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Evaluation of a Coated Filter Sampling Method for the Determination of Isocyanate Concentrations in Air

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An alternative sampling device was evaluated for the determination of isocyanates in air. Diphenylmethane and 1-(2-methoxyphenyl)piperazine were used to coat a glass fiber filter. The piperazine reacted with aromatic and aliphatic isocyanates, forming ureas. High pressure liquid chromatography was used to analyze these ureas with electrochemical detection. The mixing of the isocyanate aerosol with the reagent was facilitated by the diphenylmethane. In filter samples stored for 2 to 3 weeks, the ureas proved stable. The shelf life of the coated filter was 2 months. 2,4-Toluene-diisocyanate (584849) had detectable limits of 18.7 micrograms/cubic meter (microg/m3) and 4,4°-methylenediphenyl-isocyanate (101688) had a detection limit of 15.7microg/m3 in a 50 liter sample volume. When compared with the results obtained using a reference impinger method in laboratory sampling, the isocyanate air concentrations recorded from the coated filter method were higher. When tested in the field, air concentrations determined from the impinger samplers for more than 50 percent of the sample pairs were higher than those obtained by the filter sample method. The author concludes that this coated filter method was not reliable enough to be used for determining isocyanate aerosol concentrations in the atmosphere of a work environment.

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ABSTRACT

The evaluation of an alternative sampling device for isocyanates, a glass fiber filter coated with 1-(2-methoxyphenyl)piperazine and diphenylmethane, is presented. 1-(2-Methoxyphenyl)piperazine reacts with aromatic and aliphatic isocyanates to form ureas, which are analyzed by HPLC with electrochemical detection. Diphenylmethane, a high boiling solvent, was present to facilitate the mixing of the isocyanate aerosol with the reagent. Shelf life of the coated filter was determined to be at least two months, while the ureas were stable enough to permit storage of filter samples for two to three weeks. The lower limits of quantitation for the ureas were equivalent to 18.7 $\mu g/m^3$ of 2,4-toluene diisocyanate and 15.7 $\mu g/m^3$ of 4,4'-methylenediphenyl isocyanate for a 50-L sample volume. The coated filter was evaluated by sampling laboratory generated isocyanate aerosols and an aerosol in a foundry using side-by-side sampling of the coated filter and a reference impinger method [Warwick et al., Analyst (1981) 106, 676-685]. The isocyanate air concentrations determined from the coated-filter method were higher than those found with the reference impinger method in laboratory sampling. In the field test, the air concentrations determined from the filter samples were significantly lower than those determined from the impinger samples for more than 50% of the sample pairs. Therefore, based on the foundry results, the coated filter was judged to be unreliable for sampling isocyanate aerosol.

## INTRODUCTION

Many methods for the determination of isocyanates in air using a variety of sampling devices have been reported in the literature.[1] Current methods utilizing the impinger as the sampling device use toluene as the carrier solvent for a derivatizing reagent.[2-5] The use of toluene can create additional exposure hazards, because it evaporates during sampling. Three to five milliliters of toluene can be lost during one hour of sampling at 1 L/min. The impingers are bulky to transport and require frequent monitoring during sampling to keep a proper solvent level. Accidental spilling of the toluene from the impinger can easily occur. A coated sampling medium, such as a filter, would allow the industrial hygienist to determine isocyanate exposures without the disadvantages of the impinger. Sampling methods utilizing coated sampling devices have not always been field tested to assure reliability.[6,7] There have been some reports of field tests where agreement between a method employing a coated device and a reference impinger method was obtained,[8,9] but reports have also indicated that in field tests such devices have failed.[10-13] Failure of a coated device in these cases may be due to poor mixing of the isocyanate aerosol with the derivatizing reagent on the filter or solid sorbent. It may also result from local depletion of the reagent during sampling.

In 1982 this project was begun in order to develop an alternative sampling device for isocyanates that would determine isocyanate concentrations in air at least as accurately as a reference impinger method, but would be more convenient to use. Industrial processes using isocyanates often produce atmospheres contaminated with isocyanate aerosol rather than vapor. Therefore, a glass fiber filter coated with 1-(2-methoxyphenyl)piperazine and a high boiling solvent, diphenylmethane, was chosen to be evaluated. The solvent was present to facilitate the mixing of the isocyanate in the trapped particles with the reagent.

1-(2-Methoxyphenyl)piperazine was introduced in 1981 as a derivatizing reagent for the analysis for isocyanates.[5] It is currently used in the

United Kingdom's Health and Safety Executive Method MDHS 25[14]. This stable derivatizing reagent reacts with aromatic and aliphatic isocyanates to form ureas. For example, 2,4-toluene diisocyanate (TDI) and 4,4'-methylenediphenyl isocyanate (MDI) react with the reagent to form N,N'-bis[4-(2-methoxyphenyl)piperazine-1-carbonyl]- 2,4-toluenediamine (TDIU) and N,N'-bis[4-(2-methoxyphenyl)piperazine-1-carbonyl]-4,4'-methylenedianiline (MDIU), respectively. The 1-(2-methoxyphenyl)piperazine is acetylated with acetic anhydride to prevent it from being retained on the column during analysis of the samples by buffered reverse-phase liquid chromatography with electrochemical detection. The electroactivity of the ureas is utilized to obtain greater sensitivity and selectivity than obtainable with ultraviolet detection.

This report presents the results of the evaluation of the coated filter for shelf life prior to use, sample stability for TDIU and MDIU, and lower limits of quantitation for TDIU and MDIU. The coated-filter method was compared with an impinger method in side-by-side sampling of laboratory generated aersols and of an atmosphere at a foundry using isocyanates in a coremaking operation.

## EXPERIMENTAL

Reagents. Acetonitrile, methanol, toluene, pentane, and dimethylsulfoxide were HPLC-grade solvents purchased from Burdick & Jackson Laboratories, Inc., Muskegan, Michigan. 1-(2-Methoxyphenyl)piperazine, diphenylmethane, fenchone, diphenyl ether, triglyme, N-methylpyrrolidone, dimethylformamide, dimethylacetamide, and MDI were at least reagent grade quality and were purchased from Aldrich Chemical Company, Inc., Milwaukee, Wisconsin. For the filter shelf life experiment, some 1-(2-methoxyphenyl)piperazine was recrystallized from pentane and then protected from moisture, because it is hygroscopic. Glacial acetic acid, sodium acetate, and acetic anhydride, reagent grade, were purchased from Fisher Scientific, Cincinnati, Ohio. The distilled-deionized water was prepared in the laboratory with a Millipore system. The 2,4-toluene diisocyanate (Hylene T)® and the

Imron® paint containing 1,3,5-tris(6-isocyanatohexyl)-1,3,5-triazinetrione (HDI trimer) were from Dupont. The MDI-based Lino-cure C® was from Ashland Chemical Co.

The acetate buffer for the liquid chromatographic mobile phase was prepared by dissolving 25 g of anhydrous sodium acetate in 1 L of methanol and 1 L of distilled-deionized water. The pH of the solution was adjusted to 6.0 with glacial acetic acid, and the mobile phase was degassed with a helium purge.

TDIU and MDIU were prepared by dissolving the appropriate isocyanate (0.002 mol) in 25 mL of dimethyl sulfoxide and adding this solution to a stirred solution of 1-(2-methoxyphenyl)piperazine (0.005 mol) in dimethyl sulfoxide (25 mL). The mixture was warmed (60-90 °C) for 20-30 min. Three hundred milliliters of distilled-deionized water was added to the reacted mixture after removing it from the heat. Stirring was stopped after addition of the water. The white precipatate, which formed with the addition of the water, was collected by filtration. The compound was dried in a vacuum oven to remove the residual water. The ureas were recrystallized from toluene containing a small amount of methanol. The identities of the ureas were verified by field desorption mass spectrometry. Observed physical data for the ureas were as follows:

TDIU: mp. 212-213 °C; field desorption mass spectrum, m/e 558 ($M^+$, $C_{31}H_{30}N_6O_4$)

MDIU: mp 209-210 °C; field desorption mass spectrum, m/e 634 ($M^+$, $C_{37}H_{42}N_6O_4$)

Equipment. The liquid chromatograph consisted of two Waters 6000A reciprocating pumps, a Waters Model 680 gradient controller, a Waters Model 440 ultraviolet absorbance detector equipped with a 254-mm filter, a Waters Model 710B autosampler, an ESA electrochemical detector Model 5100A with a Model 5010 standard analytical cell and a Model 5020 guard cell. Both electrochemical cells contained high-surface area, porous graphite coulometric electrodes. Signals from the detectors were monitored with a dual-pen Soltec recorder. Quantitation of the detector signals was done with a Hewlett-Packard Model 3357 laboratory automation system.

The two detectors in the chromatography system were serially connected, with the ultraviolet detector first in line. The electrochemical detector operated in the oxidation mode with the potential of +0.80 V at the analytical cell and +0.85 V at the guard cell. Since the electrochemical detector had a very limited linear range at any gain setting, the gain was adjusted to provide the amount of sensitivity required for the particular samples being analyzed.

The column packing used to analyze all samples was Supelcosil LC-8DB, an octyldimethylsilyl bonded silica support with greatly reduced residual surface activity toward basic compounds. The first column of this packing was 15 cm long, had a particle size of 5 μm, and was preceeded by a Waters Guard-Pak C-18 precolumn. Later, the analytical column was replaced with a column 7.5 cm long with particle size of 3 μm. The internal diameter for both columns was 4.6 mm. The precolumn was also later changed to a column of Supelcosil® LC-8DB, 2 cm long with a 10-μm particle size.

The mass spectrometer was a V.G. Micromass, model 7070 HS. For the field desorption analysis of the prepared ureas, the extraction voltage was adjusted to 7000 V, and the emitter current was ramped from 0 to 25 mA while scanning over peak of interest.

Chromatographic Conditions. The sodium acetate buffer (0.15 M, ph 6.0) was combined with acetonitrile or methanol to provide appropriate isocratic conditions. Initially, a mobile phase of 75% methanol and 25% sodium acetate buffer was used. When diphenylmethane was added to the sampling system, it was then necessary to add acetonitrile to the mobile phase to obtain reproducible chromatograms. Most of the analyses were performed with a mobile phase of 40% acetonitrile and 60% of the acetate buffer. However, the field samples were analyzed using a mixture of 27% acetonitrile and 73% acetate buffer, while the urea-storage samples were analyzed with a 25%–75% combination. In all cases, the flowrate was 1 mL/min.

Coated Filters. Filters were prepared by coating a glass fiber filter (24 mm diameter, type AE, Gelman) with a solution of diphenylmethane and 1-(2-methoxyphenyl)piperazine in pentane. Two hundred microliters of this solution was gradually dropped onto the center of the filter using a syringe. This procedure allowed a specific amount of reagent to be placed on the filter. The mixture spread to the outer edges and the pentane rapidly evaporated leaving the reagent and the diphenylmethane on the filter. During sampling, the coated filter was held in a 25-mm Gelman open-faced cassette made of Delrin®. The diameter of the exposed area of the filter was 22 mm. The loading of the reagent on the filter varied from 100 to 1300 µg of reagent with either 100 or 67 µL of diphenylmethane. The loading of diphenylmethane on the filters for the laboratory generated air samples was 100 µL. However, this amount of solvent created too large a pressure drop for the personal sampling pumps used in the field. Lowering the diphenylmethane loading to 67 µL per filter sufficiently reduced the pressure drop across the filter.

The quantity of impurities in the diphenylmethane was reduced by slowly passing 8 mL of a 2:1 V/V mix of pentane and diphenylmethane through a silica Sep-Pak® (Waters Associates) using a 10-mL glass syringe. As the solvent mixture passed through the Sep-Pak, the contaminants retained by the absorbant appeared as a visible, translucent phase, providing an indication of when the capacity of the Sep-Pak® was reached.

Coated filters used in the study of shelf life were prepared with 1128-1182 µg of 1-(2-methoxyphenyl)piperazine and 100 µL of diphenylmethane. The effect of the purity of 1-(2-methoxyphenyl)piperazine, light, and time on the integrity of the coated filters was evaluated. A total of forty coated filters were prepared. Twenty were coated with unrecrystallized reagent and twenty with recrystallized reagent. Ten filters of each reagent purity were stored unprotected from the light, while the remaining filters were kept in a closed box. All filters were stored in screw cap glass scintillation vials except for five of the filters prepared with unrecrystallized reagent which

were stored in cassettes and sealed with parafilm. All five of the filters in cassettes were stored unprotected from light. All forty samples were stored at room temperature. The samples were divided into five sets of eight filters. Each set contained four filters with unrecrystallized reagent, two which had been stored in vials in the dark, one stored in a vial in the light, and one stored in a cassette in the light. Each set also had four filters with recrystallized reagent, two stored in vials in the dark and two stored in vials in the light. A set of samples was analyzed after 1, 9, 27, 35, and 56 days of storage.

Synthetic Samples. Samples for the study of the stability of the ureas were prepared by adding 10 or 100 µL of a methanol solution of TDIU and MDIU (approximately 0.1 µg/µL of each urea) to a coated filter. Sets of twelve samples, six at each level, were prepared on different days. Samples were stored protected from light and at room temperature for 1, 11, 18, and 32 days in cassettes sealed with parafilm, and were all analyzed on the same day. This type of design was used in an effort to reduce day-to-day variability in the analysis of the samples.

Control samples for the study of stability of the ureas were prepared with the filter samples by adding 200 µL of filter-coating solution and 10 or 100 µL of the methanolic solution of TDIU and MDIU to a 4-mL glass vial. The pentane and methanol in these solutions were allowed to evaporate before sealing with a screw cap and storing with the filters. Six controls, three at each level of the ureas, were prepared on each day. The control samples were worked up for analysis by adding 3-mL of methanol and 2-drops of acetic anhydride to each vial and then agitating it in the ultrasonic water bath for 15-min.

Samples for the determination of the lower limits of quantitation of the ureas were prepared as above, except that the amount of ureas added to the filters varied over a range of 0.035 to 3.03 µg per sample.

Generation System. The aerosol-generation system was constructed from relatively inexpensive materials, so that, upon completion of the experiments, it could be discarded, rather than cleaned. A schematic drawing of the system is shown in Figure 1. Laboratory air was pumped into the system with a 1/2-horsepower Gast pump. The flow of this air stream was split into two lines. One line provided the dilution air at 17 L/min, while the other, a smaller line with air at 2 L/min, operated the nebulizer. These flows were monitored with glass rotometers. The outside of the system was put together from a 2-L funnel, a 4-L funnel, a 60-cm tall pipette jar, and a 20-L jar, all made of either polypropylene or polyethylene. The bottom of the pipette jar and the stem of the 4-L funnel were cut off and the four pieces were then assembled as shown in figure 1. The seam between the pipette jar and the large funnel was sealed with 5-cm wide labeling tape on the inside as well as the outside. The smaller funnel was sealed to the other end of the pipette jar and the large funnel sealed to the 20-L jar with Klean Klay brand modeling clay. The 20-L jar served as the sampling chamber and had a small hole on the side near the bottom to serve as a vent. The clay seal made possible repeated separation of the sample chamber to add and remove samples with easy resealing of the system to keep it air tight during a generation run. The stream from the nebulizer contained the isocyanate aerosol. Static charge dissipaters were on all four sides of a 4-inch square styrofoam plate, which served as a flow disrupter. The isocyanate stream was discharged into the system 1 cm below the center of this plate. The plate created turbulence which helped to mix the dilution air and the isocyanate aerosol from the nebulizer. The 5-cm thick cardboard honeycomb, positioned 10 cm below the plate, reduced the turbulence of the air to provide an aerosol with laminar flow to the sample chamber. The critical orifices used in the sampling lines were disposable syringe needles. The one liter per minute sampling lines for the impingers used 21 gauge needles, 2.5 cm in length. The 200 mL/min lines for the filters used 26 guage needles, 1.25 cm long. Each of the needles was preceeded in line by a Millipore HV-25 mm filter. Two sampling pumps were used. A 1/4-horsepower Gast pump pulled air through the impingers, and a 1/10-horsepower General Electric pump was used for the coated filters. Six to twelve samples were taken at one time: three to six impingers, each paired with a coated filter.

Initially, a Retec X-70/N nebulizer was used in the system. This required that the isocyanate component be diluted with toluene or acetone, solvents which were compatible with the isocyanate source. However, these solvents were not compatible with the plastic housing of the nebulizer, causing it to crack, and necessitating its replacement after each run. When our supply of these nebulizers ran out and another supply could not be located, an all-glass nebulizer, similar in design, was installed in the system. The glass nebulizer did not require dilution of the isocyanate material, but its reservoir was only 5-6 mL. When the glass nebulizer was used, the generation system was in operation only about 15 min for each run, because the output of the nebulizer was great enough to empty the reservoir in less than 30 min.

Generated Samples. The aerosol-generation system was allowed to equilibrate for 5-30 minutes before sampling was begun. Each impinger contained 15-mL of a solution of 1-(2-methoxyphenyl)piperazine in toluene. The concentration of the sampling solution ranged from 38 to 49 µg/mL. A coated filter, prepared as described above, was placed in a cassette and attached to each impinger. Each filter faced downward in the sampling chamber. The generated atmosphere was sampled for 10 to 60 minutes. The first runs of the system used MDI-based Lino-cure® C as the source for the aerosol. This resin is used for sand cores and molds in foundaries and is mixed with a polyol component, such as Lino-cure® ABMR (Asland Chemical Co.). The cure rate of this mixture was so rapid that it became a soft solid before it could be placed in the nebulizer reservoir. Therefore, only the Lino-cure® C component was used to generate the aerosol. If left exposed to the air, this brown, viscous fluid would begin to solidify after several hours, depending on how much moisture was in the air. In later runs, the aerosol was generated from Imron® paint. This two component industrial paint had a cure time of four hours. The components, shale gray enamel (326-Y-67633) and HDI trimer activator (VG-Y-511), were mixed as directed on the can--four parts of the enamel component to one part of the activator. The rate of consumption of isocyanate by the reaction leading to polyurethane in the cured paint

relative to the rates of mixing of the aerosol with the sampling reagent and the subsequent urea formation was not monitored in these experiments.

Immediately after sampling, toluene was added to the impingers to restore the 15-mL pre-sampling volume. These samples were then transferred to 20-mL glass scintillation vials. The filters were removed from the cassettes and placed in 20-mL scintillation vials.

Analysis. A 2-mL aliquot of each impinger sample was prepared for analysis. The 1-(2-methoxyphenyl)piperazine in each aliquot was acetylated with a drop of acetic anhydride. The aliquot was taken to dryness with warming at 60 °C and under a stream of nitrogen. The residue was then reconstituted in 2-mL of methanol. After the addition of the methanol, each sample was agitated for 15 min in an ultrasonic water bath. Each filter sample was extracted with 3 mL of methanol. Reagent in the filter extract was acetylated with 1-2 drops of acetic anhydride. These samples were also agitated in the ultrasonic bath for 15 min. The filter extracts were filtered with a 25-mm Millipore HV filters (0.45 μm pore size) to remove any particulate in the sample.

Standards for TDIU, MDIU, and 1-(2-methoxyphenyl)piperazine were prepared by diluting aliquots of stock solutions (approximately 0.5 μg/μL) of each compound in methanol to the appropriate concentrations (0.0069-50.0 μg/mL). The 1-(2-methoxyphenyl)piperazine in the standards was acetylated with 2 drops of acetic anhydride before dilution with methanol to the mark of the volumetric flask. Standards for the urea from HDI trimer were prepared by adding known amounts of a toluene solution of the HDI trimer component of the Imron® paint to 15 mL of the impinger sampling solution. After allowing these solutions to stand for at least 30 min, three to five 2-mL aliquots were prepared as described for impinger samples. The amount of isocyanate present in the solution was based on the percent of HDI trimer reported on the material safety data sheet provided with the paint.

The samples and standards were analyzed by isocratic reverse phase liquid chromatography under appropriate conditions as previously described. The injection volume of each solution into the chromatograph was 10 µL. All analyses were done at ambient temperature.

## DISCUSSION OF RESULTS

The most reasonable approach to a convenient and accurate sampling system for isocyanates, seemed to be a glass fiber filter coated with 1-(2-methoxyphenyl)piperazine along with a high boiling solvent, which would facilitate mixing of the derivatizing reagent with the isocyanates being sampled. The criteria for selecting a solvent to coat on the filter were boiling point, solvent miscibility with water, and yield of the derivatizing reaction in the solvent. The search for a solvent began with the selection of several which had a boiling point higher than 150 °C. Table 1 lists the solvents considered. Diphenylmethane met all of the criteria for use as the carrier solvent on the filters. This compound is a solid at room temperature, but melts at 26-27 °C. When mixed with 1-(2-methoxyphenyl)piperazine, a solid which melts at 22-24 °C, the mixture remained a viscous liquid.

The diphenylmethane eluted near MDIU under the HPLC conditions used. However, as diphenylmethane was not electroactive, it did not interfere with the quantitation of the MDIU with the electrochemical detector. There was an impurity in the diphenylmethane which was electroactive and caused some problems in the quantitation of TDIU at low concentrations. To reduce this contamination, a 2:1 mixture of pentane and diphenylmethane was slowly passed through a silica Sep-Pak. As shown in the chromatograms in Figure 2, this procedure successfully reduced the contamination to a level such that it could be adequately separated from TDIU, which had a retention time of about 2 min. The 1-(2-methoxyphenyl)piperazine was then dissolved in this mixture.

To determine if 1-(2-methoxyphenyl)piperazine would remain on the filter in the presence of diphenylmethane during sampling, air at various flowrates was pulled through filters, which were coated with about 100 µg reagent and 100 µL of diphenylmethane. In each case, the period of air flow was 60 min. The amount of reagent remaining on the filters was compared by liquid chromatographic analysis to a coated filter which had had no air drawn through it. At 1.0 L/min, only about 75% of the reagent remained on the filter after 60 min. At slower flowrates a smaller fraction of the reagent was lost, and at 250 mL/min no loss was detected. It was not determined whether this result was due to the slower flowrate or the smaller sample volume. Although this evaluation was done at the lowest loading of reagent used on the filters, the slower flowrate was used for all sampling. Since 250 mL/min is not an easily obtainable flowrate with personal sampling pumps, a flowrate of 200 mL/min was used in the field test of the coated filter. During the analysis of the laboratory and field samples, a significant amount of reagent was found on the filters, even when more than 60 L of air had been sampled.

A storage study was done to determine the shelf life of a coated filter before use. The variables for this evaluation of the coated filters included time, purification of the reagent by recrystallization, storage in light or darkness, and storage in a glass screw-cap vial vs. storage in a cassette sealed with parafilm. A graphical representation of the data is shown in Figure 3. The recovery is based on the weight of reagent used to prepare the coating solution. Since the amount of 1-(2-methoxyphenyl)piperazine (1129 or 1182 µg per filter) resulted in a solution with a concentration which was above the range of the detector, it was necessary to dilute each filter extract by a factor of ten to obtain reliable quantitation and not overload the detector. No artifacts were observed in the extracts of the filters with either detector. The recovery of reagent from filters stored in cassettes was lower than that from filters stored in vials, except on day 1. A possible explanation is that some of the coating solution was absorbed by the fluoroelastomer o-ring which held the filter in place in the cassette. The odor of the

diphenylmethane was detected on o-rings which had contacted a coated filter. However, the data from this experiment indicate that no significant loss or degradation of reagent occurs with storage up to 56 days.

The study to evaluate the stability of the ureas on the filter was planned so as to reduce day-to-day variability of sample analysis. A set of samples, as decribed in the experimental section, was prepared on different days using a freshly prepared stock solution each day. It was necessary to use a new lot of filters for samples stored for 1 and 11 days. All of the samples were stored at room temperature in the dark and were analyzed on the same day. The recovery of each sample was based on the weight of each urea used to prepare the stock solution. The recovery was calculated as the ratio of the amount of urea found in the sample to the amount added to the sample, times 100. The average recoveries for each day at each level are plotted in Figure 4, and the average recoveries for the control samples are plotted in Figure 5. The pooled relative standard deviation for the average recoveries of TDIU on the filters at the 10-µg level was ±8.0%, while at the 1-µg level it was ±11%. For MDIU, the pooled relative standard deviation of the average recoveries from the filters was ±4.3% at the 10-µg level and ±12% at the 1-µg level. The pooled relative standard deviation for the average recoveries of the control samples was ±2.7% for TDIU and ±3.0% for MDIU at the 10-µg level, and ±4.8% for TDIU and ±4.4% for MDIU at the 1-µg level. The data in Figures 4 and 5 seem to indicate that the MDIU was slightly less stable than TDIU, and that when TDIU is stored on the coated filter, some interferent becomes significant with prolonged storage at low levels.

The analytical range was examined by determining the recoveries of each urea over a range of loadings. The percent relative standard deviation of the average recovery from the filter was plotted against the loading of the urea on the filter, as shown in Figure 6. The variability of the recovery determinations tended to increase at lower loadings, but in most instances the precision was acceptable even at the lowest loadings. Factors which

affected the limit of quantitation for TDIU (0.3 µg per filter sample) were the large reagent peak and impurities, both of which began to interfere at higher detector sensitivities. The recovery of MDIU appeared to become unacceptable at low loadings (Figure 7) and, thus, determined the limit of quantitation (0.2 µg per filter sample) of this urea. These limits of quantitation for the ureas were equivalent to 19 $\mu g/m^3$ of TDI and 16 $\mu g/m^3$ of MDI for an air sample volume of 50 L.

The experiments in which laboratory-generated aerosol was sampled using sets of impingers paired with coated filters are summarized in Table 2. The most significant information gained from the filter samples collected using the generation system was that the loading of the reagent on the filter was critical to derivatizing the isocyanates collected. Reagent loading of at least 1116 µg gave promising results. When using this loading on the filter, the concentration of isocyanate as determined from the filter samples was always greater than that determined from the impingers. A plot of impinger concentration versus the corresponding filter concentration is shown in Figure 8. The ratio of the pairs of samples ranged from 1 to 12.

The precision of the determinations of the concentration of the isocyanate in the generated aerosol, based on the analysis of the impinger samples, was 15-20% during the first six months of operation. Later, there appeared to be a gradient which developed within the generation sample chamber, causing the aerosol to be nonhomogeneous. A possibile reason for the change was that the static charge dissipaters in the mixing area of the system became coated with polymerized aerosol. Since the charge dissipaters were alpha particle emitters, it would have taken very little coating to reduce their effectiveness. Since the results from the filters with high reagent loading always yielded a higher concentration than the impingers, we concluded that the coated filters were trapping the particles in the aerosol and converting the isocyanate to the urea at least as quantitatively as were the impingers. Analysis of blank coated filters revealed no positive interference.

The field test of the coated filter was done in an aluminum foundry that used a no-bake polyurethane (MDI-based) binder system to form the sand cores for use in the casting molds. The binders were a liquid phenol formaldehyde resin and a MDI-derived prepolymer in solvents. The basic arrangement of the areas sampled is shown in Figure 9. The binders and the sand were mixed in area A, which was elevated above the core machines. The mixture of sand and binders was transported to the core machines below. At the core machines, areas B through G, gaseous N,N-dimethylethylamine was introduced and, as it contacted the binder coated sand, it catalyzed an immediate curing or hardening at room temperature. Pairs of samplers, each containing an impinger with 1-(2-methoxyphenyl)piperazine in toluene and a filter coated with 1034 µg of 1-(2-methoxyphenyl)piperazine and 67 µL of diphenylmethane, were taken on two consecutive days, covering five working shifts. The results from these samples are listed in Table 3. The samples were all analyzed within two weeks after being collected.

While preparing the field samples for analysis, a strong amine odor was detected. The amine in the samples was later suspected of fouling the electrochemical detector cell. A gradual loss in sensitivity was observed, especially during the analysis of the impinger samples. However, the rate of change of the response was slow enough that quantitation of the samples was still possible.

In Area A, where the phenolic resin and isocyanate components for the procedure were freshly mixed, the ratio of the filter result to the impinger result was always greater than one. While there were some sample pairs from the other areas which indicated reasonable agreement between the two methods (ratio of filter result to impinger result greater than one), twelve of the nineteen pairs of samples in those areas had ratios of 0.5 or less. A possible explanation for this may be that the polymerization reaction in the aerosol proceeded more rapidly after the amine catalyst was added, causing the isocyanate in the aerosol to be consumed by the polymerization reaction before it could mix with the reagent on the filter and react to form the urea.

## CONCLUSIONS AND RECOMMENDATIONS

In the laboratory experiments on determining isocyanates in aerosol, a glass fiber filter coated with 1 mg of 1-(2-methoxyphenyl)piperazine and 67 µL of diphenylmethane seemed to be an adequate substitute for an impinger containing 1-(2-methoxyphenyl)piperazine in toluene. The precision of the analysis for the ureas derived from the isocyanates trapped on the coated filter was acceptable. The stability of the ureas is not affected by the filter; however, the ureas themselves may be unstable with time. The shelf life of the coated filter was sufficient, with no artifact formation after two months of storage. Results from the laboratory generated samples suggested that the coated filter was more efficient in collecting the aerosol particles than the impinger. However, results from the field study revealed an industrial hygiene situation where the coated filter did not consistently perform as well as an impinger. In more than 50% of the field sample pairs, the concentration determined from the filter sample was significantly less than the concentration obtained from the impinger sample. Therefore, the coated filter cannot be considered a reliable sampling method for isocyanates.

Future efforts to develop an accurate method of sampling for isocyanates should use an interdisciplinary approach. More detailed information concerning the isocyanate-based systems as they are being used in industry is needed. Information, such as particle size of the aerosol being sampled, rate of mechanical mixing of the derivatizing reagent and the isocyanate, composition of the aerosol sampled, and the effect of particle size on the kinetics of the reaction of the isocyanate with the derivatizing reagent may provide insight as to what requirements are necessary for an isocyanate sampler. A long-term, flexible project would be needed, due to the wide variety of industrial hygiene situations where isocyanates are used and the kind of information which is required. The development of an accurate and convenient sampler for isocyanates needs more basic research to characterize the aerosol being sampled.

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Table 1

Solvents Considered for Reagent Carrier Solvent on Filters

| Compound | Boiling Point (°C) | Misicible with Water | Yield of TDIU[a] |
|---|---|---|---|
| Fenchone (1,3,3-trimethyl-2-norbornanone) | 195 | no | 0% |
| Diphenyl ether | 222 | no | -[b] |
| Triglyme (2,5,8,11-tetraoxadodecane) | 217 | yes | 63% |
| N-Methyl-2-pyrrolidone | 202 | yes | 50% |
| Dimethylformamide | 153 | yes | -[b] |
| Dimethylacetamide | 158 | yes | -[b] |
| Diphenylmethane | 261 | no | 100% |
| Dimethyl sulfoxide | 189 | yes | 100%[c] |

[a] Percent conversion of TDI to TDIU after reaction with 1-(2-methoxyphenyl)piperazine in listed solvent. Comparison was made against same quantity of TDI reacted in a solution of 1-(2-methoxyphenyl)piperazine in toluene. 100 µg of TDI was added to 10 mL of each derivatizing solution. Concentration of derivatizing reagent in all solvents was approximately 43 µg/mL. Sample solutions were analyzed by HPLC.

[b] Not investigated because TLV too low

[c] 44-66% when 50% water present

Table 2

Average Air Concentrations of Isocyanate in Laboratory Generated Aerosol

| Set #[a] | Type of Isocyanate | Reagent Loading (mg) | Isocyanate Concentration ($mg/m^3$)[b] Impinger $\bar{X}$ | Impinger s | Filter $\bar{Y}$ | Filter s | Ratio $\bar{Y}/\bar{X}$ |
|---|---|---|---|---|---|---|---|
| 1 | MDI[c] | 202 | 344 | 53 | -[d] | - | 0.01 |
| 2 | MDI[c] | 1313 | 2.0 | 0.3 | 2.0 | 0.3 | 1.0 |
| 3 | $(HDI)_3$ [e] | 1380 | 0.07 | 0.002 | 0.13 | 0.06 | 1.8 |
| 4 | paint[f] | 1380 | 0.63 | 0.06 | 2.2 | 3.1 | 3.4 |
| 5 | paint[f] | 1116 | 0.09 | 0.02 | 0.45 | 0.35 | 5.0 |
| 6 | paint[f] | 1116 | 0.20 | 0.03 | 2.4 | 1.1 | 12 |
| 7 | paint[f] | 1116 | 0.12 | 0.05 | 0.32 | 0.08 | 2.7 |
| 8 | paint[f] | 1225 | 0.15 | 0.17 | 0.58 | 0.46 | 3.9 |
| 9 | paint[f] | 1225 | 0.17 | 0.16 | 0.39 | 0.44 | 2.3 |

[a] Room temperature for each set of samples was 68-72 °F; relative humidity was 42-81%; sampling time was 7-60 min.; sampling rate for the impingers was 800-950 mL/min.; sampling rate for the filters was 180-200 mL/min.

[b] $\bar{X}$ = average concentration from impinger samples; $\bar{Y}$ = average concentration from filter samples; s = standard deviation

[c] MDI component of Lino-Cure® C

[d] No isocyanate detected

[e] HDI trimer component of Imron® paint

[f] HDI trimer-based Imron® paint mix

Table 3

Field Test Data

| Area | Day | Shift | Concentration MDI Impinger ($\mu g/m^3$) | Concentration MDI Filter ($\mu g/m^3$) | Concentration Ratio (filter/impinger) |
|---|---|---|---|---|---|
| A | 1 | 1 | 3.5 | 10 | 2.9 |
| | 1 | 3 | 0.09 | 4.1 | 46 |
| | 2 | 1 | 1.1 | 10 | 9.7 |
| | 2 | 2 | 3.4 | 13 | 3.9 |
| B | 1 | 1 | 3.9 | 0.90 | 0.2 |
| | 2 | 1 | 0.38 | -[b] | - |
| C | 1 | 1 | 5.9 | 0.59 | 0.1 |
| | 1 | 2 | 0.87 | 0.30 | 0.3 |
| | 2 | 2 | 9.3 | 0.53 | 0.06 |
| D | 1 | 2 | 1.8 | 0.32 | 0.2 |
| | 2 | 1 | 2.2 | 4.2 | 1.9 |
| | 2 | 2 | 23 | 44 | 1.9 |
| E | 1 | 1 | -[a] | -[b] | - |
| | 1 | 2 | -[a] | 0.53 | - |
| | 1 | 3 | 0.42 | 0.49 | 1.2 |
| | 2 | 1 | 0.44 | -[b] | - |
| | 2 | 2 | 0.82 | -[b] | - |
| F | 1 | 2 | -[a] | -[b] | - |
| G | 1 | 1 | 13 | 0.86 | 0.07 |
| | 1 | 2 | 0.26 | -[b] | - |
| | 1 | 3 | 2.3 | -[b] | - |
| | 2 | 1 | 18 | 0.21 | 0.01 |
| | 2 | 2 | 1.4 | 2.2 | 1.6 |

[a] Less than 0.1 µg of MDI per impinger sample was detected. This was equivalent to an air concentration of 0.25 $\mu g/m^3$ for a representative sample volume of 400 L.

[b] Less than 0.01 µg of MDI per filter sample was detected. This was equivalent to an air concentration of 0.13 $\mu g/m^3$ for a representative sample volume of 80 L.

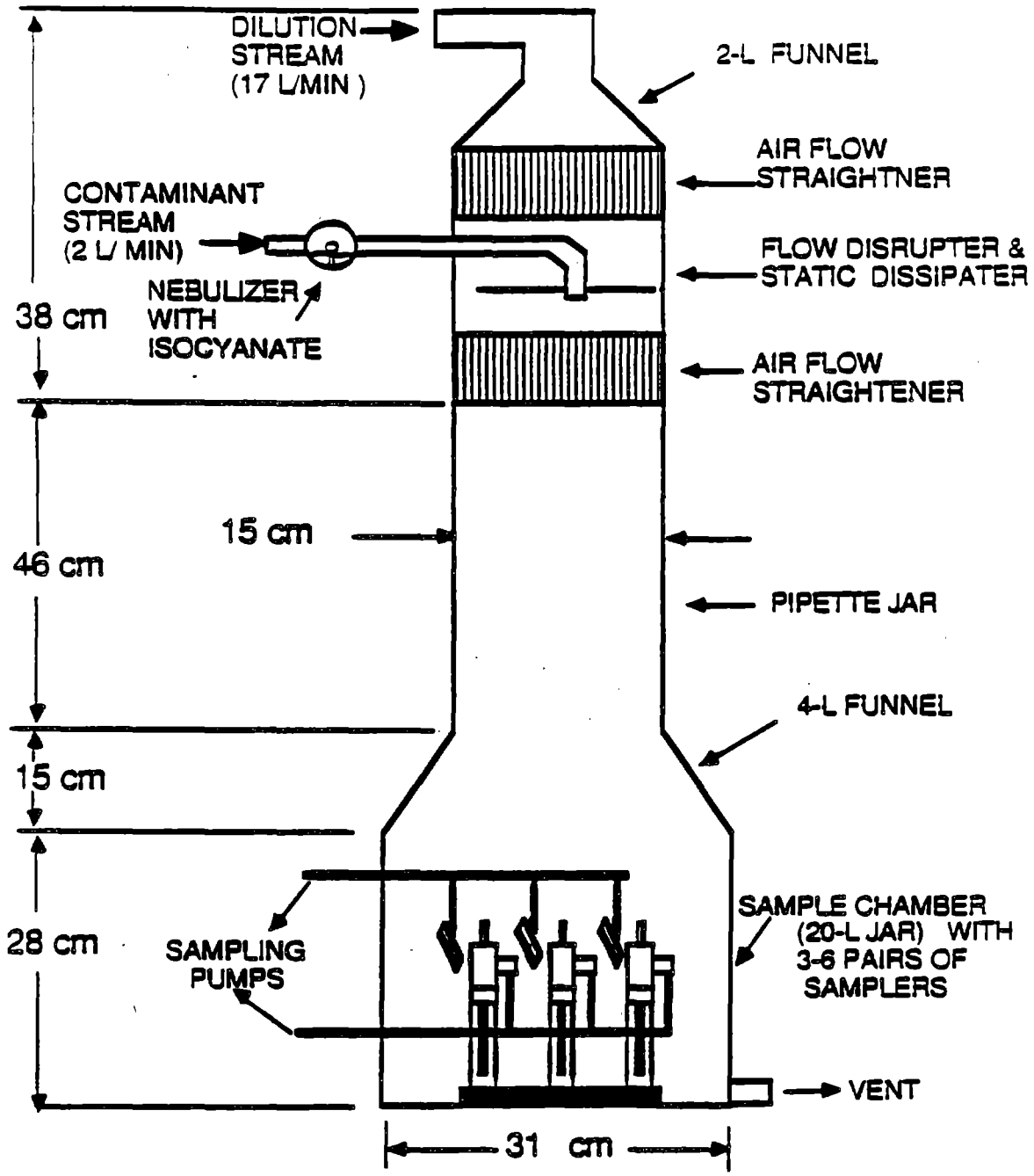


Figure 1. Schematic drawing (not to scale) of system for generation of isocyanate aerosols.

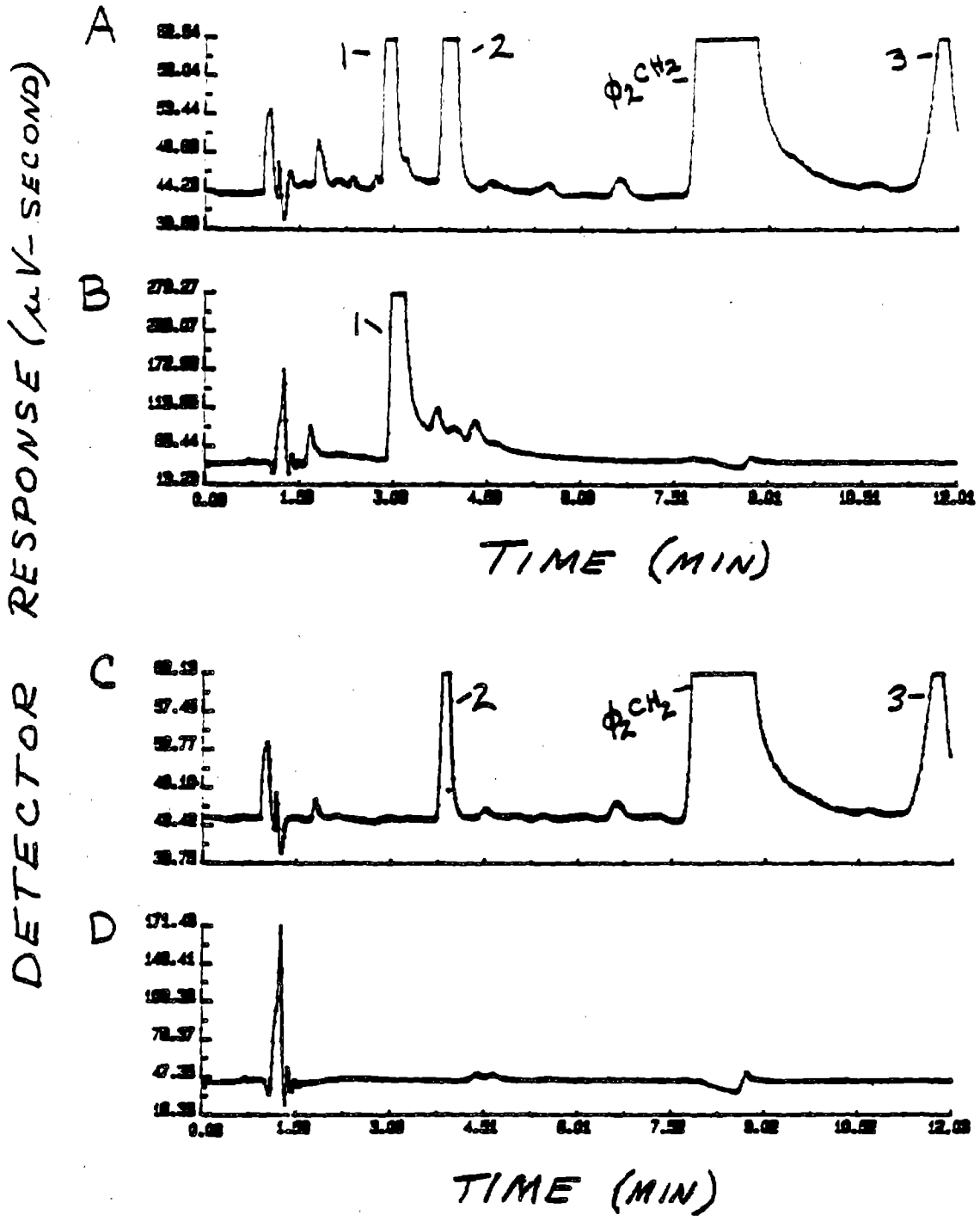


Figure 2. Chromatograms of diphenylmethane before (A and B) and after (C and D) cleanup by passing through a silica Sep-Pak. Chromatograms A and C are the UV response, and chromatograms B and D are the electrochemical response. Peak 1 was the only electroactive compound of the four observed with UV detection. The identities of peaks 1-3 are unknown, but the peaks are from diphenylmethane. The HPLC mobile phase was 73% of a 0.15 M sodium acetate in 1:1 methanol-water (pH 6.0) and 27% acetonitrile.

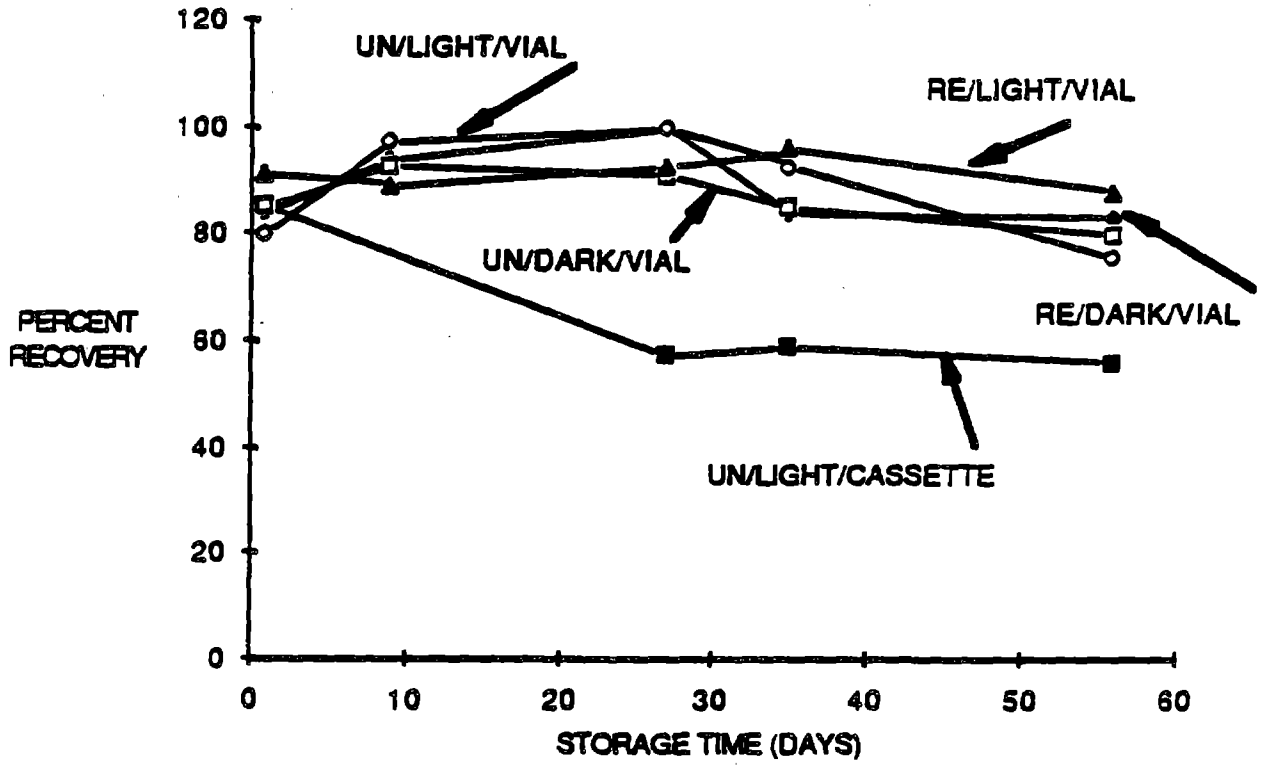


Figure 3. Plot of data from shelf life experiment. The percent of 1-(2-methoxyphenyl)piperazine recovered vs. the amount of time the filters were stored is shown. The variables of the experiment were whether the 1-(2-methoxyphenyl)piperazine on the filter was recrystallized (RE) or unrecrystallized (UN) and whether the filter was stored in light or dark and in a vial or a cassette. Points are the average of two samples, except only one determination per point was obtained for filters coated with unrecrystallized reagent and stored in the light in either a cassette or a vial.

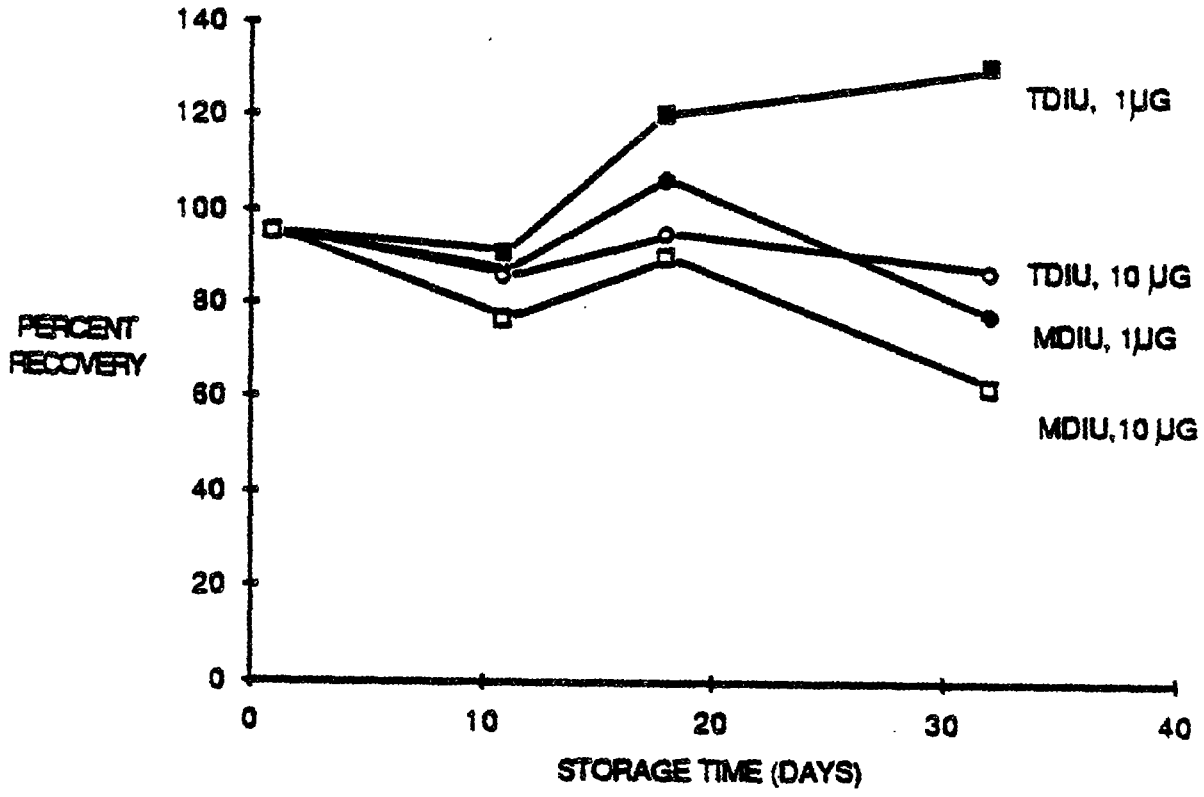


Figure 4. Plot of data from study of stability of TDIU and MDIU on coated filters. Percent recovery vs. storage time is shown. The results for the 10-µg samples are plotted separately from the results for the 1-µg samples for each urea. Each point is the average of 5-6 samples.

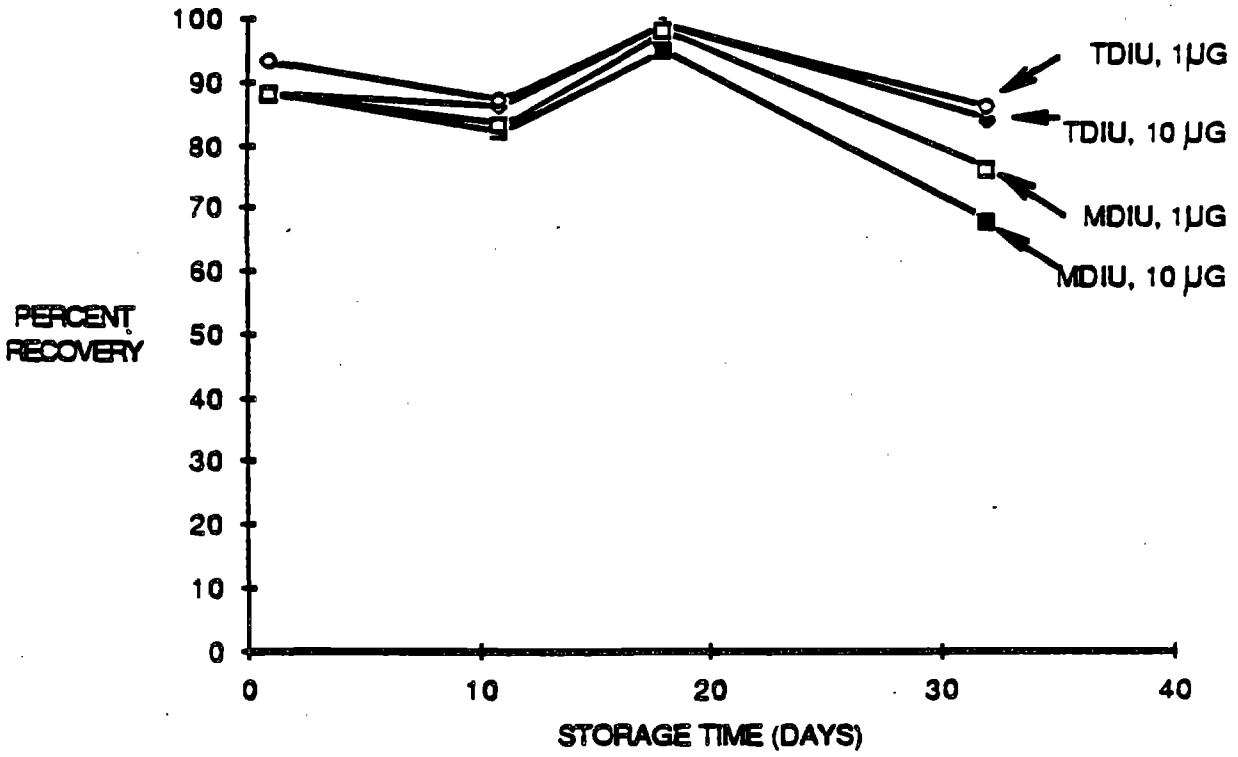


Figure 5. Plot of average recovery from the control samples for the study of the stability of TDIU and MDIU on coated filters vs. storage time. The results for the 10-µg samples are plotted separately from the results for the 1-µg samples for each urea. Each point is the average of 3 samples.

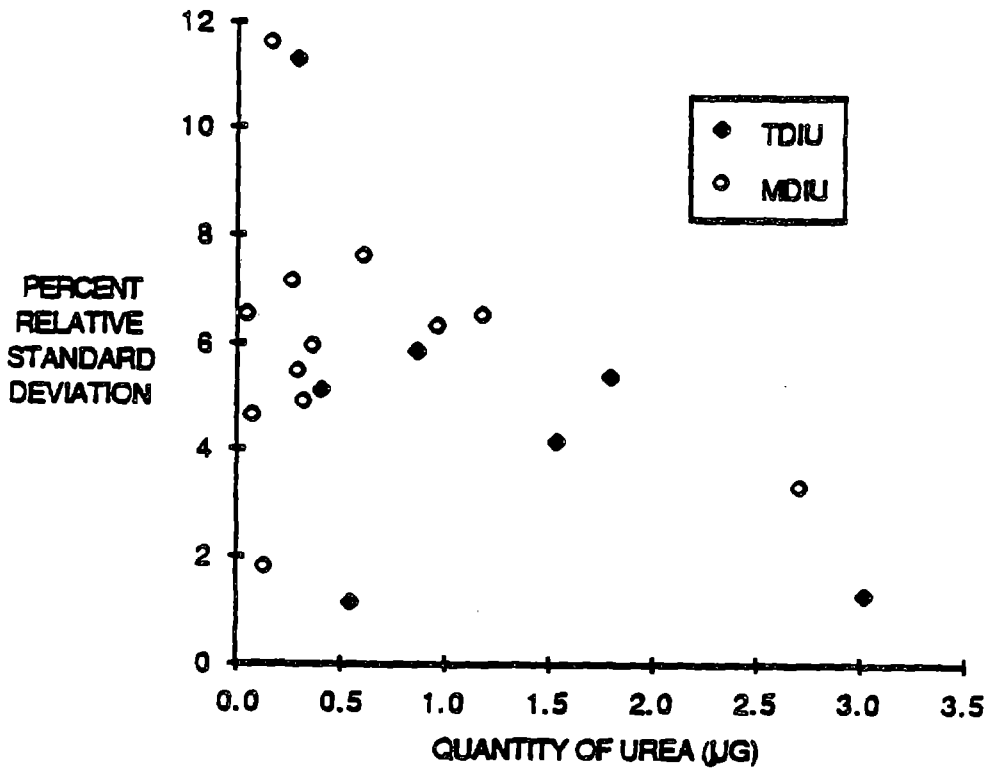


Figure 6. Plot of percent relative standard deviation vs. the loading of TDIU or MDIU in synthetic samples. Each point is the average of 5-6 samples.

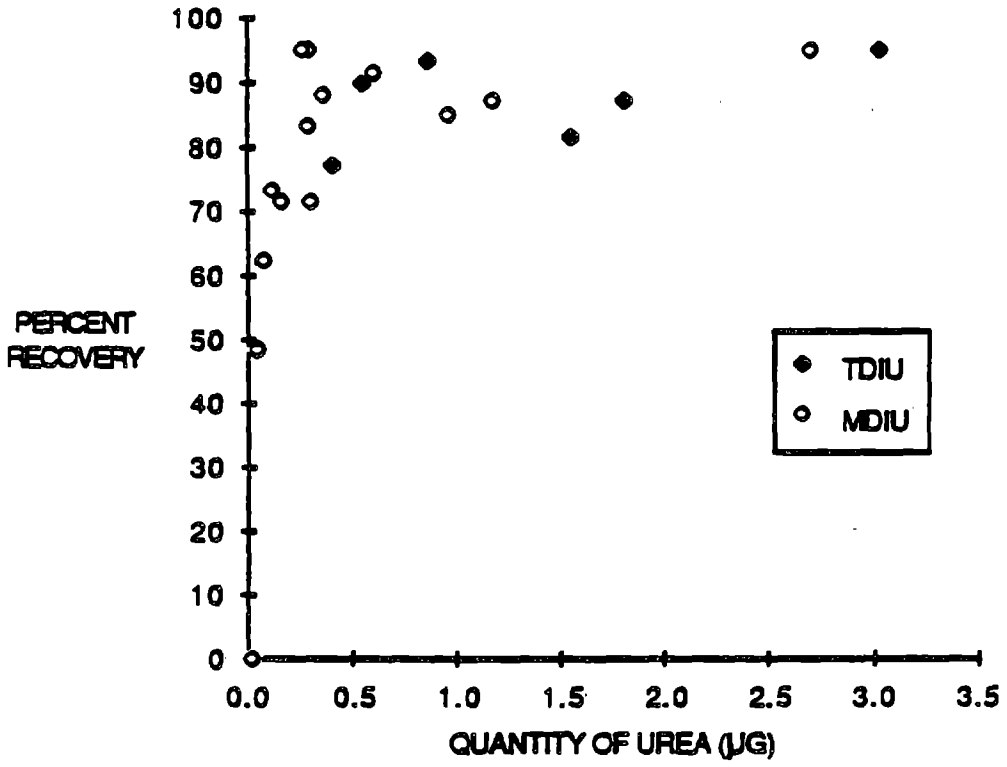


Figure 7. Recovery of MDIU and TDIU from coated filters. Each point is the average of 5-6 samples.

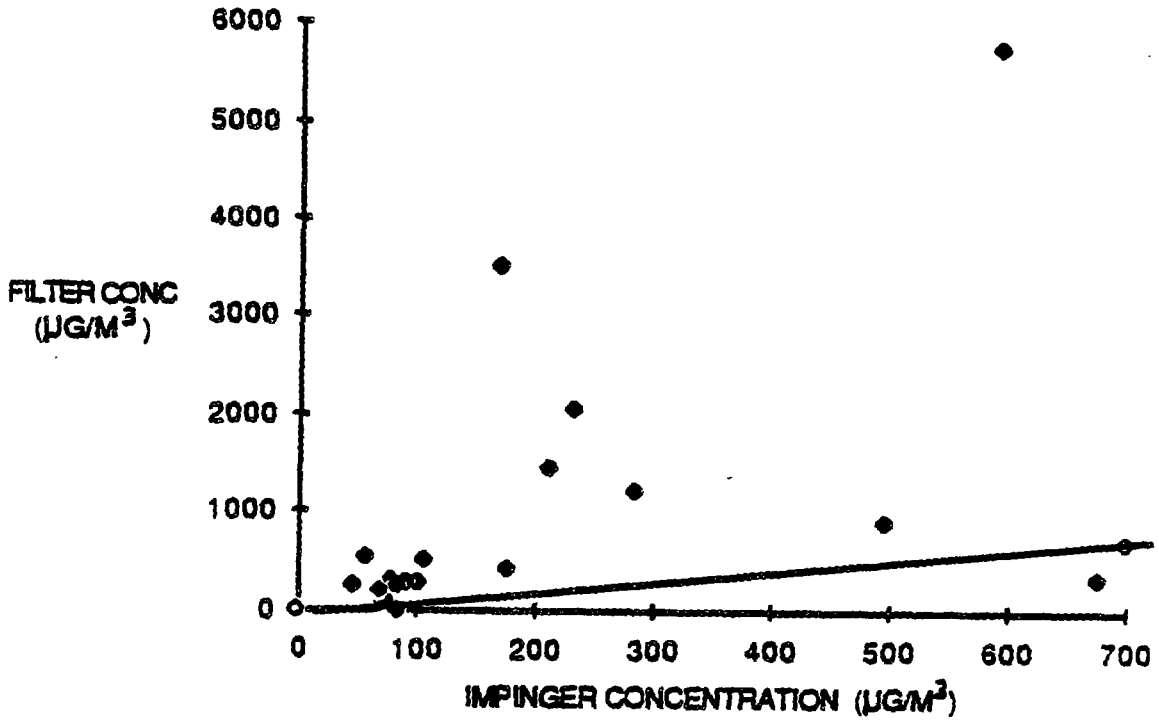


Figure 8. Scatter plot of paired determinations of isocyanate in laboratory-generated aerosol. The concentration determined from the impinger sample is plotted against the concentration determined from the corresponding coated filter. The straight line indicates where the concentration determined from the impingers would equal the concentration determined from the coated filters.

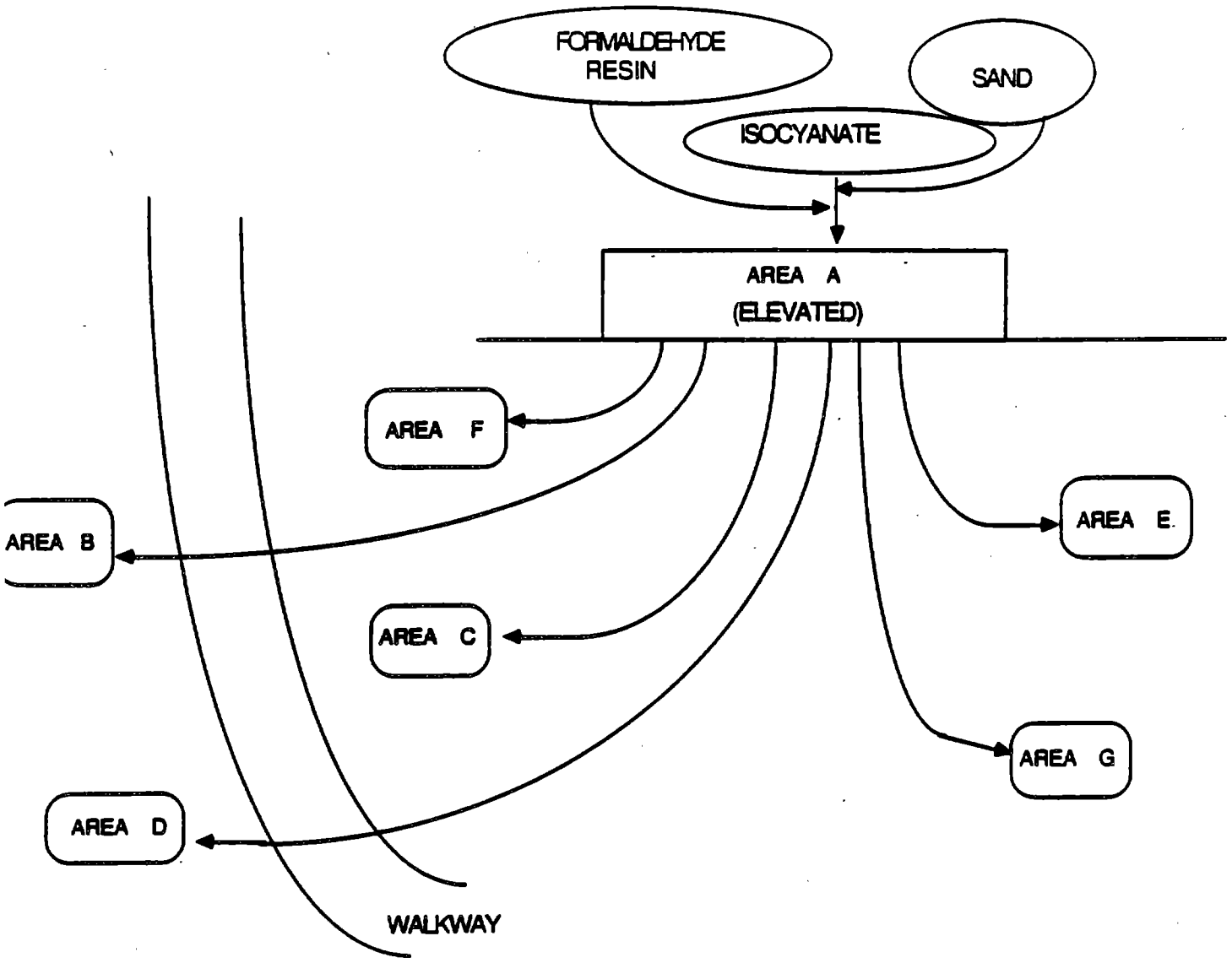


Figure 9. Layout of areas sampled during the field test of the coated-filter method at a foundry.