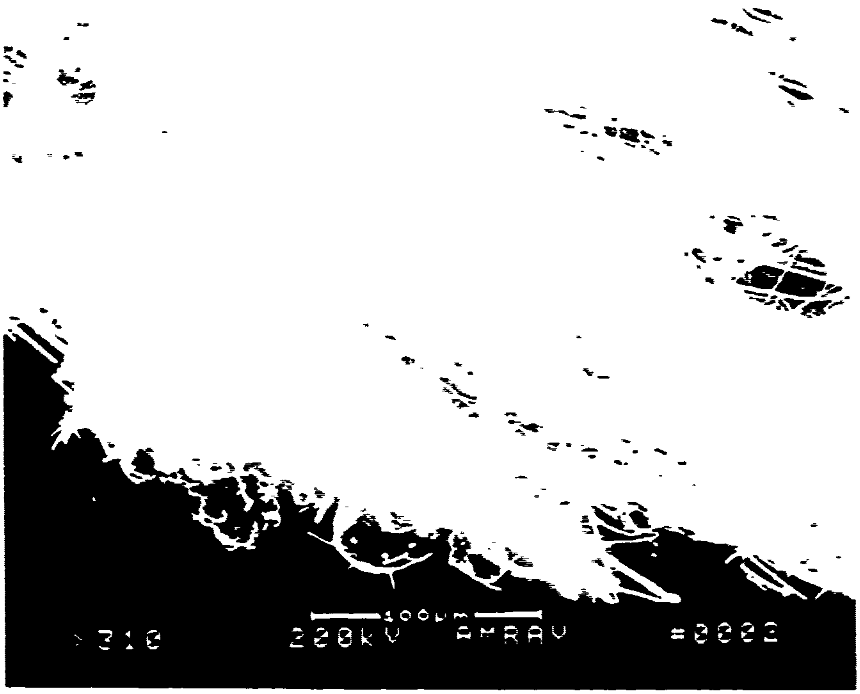


Figure 5c: Side Photograph of Polyurethane Particles. These partilces were collected on the surface of a treated glass fiber filter at 310 power and viewed using SEM.

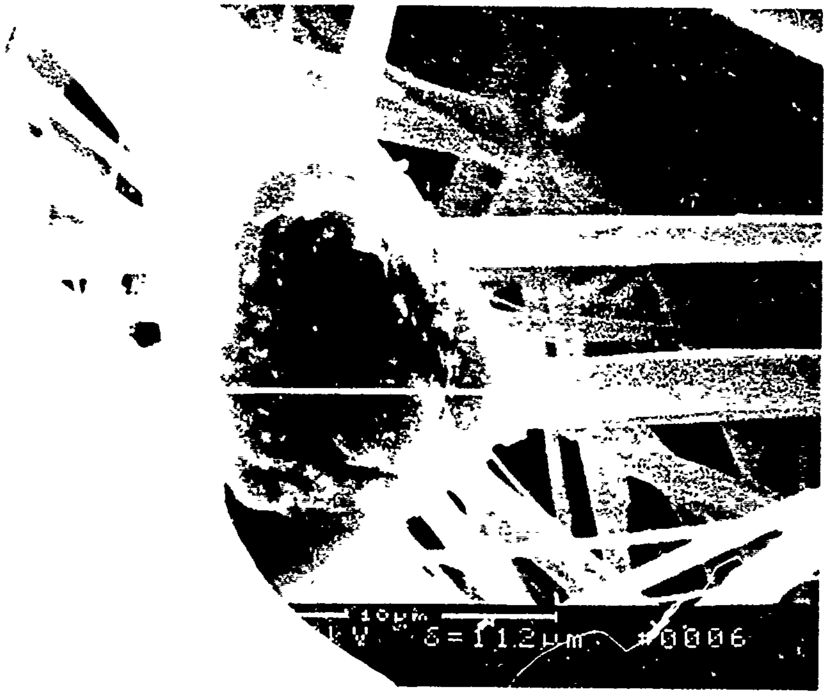


Figure 5d: Polyurethane Particle (11.2 micron) on Treated Glass Fiber Filter. This photograph shows carbon dioxide gas bubbles present after being generated and released from the inside.

Figure 6a is a photograph of this untreated glass fiber filter at 144 power. Again, there are large masses of aerosol particles which are grouped together. Some of the particles are spherical and some are distorted shapes with various sizes. It is apparent that all of the particles are again attached to the outer surface and fibers. Figure 6b shows a close up (560X) of one of the agglomerates on the untreated filter. This agglomerate is over 100 microns in diameter. Note in each of these photographs that the large and small particles appear only on the top layer of the filter. In Figure 6c shows a previously polymerized spherical 10 micron particle along with another particle which polymerized after attaching itself to several of the glass fiber filters. A particle observed on the filter and analyzed using X-Ray defraction is shown in Figure 6d.

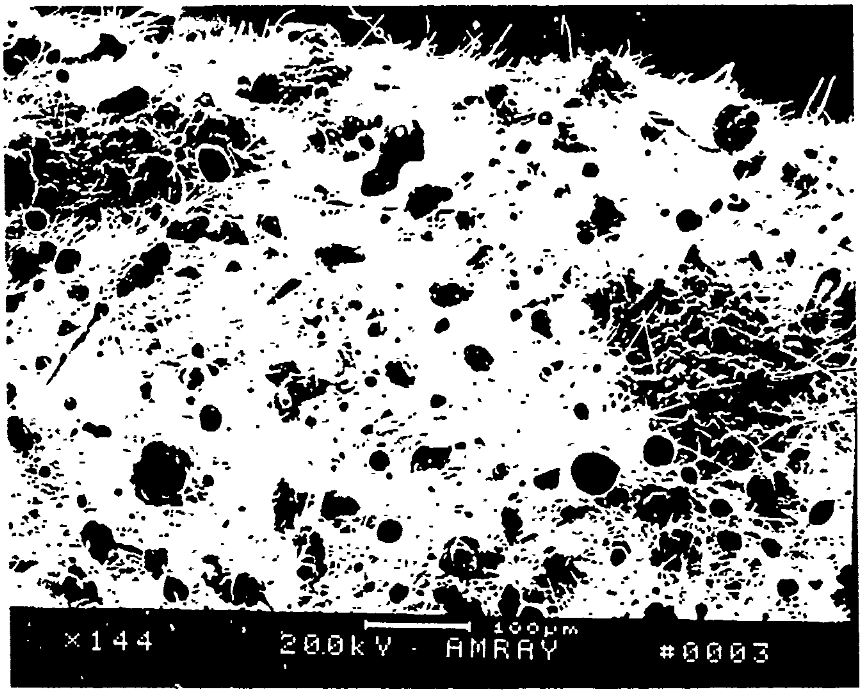


Figure 6a: Polyurethane Particles on Untreated Glass Fiber Filter.

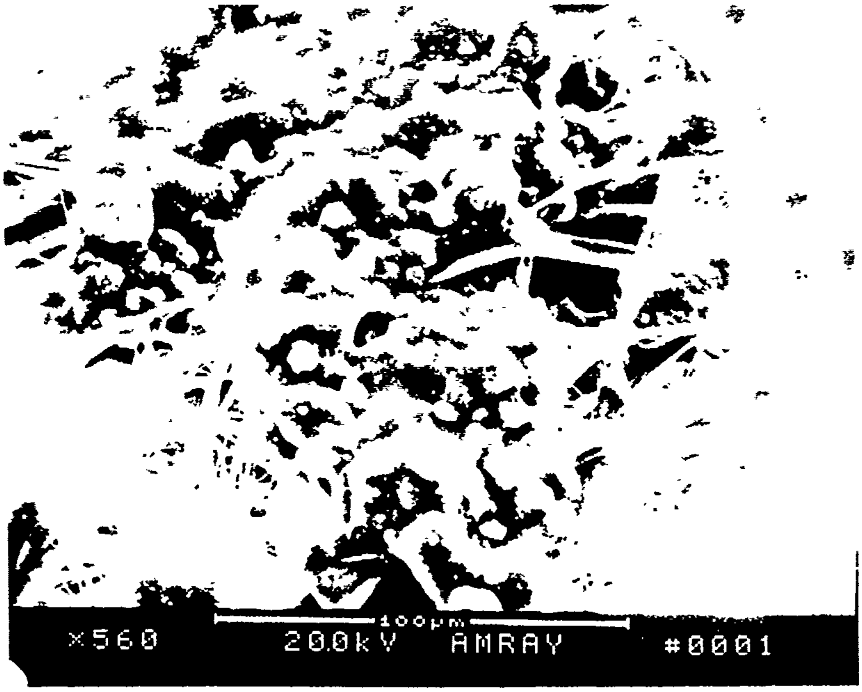


Figure 6b: Polyurethane Particle (100 microns) on Untreated Glass Fiber Filter.

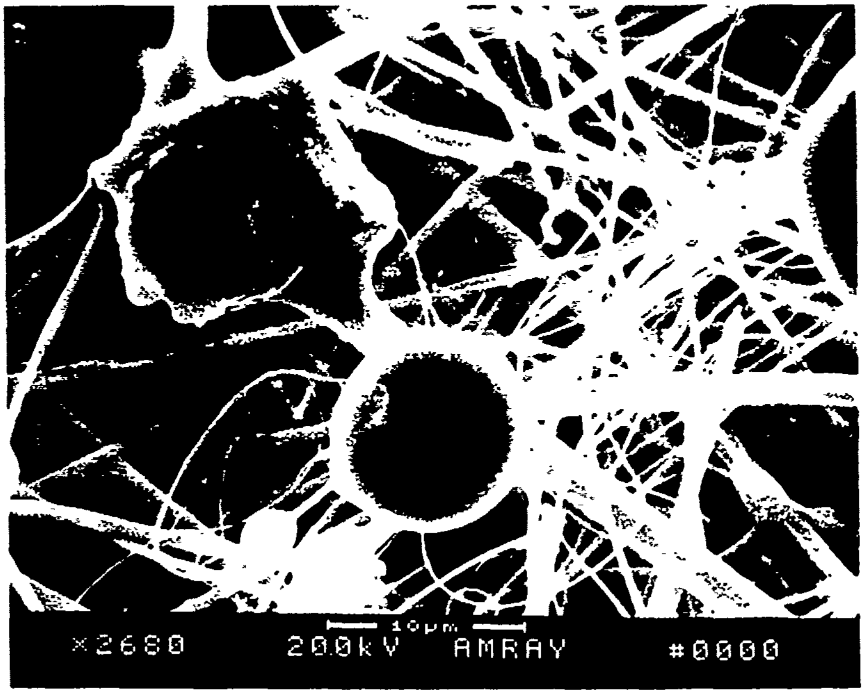


Figure 6c: Spherical (10 micron) and Irregular Shaped Particles. These particles were collected on untreated glass fiber filters and viewed by SEM at 2680 power.

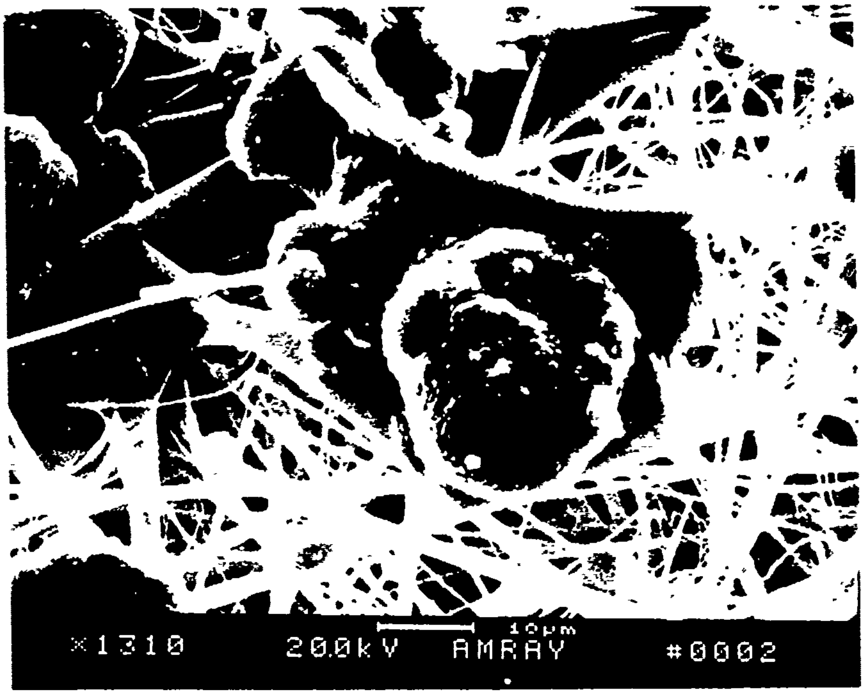


Figure 6d: Polyurethane Particles Used in X-Ray Defraction Analysis. This particle was collected on untreated glass fiber filters and analyzed using X-Ray defraction in order to verify it was a paint particle.

Using the Series II X-Ray Analyzer, I was able to analyze this particle and determine the elements it contained. Table 1 lists all the elements present in the particle that the X-Ray Analyzer can quantify by weight percent. Figure 7 shows the complete spectrum analyzed by the analyzer. The abbreviation of TI is for titanium which is present in polyurethane paints to enhance the pigmentation. Also, SI is for silica which is present and is used as a thickening agent and alternative paint whitening agent. This form of silica is noncrystalline and relatively harmless in the paint mixture.

Table 1. Percent by Weight of Listed Elements.

Element	Percent By Weight
Si	75.35
Mg	0.67
Fe	5.42
Ca	1.24
Mn	0.57
Na	2.84
S	9.64
Cl	0.10
K	0.91
Al	3.26

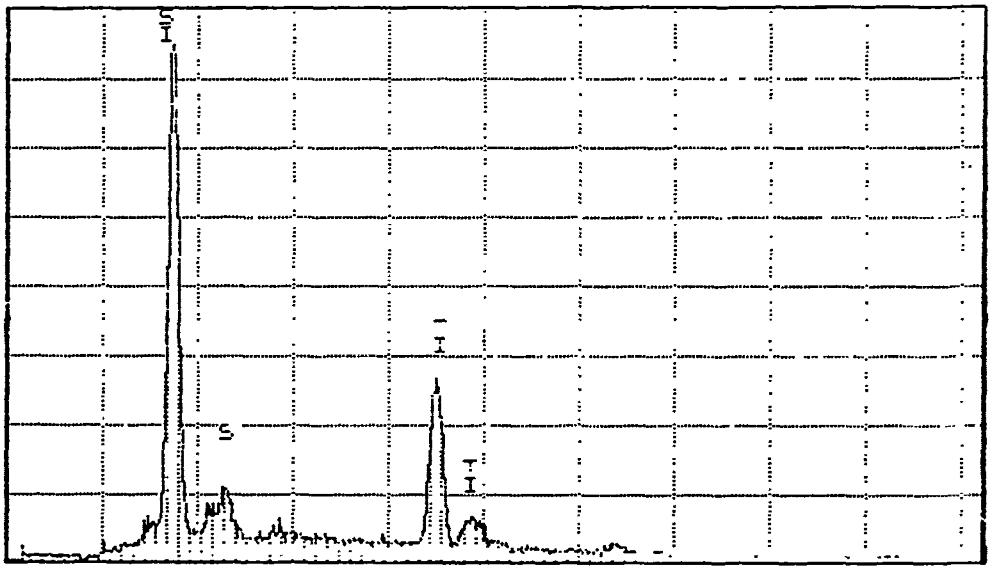


Figure 7: X-Ray Defraction Analyzer Spectrograph.

The results of performing side-by-side vapor sampling using both the OSHA and NIOSH methods are in Table 2. All measurements are reported in micrograms per cubic meter (ug/m^3).

Table 2. Side by Side Vapor Sampling Results.

Sample #	NIOSH 5521 Method (ug/m3)	OSHA 42 Method	Time Length From Start (min)
1	0.507	0.537	0
2	0.374	0.538	19
3	0.561	0.421	37
4	0.791	0.474	55
5	0.547	0.440	72
6	0.769	0.366	90
7	0.324	0.302	107

By using the statistical package SAS I compared the two data sets using a paired t-test. The results revealed a P-value of .17 which means that the values are not significantly different at the 17 percent level.

While running some of the analysis it was apparent that the OSHA 42 method has a much easier sample preparation method than the NIOSH 5521. All seven samples of the OSHA 42 method were prepared in one hour and fifteen minutes. However, preparation of each sample for the NIOSH 5521 method took more than 45 minutes. It took approximately 20 minutes to heat and blow dry the sample. Adding methanol and sonic mixing took another 15 minutes. Another 10 minutes were needed to prepare the sample vials, crimp the samples and allow the heated containers to cool off before adding methanol. This is an observation I felt affects the accurate reporting of isocyanate concentrations. Since the shelf life for the NIOSH 5521 method is only seven days, it is difficult for analysts to prepare and analyze all the samples in the appropriate amount of time.

The results of the dual OSHA filters showed that the first sampler did in fact allow some of the isocyanates go through its filter and were collected on the second filter. On the first filter, I collected an isocyanate concentration of 1.25 microgram per cubic meter and on the second filter I collected 0.07 micrograms per cubic meter. This amounts to a 5.3 percent loss in total free isocyanates. There are three reasons why this might have occurred. The first one is due to the complete saturation of the first filter. The second reason could have been because the reaction between the derivatizing agent and the isocyanates were too slow for them to react fully before it was through the filter and on to the second. The second reason is why I continued some of my study in area of reaction rates. The third reason is that the vapor passed through the filter without contacting the derivatizing agent.

To determine if the reaction was rapid enough to be used effectively with the OSHA 42 method, I studied several different reactions using an FTIR Spectrometer. Figure 8 is a baseline scan of the polyethylene sheeting in the FTIR. This baseline scan allowed me to identify the peaks due to sheeting.

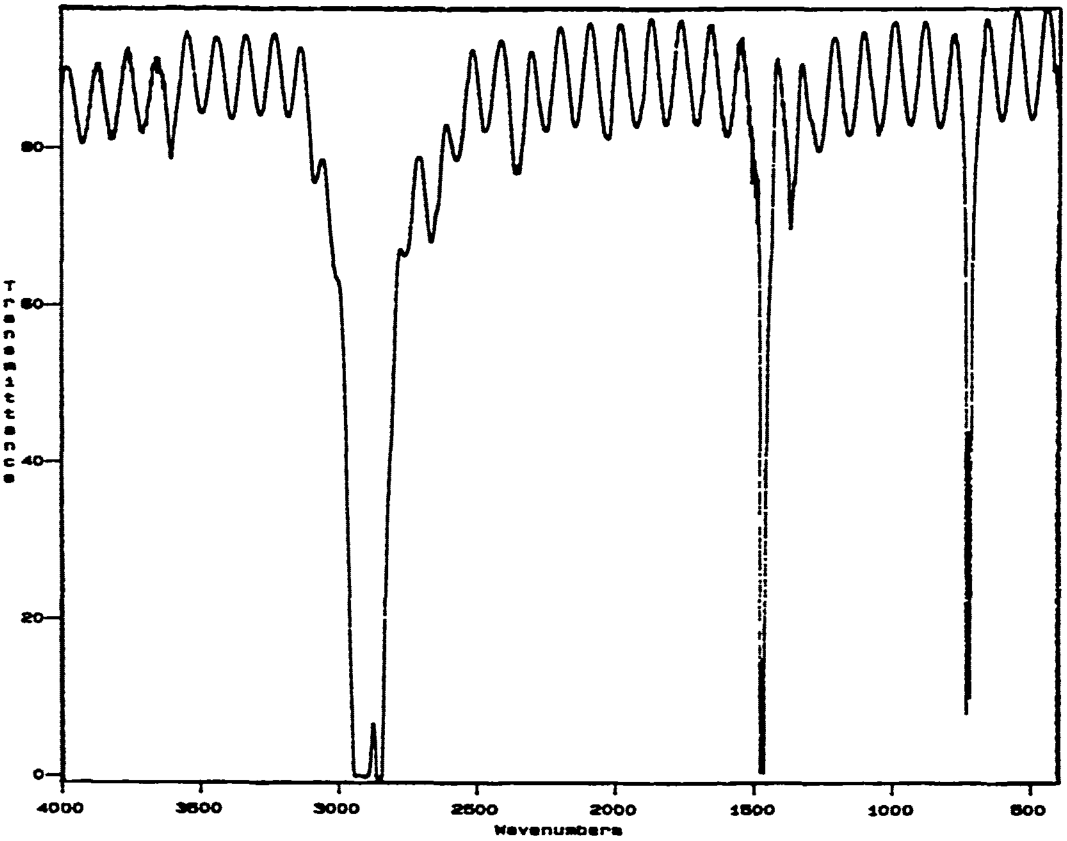


Figure 8: Baseline Polyethylene FTIR Scan.

A scan of reagent grade HDI is shown in Figure 9. This scan serves as the baseline of HDI in the FTIR. Note that the isocyanate peak appears at 2250 cm $^{-1}$.

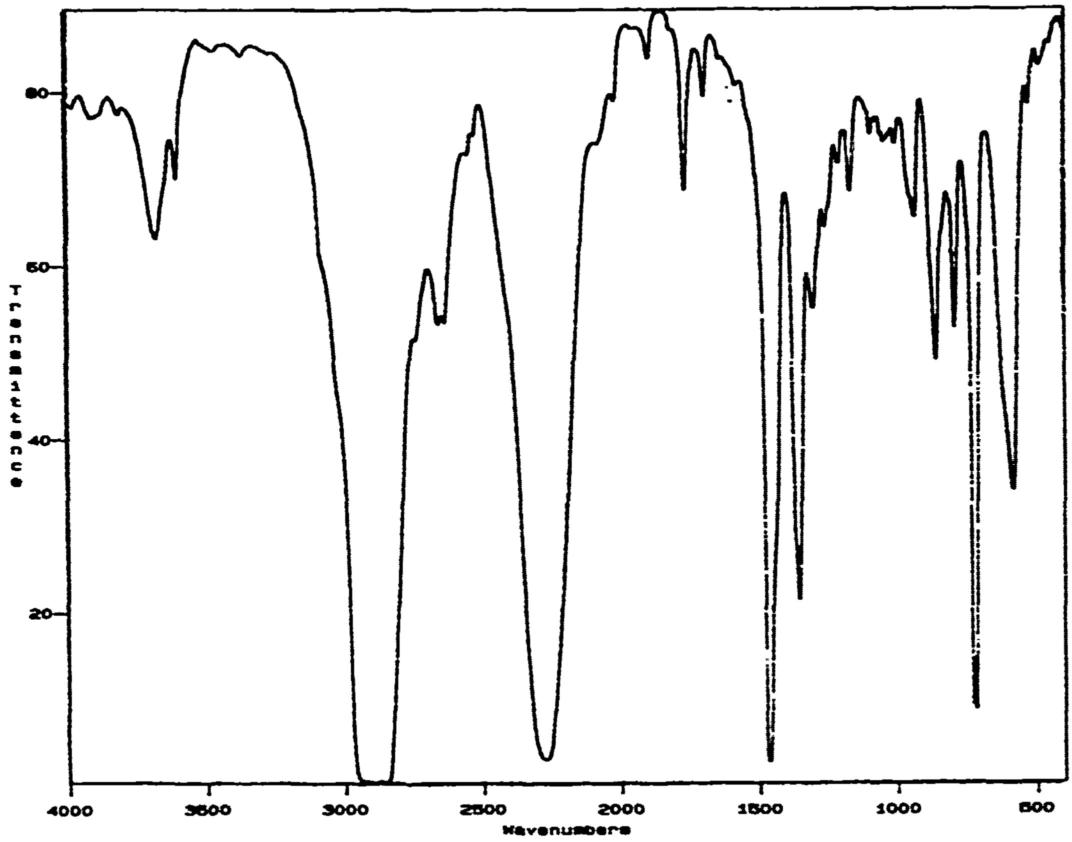


Figure 9: FTIR Scan of 100% HDI.

Figure 10 is a scan of the hardener portion of some polyurethane paint. The hardener portion of the two component polyurethane paint is the one which contains the isocyanates. Here you can see the distinctive peak at approximately 2250 cm $^{-1}$. If you look carefully you can tell that there are actually two peaks overlapping here.

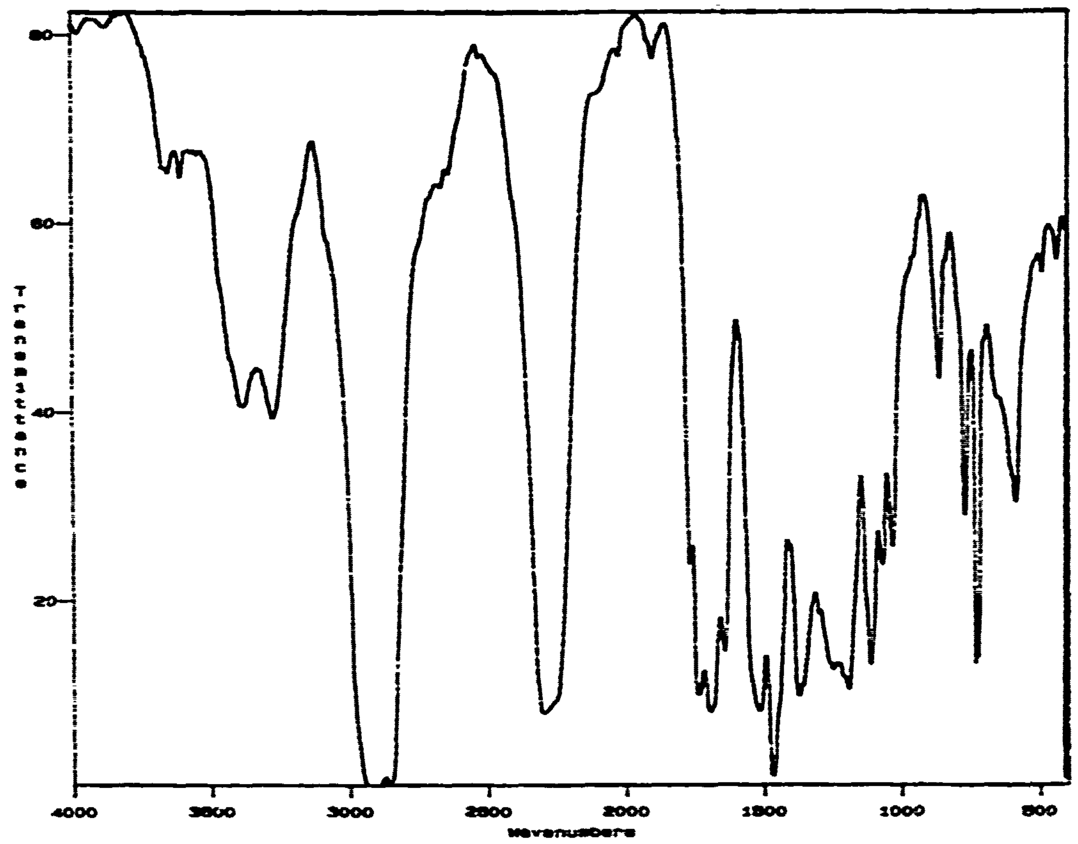


Figure 10: FTIR Scan of Polyurethane Paint Hardener.

In Figure 11 is the baseline scan of 100% 1-(2-pyridyl)-piperazine. This peak appears at approximately 2350 cm^{-1}. In later scans which contain both piperazine and isocyanates, the different peaks can be seen.

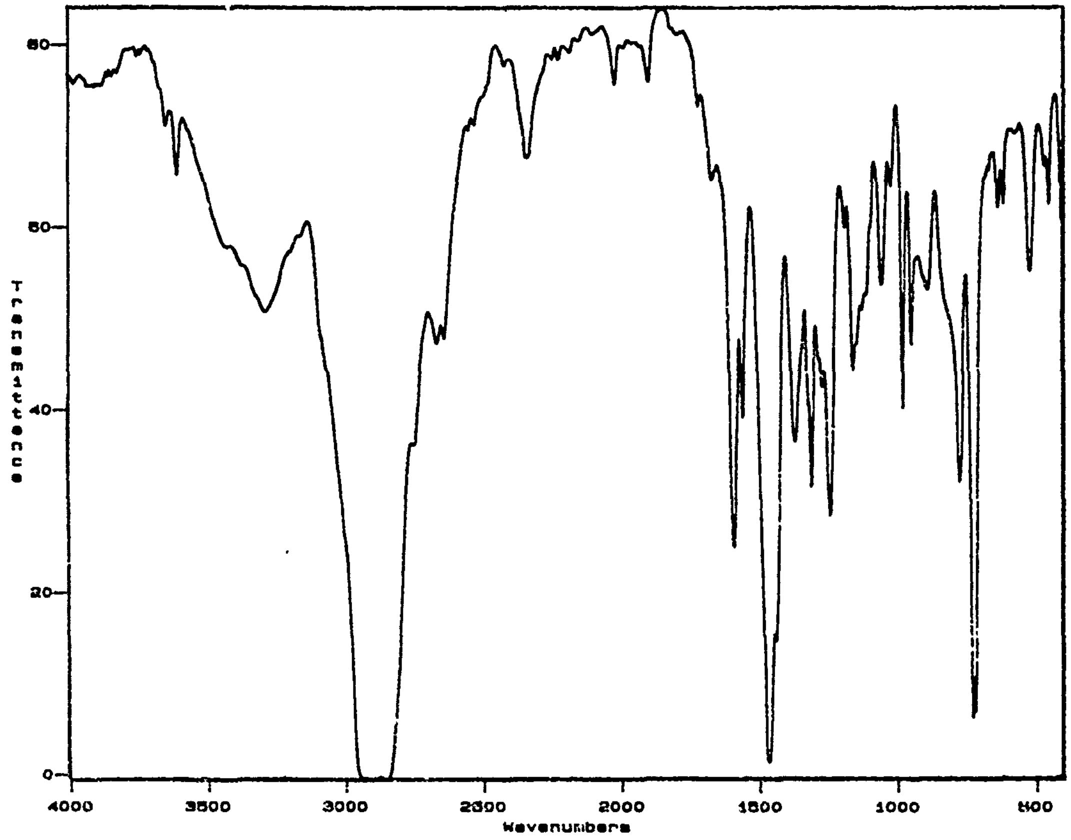


Figure 11: FTIR Baseline Scan of 100% 1-(2-pyridyl)-piperazine.

Figure 12 is a scan of polyurethane paint and 1-(2-pyridyl)-piperazine derivatizing over a period of 20 minutes (22 scans). The resolution was set for 8 scans at 16 cm^{-1} and each run lasted for a total of 7 seconds. In order to determine if the NIOSH and OSHA methods are underestimating due to slow reactions with the derivatizing agent I scanned this reaction on the FTIR. The peak at 2250 cm^{-1} continues to diminish for up to 20 minutes. From this data I conclude that the derivatization reaction which is assumed to be instantaneous, actually has a time constant of 8 to 12 minutes.

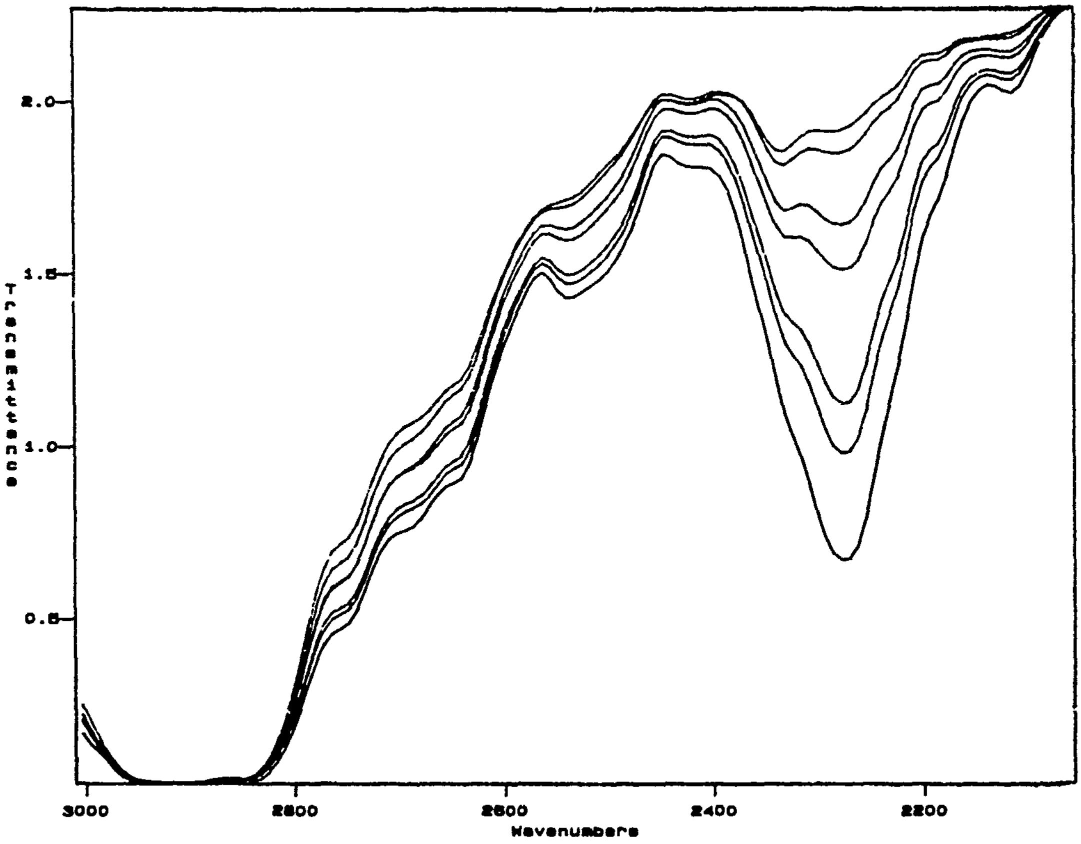


Figure 12: FTIR Scan of Polyurethane Paint and 1-(2-pyridyl)-piperazine.

In Figure 13 I scanned two component polyurethane paint over a period of 12 days to see how long this polymerization process would take. One drop of HDI hardener was added to one drop of polyurethane paint between two layers of polyethylene sheeting and mounted in the FTIR pathway. As you can see in the graph, the process takes up to 12 days for full polymerization of the paint.

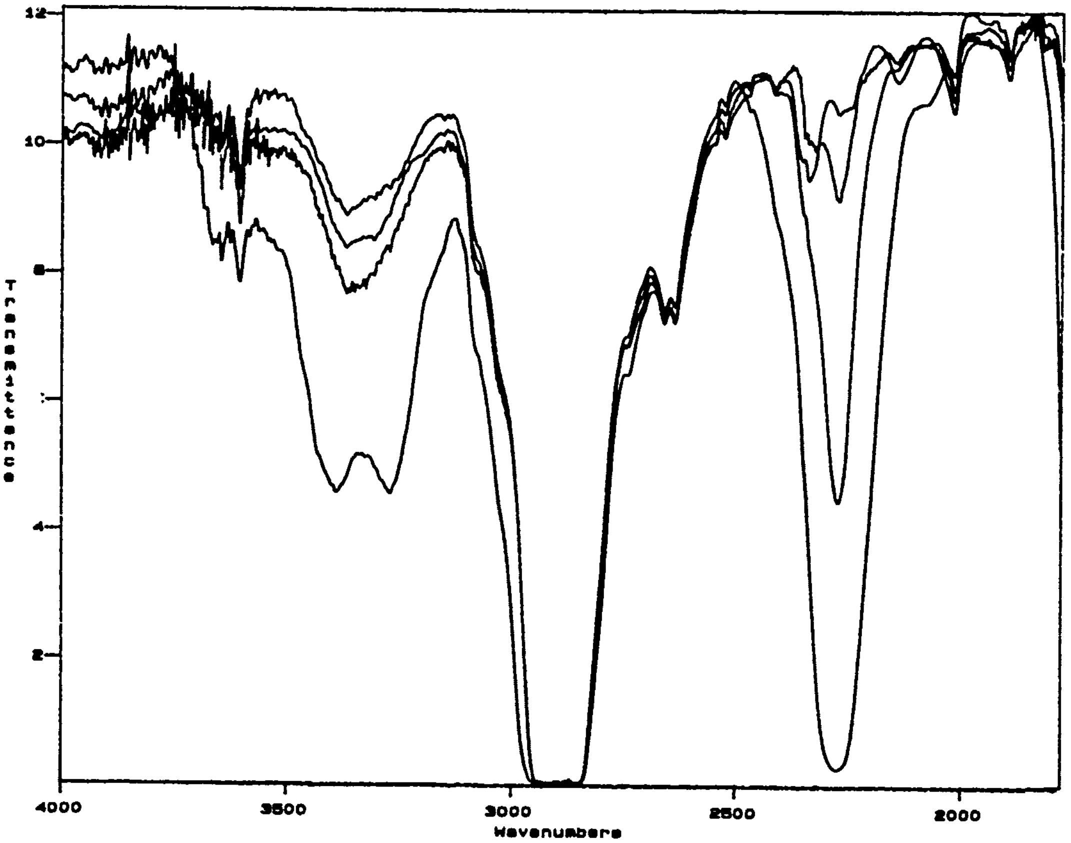


Figure 13: FTIR Scan of Polyurethane Paint Polymerizing Over a 12 Day Period.

In Figure 14 two component polyurethane paint and hardener were added to 1-(2-pyridyl)-piperazine between two sheets of polyethylene sheeting. The resolution was again set for 8 scans at 16 cm^{-1}. This is a series of 11 scans between 0 seconds and 1200 seconds. After the seventh scan (420 seconds) more piperazine was added in order to drive the isocyanate peak at 2250 as low as it would go. When this was done, the piperazine peak at 2350 also grew slightly and then diminished on later scans.

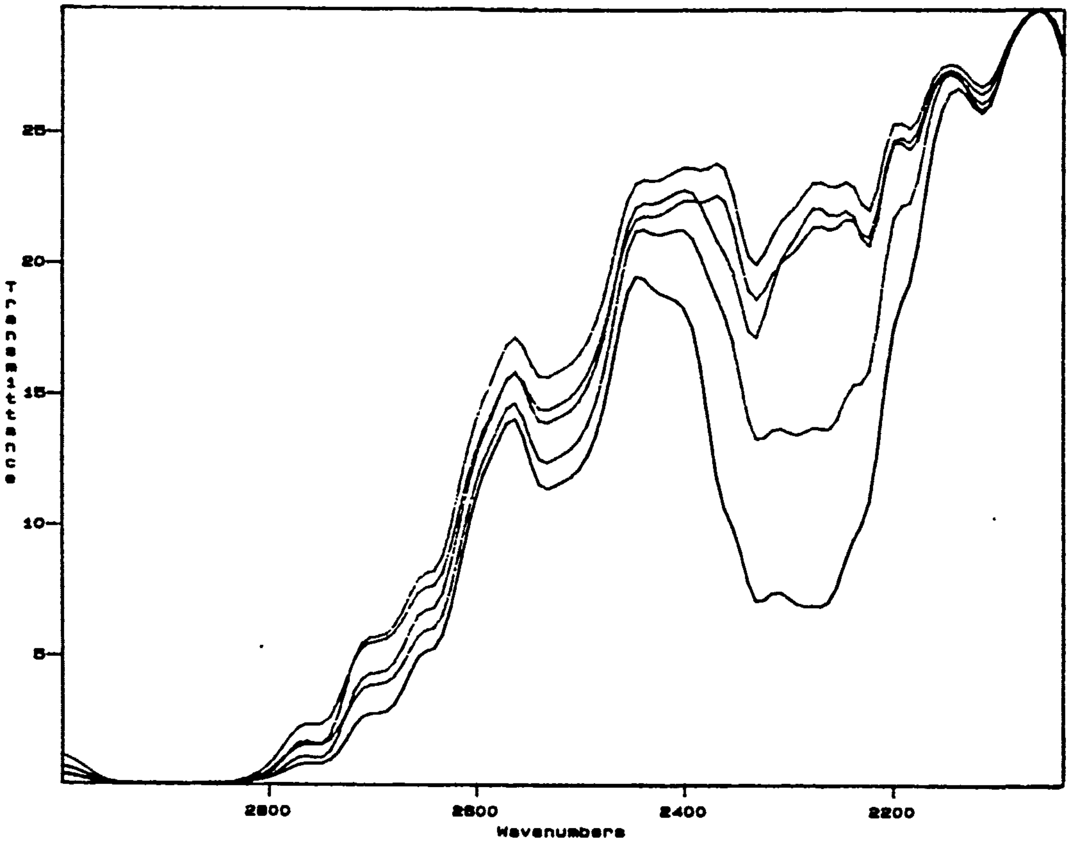


Figure 14: FTIR Scan of Polyurethane Paint and 1-(2-pyridyl)-piperazine (driven to completion).

In order to determine the particle size distribution for the sampling conducted during my research, I used a Cascade Impactor. Two samplings were taken during a normal spray painting operation of an airplane. Spraying was conducted inside a building with marginal ventilation. During the first 15 minute sample only a light coat of paint was applied. During the 21 minute sample a heavier coat of paint was applied. In both cases, stage 4 was the heaviest stage of the eight. See Table 3 for the cascade impactor cut line for each stage.[12] See Table 4 for the individual weights by stage for each sample as well as the total weight sampled. The range of particle diameters for stage 4 is from 6.0 to 9.8 microns in diameter.

One method of approximating the amount of isocyanate per stage is to multiply the total sample mass by the percent by weight of isocyanates in the mixture. In this case isocyanates were 30 percent by weight in the paint mixture. The approximate amount of isocyanates total using this method were 14.3 mg/m^3 and 15.6 mg/m^3 respectively. These results are over exaggerated and well above any measurements recorded by either the NIOSH or OSHA methods during my research.

Table 3. Cascade Impactor Cut-Lines.

Series 290 Impactor Cut-Points at 2.0 LPM

Stage No.	Cut-Point in Microns
1	21.3
2	14.8
3	9.8
4	6.0
5	3.5
6	1.55
7	0.93
0.52	0.52
Back-Up Filter	0.0

Table 4. Mass Results Per Stage of Cascade Impactor.

Sample No.	Stage No.	Total Weight on Filter (mg)	Estimated HDI on Filter (mg)
1	1	0.135	0.040
	2	0.186	0.056
	3	0.300	0.090
	4	0.364	0.109
	5	0.282	0.085
	6	0.002	0.001
	7	0.008	0.002
	8	0.154	0.046
	Total =	1.431	0.429
2	1	0.229	0.069
	2	0.318	0.095
	3	0.361	0.108
	4	0.592	0.178
	5	0.413	0.124
	6	0.181	0.054
	7	0.096	0.029
	8	0.000	0.000
	Total =	2.190	0.657

CONCLUSIONS AND RECOMMENDATIONS

The results of this evaluation show that the NIOSH 5521 method is the better method for sampling aerosol isocyanates. However, this method does require that close attention be taken to ensure that the sample nozzle inlet and outlet are kept clean. Otherwise the openings fill with paint increasing the air velocity in the nozzle. By speeding up the sampling stream fewer aerosol particles will be captured in the derivatizing fluid and the isocyanate concentration underestimated.

For sampling vapors, the OSHA 42 method is as effective as the NIOSH method and has two advantages over the NIOSH method. First, the OSHA method eliminates the requirement that 15 milliliters of volatile liquid be placed on the workers near their breathing zone. Secondly, the OSHA method requires less time for sample preparation and uses only a single integrator during the analysis. Thus the sampling analysis can be completed and results returned to the Industrial Hygienist in a shorter amount of time. Corrective action can be taken sooner providing better protection of the workers. It should be noted that some of the isocyanates were not collected on the first treated filter but on the second filter. Up to 5 percent of the isocyanates may be lost due to slow reactions or break through. Further studies in this area are needed to determine at what concentrations or sampling times are two in line filters required.

The OSHA 42 method is not effective in the collection of aerosol particles. The particles have such poor contact with the derivatizing agent coating on the glass fiber filters that very little derivatization actually takes place and the isocyanate concentrations are underestimated. Microscopic evaluation of both the treated and untreated glass fiber filters showed that all of the particles were collected on the surface of the filter and none in the matrix where better contact with the derivatizing agent would have occurred.

Measurement of reaction rates using an FTIR revealed that the reaction between the derivatizing agent and the isocyanates are not as fast as commonly believed. This supports the study conducted by Wu, Sttoyanoff and Gaind which showed that the ratio of the rate of change was 49 for 1-(2-pyridyl)-piperazine when compared to the rate of reaction between water and isocyanates. Tryptamine has a ratio value of 98 and 1-(2-methoxyphenyl)-piperazine has a ratio value of 100. Further studies should be made to compare other derivatizing agents such as tryptamine and 1-(2-methoxyphenyl) piperazine on treated glass fiber filters for sampling vapor isocyanates since they have reported higher reaction rates.

After viewing all of my data, I feel that the use of solid sampling material such as glass fiber filters is not effective when sampling for aerosol isocyanates since it allows only limited contact between the derivatizing agent in the matrix and the aerosol particles collected on the surface of the filter. Further studies should be done in order to develop a better design for the aerosol sampler.

REFERENCES

1. **Occupational Safety and Health Administration:** *Job Health Hazards Series:* Toluene Diisocyanate (TDI). U.S. Department of Labor, Washington D.C., 1975.

2. **Purnell, C., Walker, R.:** Methods for the Determination of Atmospheric Organic Isocyanates A Review. *The Analyst*, 110:893-905, 1985.

3. **American Conference of Governmental Industrial Hygienist (ACGIH):** *Threshold Limit Values and Biological Indices*, Cincinnati, OH, 1992.

4. **Dharmarajan, V., Lingg, R.S., Booth, K.S., and Hackathorn, D.R.,:** Recent Developments in the Sampling and Analysis of Isocyanates in Air. *American Society for Testing and Materials*, Philadelphia, page 190-202, 1987.

5. **Rudzinski, W.E.:** Analysis of Isocyanates in Spray-Paint Operations. Southwest Texas State University, San Marcos, TX, page 34-1 to 34-20, 1992.

6. **Willisamson, K.S.:** Studies of Diisocyanate Workers (2). *Trans Assoc Ind Med Off*, 15:29-35, 1965.

7. **Munn, A.:** Experience with Diisocyanates. *Trans Assoc Ind Med Off*, 9:134-38, 1960.

8 **Friebil, H., Lushtrath, H.:** The effect of toluene diisocyanate (Desmodur T) on the respiratory passages. *Arch Exp Pathol Pharmakol*, 227:93-110, 1955.

9. **Wu, W.S., Stoyanoff, R.E., and Gaind, V.S.:** Application of Tryptamine as a Derivatizing Agent for Airborne Isocyanate Determination, Part 4. Evaluation of Major High-Performance Liquid Chromatographic Methods Regarding Airborne Isocyanate Determination With Specific Investigation of the Competitive Rate of Derivatization. *The Analyst*, 115:21-25, 1991.

10. **National Institute of Occupational Safety and Health:** *NIOSH Manual of Analytical Methods, Method 5521*, Cincinnati, OH, 1989.

11. **Occupational Safety and Health Administration:** *OSHA Analytical Methods Manual, Method 42*, Salt Lake City, UT, OSHA Analytical Laboratory, 1989.

12. **Grasby-Anderson Cascade Impactor:** *Instruction Manual, Bulletin Number 290 I.M.-3-82*, page 17.

APPENDIX A

HP 1090 STANDARD OPERATING CONDITIONS

1. **Start up Liquid Chromatograph (LC) and prepare to run.**

a. Turn on LC.

b. Insure waste container is empty.

c. Insure solvent reservoirs contain adequate solvent.

d. Turn on helium in order to degas the solvent. Insure solvent degasses at least 1 hour before running the analysis.

e. Turn lamp on (allow to stabilize for 1 hour).

f. Load appropriate LC method (flow, %B, detector wavelength, run time, etc.). Note: Be sure to enter the injection volume (INJ VOL) again, even if it is correct in the method. This is necessary due to a software glitch.

g. After degas, turn solvent pump ON. Allow to run 15 minutes to stabilize flow and pressure. Press PLOT key on the integrator to determine stability of the baseline; press STOP when satisfied baseline is straight.

h. Activate INJECTOR WASH; press 1 and ENTER. Watch syringe plunger fully withdraw. Allow syringe to flush for 20 seconds, then press 0 and ENTER.

i. Turn on compressed air supply at the cylinder valve.

2. **Making the run:**

a. Load the autosampler tray; load from the right and work to the left. NOTE: The first (closest) slot is number 0, followed by 1-9 for the first row. It is important to remember this when programming the LC run sequence.

b. Program the run sequence. NOTE: If the run is going to be made overnight/over the weekend, it is important to de sure the last sequence step is verified to be "0" for pump, lamp, and oven. This will automatically turn these functions off when the run is complete.

c. Make sure the integrator power is ON.

d. Check integrator parameters by pressing LIST twice. Load parameters manually or using the appropriate method file, and load calibration file if desired.

e. Press LAMP ON again to calibrate the detector.

f. To start, press SEQUENCE, START, and ENTER.

3. **Post-run and shut-down:**

a. Turn the lamp OFF.

b. VERY IMPORTANT STEP: For the reverse-phase columns, place pure water into the solvent channel which delivered the aqueous phase (usually acid or buffer solutions). First flush with 100% water for 20 min, and perform at least 2, 30 second injector washes. This removes buffer salts/acids from the entire system. Follow water flush with 50/50 acetonitrile/water (2 minutes), then 80/20 acetonitrile/water (15 minutes).

c. Flush the column for 10 minutes with the solvent mixture recommended by the column manufacturer. This is usually 50/50 acetonitrile/water for reverse-phase columns.

d. Turn pump OFF.

e. Turn LC OFF.

f. Turn off helium and compressed air supplies.

g. Unload samples and discard into propter waste containers.

APPENDIX B

ISOCYANATE METHOD (NIOSH 5521)

Method: NIOSH 5521
Instrument: LC
Column: RP-8 Cartridge Column
Flow: 1 ml/min
Mobile Phase: 55% buffered water/45% methanol
Oven Temp: ambient
Run Time: 15 min
DAD Detector: Sample, 242, 8; Reference, 390, 16
EC Detector: +0.80 V vs. Ag/AgCl
Inj Volume: 20 uL
Channel A (left): methanol
Channel B (center): buffered water (see below)
Channel C (right): HPLC grade water (for column flush)
Detection Limits 1.0 ug

The electrochemical detector (EC) must be connected to the HPLC by disconnecting the injector wash and connecting the green hose in it's place. When finished or at the end of each day the injector wash must be reconnected in order to wash the injection system. The injector must be washed to prevent clogging by the buffer solution.

The EC electrode must be cleaned and pretreated at the beginning of each day of use. However, the mobile phase must be flowing during pretreat. Also, the chromatographs and results will be much better if the EC is zeroed periodically.

Integrator Settings

DAD	EC
Zero = 10	Zero = 20
Att 2^ = 3	Att 2^ = 8
Cht Sp = 0.3	Cht Sp = 0.3
Ar Rej = 250	Ar Rej = 100000
Thrsh = 2	Thrsh = 5
Pk Wd = 0.04	Pk Wd = 0.08

Sample Preparation

Add 25 ul acetic anhydride to each sample. Evaporate to dryness under gentle stream of nitrogen while warming on a hot plate at 60 °C. Redissolve in 5.0 mL methanol and agitate in ultrasonic bath for 15 minutes.

Standard Preparation

Prepare a 10.0 ug/ml stock solution of each isocyanate solution to be analyzed. For HDI add 7.6 mg to a 250 mL volumetric flask, dilute to mark with methanol. Be sure to use the proper isocyanate urea (made from 1-(2-methoxyphenyl)-piperazine). Agitate in ultrasonic water bath until clear. Make analytical standards covering a range of 0.1 ug/mL to 4.0 ug/mL.

Calculations

Prepare HDI plot: plot area response (y-axis) vs. ug isocyanate/mL (x-axis). Find the ug of each isocyanate in each sample by using the chart (or a calculator with quadratic regression or graphics program on a computer with second order regression), then multiply by 5 (dilution factor). Express as mg/m^3 by dividing the micrograms (ug) in each sample by the air volume in liters. Remember, ug/L is the same as mg/m^3.

$$\text{Isocyanate, } mg/m^3 = \frac{\text{ug isocyanate from chart X 5}}{\text{air volume (liters)}}$$

Buffer Solution

The buffer solution is prepared by adding 705 g anhydrous sodium acetate in 500 mL water. Add 500 mL HPLC grade methanol. Glacial acetic acid is added to adjust the pH to about 6.0. Only a couple of drops of acid are needed to reach this pH. It is not important that the pH be exactly 6.0, but somewhere close to this value. Be sure to flush the column and injector thoroughly with a 1:1 mixture of distilled water/ methanol after the run is finished to prevent the buffer from clogging the system.

APPENDIX C

ISOCYANATE METHOD (OSHA 42)

Method: OSHA 42
Instrument: LC
Column: RP-18 Cartridge column
Flow: 1 mL/min for single analytes
Mobile Phase: 50% buffered water/50% acetonitrile
Oven Temp: ambient
Run Time: 10 min with no guard column
Detector: Sample, 254, 8; Reference, 390, 16
Inj Volume: 20 ul
Channel A (left): acetonitrile
Channel B (center): buffered water (see below)
Channel C (right): HPLC grade water (for column flush)
Detection Limits: HDI, 0.0006 mg

Integrator Settings

Zero = 10
Att 2^ = 3
Cht Sp = 0.3
Ar Rej = 250
Thrsh = 3
Pk Wd = 0.10

Sample Preparation

Take the glass fiber filter out of the cassette and place into a screw-top test tube. Add 2.0 mL of 10% DMSO/acetonitrile to each tube and cap. Shake periodically and let the filters desorb for one hour. Filter each sample using a syringe filter into a autosampler vial, cap, and analyze.

Standard Preparation

Prepare a 1.0 mg isocyanate/mL stock solution of each isocyanate to be analyzed as follows:

HDI: Add 29.4 mg HDI urea to a 10 mL volumetric flask; dilute to volume with DMSO to obtain a 1.0 mg HDI/mL solution.

Make analytical standards covering a range of 0.5 ug/mL to 4.0 ug/mL by adding 0.5 uL - 4.0 uL of the stock standards to 1.0 mL of 10% DMSO/acetonitrile which has been added to a autosampler vial. Use a 10 microliter syringe to add the stock solution to the autosampler vials as shown below:

0.5 ug/mL standard: 0.5 uL isocyanate stock standard
1.0 ug/mL standard: 1.0 uL isocyanate stock standard
2.0 ug/mL standard: 2.0 uL isocyanate stock standard
4.0 ug/mL standard: 4.0 uL isocyanate stock standard

If the peak areas found in the samples are above the range of the standards, make dilution's and rerun, applying the proper dilution factor during the calculations.

Calculations

Prepare a plot for HDI by plotting the area response (Y-axis) vs. ug isocyanate/mL (x-axis). Find the ug of each isocyanate in each sample by using the chart (or a calculator with quadratic regression), then be sure to multiply by 2, (dilution factor). Express as mg/m^3 by dividing the micrograms (ug) in each sample by the air volume in liters. Remember, ug/L is the same as mg/m^3.

$$\text{Isocyanate, mg/m}^3 = \frac{\text{ug isocyanate from chart X 2}}{\text{air volume (liters)}}$$

Buffer Solution

Prepare a fresh buffer solution weekly. Old buffer solution will grow large amounts of bacteria that will clog the HPLC if used. The buffer solution is prepared be adding 0.38 g of HPLC grade ammonium acetate to 500 mL water. Glacial acetic acid is added to adjust the pH to about 6.2. Only a couple of drops of acid are needed to reach this pH. Be sure to flush the column and injector thoroughly with 1:1 mixture of distilled water/ acetonitrile after the run is finished to prevent the buffer from clogging the system.

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