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*Laboratory Development and
Field Evaluation
of a Generic Method for
Sampling and Analysis
of Isocyanates*

Revised Final Report

Prepared for:

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August 1995

**RADIAN
CORPORATION**



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Disclaimer

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Abstract

The U.S. Environmental Protection, under the authority of Title III of the Clean Air Act Amendments of 1990, requires the identification and evaluation of a sampling and analysis method for the following isocyanates: hexamethylene-1,6-diisocyanate; 2,4-toluene diisocyanate; methylene diphenyl diisocyanate; and methyl isocyanate. A laboratory study was performed to develop a sampling and analysis method. This effort was followed by three field validation tests using the approach specified in the EPA Method 301 protocol. The sampling method employed was a modification of the EPA Method 5, using a derivatizing agent to stabilize the isocyanates for subsequent analysis. Samples were analyzed by high performance liquid chromatography under conditions adequate to separate and quantify all four compounds. The method bias and precision met the 301 criteria for an acceptable method as tested at the specified source types.

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Section 1 Introduction

Sampling and analytical methods for a particular analyte or group of analytes can be evaluated and validated by demonstrating their performance in field tests, thereby establishing the precision and bias of the methods experimentally. Few methods have been fully evaluated for sampling and analyzing the organic compounds listed in Title III of the Clean Air Act Amendments (CAAA) of 1990. For some analytes, methods have been developed and evaluated for sample analysis, but not for sample collection. Field validation may be performed by side-by-side comparison of a candidate method to a validated method to establish comparable performance for the same analytes in the same matrix (same source category). Another procedure for validation of a method is to spike known quantities of analytes into the collection apparatus in the field so that the precision and bias of the method can be demonstrated from sample collection through analysis.

The U.S. Environmental Protection Agency (EPA), under the authority of Title III of the CAAA of 1990, requires the identification and validation of sampling and analytical methods for the isocyanate compounds which are listed among the 189 hazardous air pollutants identified in Title III. These isocyanate compounds are listed in Table 1-1. The laboratory developmental phase of the method was accomplished under Work Assignments 11, 21, and 40 on EPA Contract No. 68-D1-0010. The field evaluation of the method was accomplished under Work Assignments 55 (TDI), 66 (MDI), and 71 (HDI, MI, MDI, and TDI).

In all, three field tests were performed to accomplish the isocyanate field evaluation.

Table 1-1. Isocyanates Listed in the Clean Air Act Amendments of 1990

Hexamethylene-1,6-diisocyanate (HDI)
2,4-Toluene diisocyanate (TDI)*
Methylene diphenyl diisocyanate (MDI)
Methyl isocyanate (MI)

* The 2,6-TDI isomer may also be present but is not listed in the CAAA.

The objective of this work was to develop and evaluate the isocyanate sampling and analytical test method through field testing at operating stationary sources. The method was evaluated by collecting flue gas samples for the analysis of the individual isocyanate and evaluating the data for bias and precision. EPA Method 301, *Field*

Validation of Pollutant Measurement Methods from Various Waste Media, was used as the model for the experimental design of this method evaluation project. Analyte spiking was used with quadruplicate (QUAD) sampling trains to generate the required data. Each field evaluation was performed at an industrial facility which used a specific isocyanate in its manufacturing process. Only two of the quadruplicate trains were spiked for each run. The two unspiked trains were used to establish the background level of the target compound in the stack gas.

The sampling method utilizes a Method 5-type sampling train, which operates with a solution of 1-(2-pyridyl) piperazine and toluene in the impingers. Stack gas is extracted from the source through a heated, glass-lined probe and drawn through the impingers. Any isocyanate present in the stack gas reacts rapidly with the piperazine to form an isocyanate derivative. The quantity of isocyanate is determined by first evaporating the impinger solution to dryness and redissolving the derivatized isocyanate in acetonitrile followed by high performance liquid chromatographic (HPLC) analysis.

This report discusses the details of the laboratory developmental work and the three field evaluation studies. Section 2.0, Conclusions and Recommendations, summarizes the results and provides recommendations. Section 3.0 discusses the experimental approach for the laboratory and field studies and Section 4.0 provides a discussion of the results. The analytical instrument performance and associated quality control data are provided in Section 5.0. Section 6.0 presents the method quality control and EPA Method 301 statistical procedures.

Section 2.0 Conclusions and Recommendations

Based upon the results of the laboratory studies and three field test evaluations at three different source categories, the following conclusions can be made concerning the validity of the method as tested under the conditions described in this report:

2.1 Field Test #1 (TDI)

- The calculated values for precision (%RSD) for both the spiked and unspiked trains, 3.55 and 4.72, respectively, are both well within the acceptance criteria of less than 50% RSD found in Section 6.3 of the EPA Method 301. Therefore, the method as tested at a flexible foam manufacturing facility meets the precision requirements;
- The method bias, at the concentration levels tested, was found to be significantly different from zero at the 95% level of confidence when the data from all eight runs (minimum of six runs required) were used in the calculations. A correction factor of 1.053 would be required if all eight runs are included in the bias calculation. Good technical reasons exist for excluding one of the eight QUAD runs. If this run is statistically eliminated, no bias correction is required. In either case the correction factor is well within the acceptance criteria of 0.7 to 1.3 found in Section 1.2 of the EPA Method 301. Therefore, the method as tested at this source meets the bias and correction factor requirements; and
- The method as tested is sufficiently robust to allow testing at sources similar to the source tested in this study where the stack gas moisture is less than 1% by volume, the stack temperature is less than 30°C and the presence of other compounds that may interfere with the analysis is minimal.

2.2 Field Test #2 (MDI)

- The calculated values for precision (%RSD) for both the spiked and unspiked trains for eleven runs, 4.25 and 28.2, respectively, are both well within the acceptance criteria of less than 50% RSD found in Section 6.3 of the EPA Method 301. Therefore, the method as tested at a pressed board manufacturing facility meets the precision requirements;
- The method bias, at the concentration levels tested, was found to be significantly different from zero at the 95% level of confidence when the data from all eleven runs (minimum of six runs required) were used in the calculations. A correction factor of 1.084 would be required if all eleven runs were included in the bias calculation. The correction factor is well within the acceptance criteria of 0.7 to 1.3 found in Section 1.2 of the EPA Method 301. Therefore, the method as tested at this source meets the bias and correction factor requirements; and

- The method as tested is sufficiently robust to allow testing for MDI at sources similar to the source tested in this study where the stack gas moisture is less than 5% by volume, the stack temperature is less than 45°C and the presence of other compounds that may interfere with the analysis is minimal.

2.3 Field Test #3 (HDI, MDI, MI and TDI)

- The calculated values for precision (%RSD) for the spiked trains for HDI, MDI, MI, and TDI, (3.3, 2.8, 3.7, and 2.9, respectively) are all well within the acceptance criteria of less than 50% RSD found in Section 6.3 of the EPA Method 301. Therefore, the method as tested at a paint spray booth meets the precision requirements for a valid method.
- The method bias for HDI and MI, at the concentration levels tested, were found to be significantly different from zero at the 95% confidence level when the data from all twelve runs (minimum of six required) were used in the calculations. A correction factor of 0.9798 for HDI and 0.9701 for MI (acceptable range 0.7 to 1.3) would be required if all twelve runs are included in the bias calculation. The method bias for TDI and MDI were not significantly different from zero. Therefore, the method meets the bias criteria for a valid method for all four isocyanates as tested at a paint spray booth.
- The method as tested is sufficiently robust to allow testing at sources similar to the source tested in this study where the stack gas moisture is less than 1% by volume, the stack temperature is less than 30°C and the presence of other compounds that may interfere with the analysis is minimal.

Recommendations:

- Compile data and comments relative to testing at similar or different source categories in order to further evaluate/refine the method.
- Document the sampling and analytical protocols following the Environmental Monitoring Management Council (EMMC) and CFR 40, Subpart 60 formats for similar sampling and analytical methods.

Section 3 Experimental Approach

In order to ensure compliance with the CAAA, it is necessary to be able to accurately measure the emissions of the listed isocyanates from stationary sources. Since no validated method(s) for measuring these compounds existed at the time this work was begun, a laboratory study was initiated to develop a single sampling and analysis procedure that would be amenable to all four isocyanates. The source test method developed would be required to satisfy the quality control criteria for method precision, bias, detection limit, and ruggedness typically required for source test methods. A method for measuring the emissions of isocyanates from stationary sources was developed in a step wise approach.

3.1 Laboratory

The laboratory development of the method followed the approach outlined below.

- Perform a literature search relative to the four isocyanates with emphasis on sampling and analytical methods and the chemistry of the compounds;

The literature review provided information on the isocyanates relative to their uses, physiological effects, reactivity and previous approaches to sampling and analysis reported by other investigators. Due to the reactive nature of the isocyanates, two derivatization techniques were selected as possible approaches to developing a viable method.

- Evaluate the most promising sampling and analysis approaches;

The first approach that was evaluated was the reaction of isocyanates with a simple alcohol to form a stable urethane. No peaks were observed for the derivatized HDI and MI because the compounds have no chromophores detectable at 254 nm using HPLC as the analytical technique. Since a single analysis technique for all four compounds was desirable, a second derivatization technique was investigated. The use of 1-(2-pyridyl) piperazine (1,2-pp) produced derivatives of all four isocyanates with chromophores displaying sufficient absorptivity to provide acceptable detection limits.

- Perform dynamic spiking of the compounds into a prototype sampling train;

To simulate actual sampling conditions, a spiking apparatus was developed and used to dynamically spike a proposed sampling train configuration. The results of this experiment were used to identify and evaluate modifications to both the sampling and analysis approaches.

3.2 Field

The results of the laboratory experiments were used to formalize the train configuration and sample recovery procedures for actual field evaluation of the method. The procedures outlined in EPA Methods 1-5 were incorporated along with the safety considerations necessary for using toluene as the solvent in the impingers. It then became necessary to identify manufacturing facilities that used one or more of the four isocyanates and then obtain permission to visit each facility for the purpose of collecting samples using the proposed method.

Section 4 Results and Discussion

4.1 Laboratory Development

The results obtained from the development of a source sampling method for the four isocyanates listed in the CAAA are discussed in the following sections.

4.1.1 *Literature Search and Background Information*

Isocyanates are used extensively in the production of polyurethane materials such as flexible foam, enamel wire coatings, paint formulations, and in binders for the pressed board industry. Because of their widespread use and known adverse physiological effects such as bronchial asthma, allergic eczema, and skin irritation, several isocyanates have been listed in Title III of the Clean Air Act Amendments. The isocyanates of interest include:

- 2,4-toluene diisocyanate (TDI);
- methylene diphenyl diisocyanate (MDI);
- hexamethylene-1,6-diisocyanate (HDI); and
- methyl isocyanate (MI).

The aromatic isocyanates (TDI and MDI) are used in the production of urethane foams and pressed boards. The aliphatic isocyanate, HDI, is used as a hardener in automobile spray paint and MI is used in organic synthesis and as an additive to adhesives in polymer technology. Table 4-1 lists the physical properties, Table 4-2 lists the reactivity data, and Figure 4-1 shows the structures of each of the isocyanates.¹ The isocyanate 2,6-TDI is not included in Title III of the Clean Air Act Amendments, but because it is present as a large percentage of the total isocyanates when 2,4-TDI is used it is included as part of the analysis, but excluded from the validation procedure.

Table 4-1. Physical Properties of Isocyanates

Parameter	TDI	HDI	MDI	MI
Chemical Family	Aromatic Isocyanate	Aliphatic Isocyanate	Aromatic Isocyanate	Aliphatic Isocyanate
Chemical Name	2,4 toluene diisocyanate	hexamethylene-1,6-diisocyanate	methylene diphenyl diisocyanate	methyl isocyanate
CAS Number	584-84-9	822-06-0	101-68-8	624-83-9
Formula	C ₉ H ₆ N ₂ O ₂	C ₆ H ₁₂ N ₂ O ₂	C ₁₉ H ₁₆ N ₂ O ₂	C ₂ H ₄ NO
Physical Form	Liquid	Liquid	Solid	Liquid
Color	White to Pale Yellow	Colorless	White to Yellow	Colorless
Odor	Sharp, Pungent	Sharp, Pungent	No Odor	Sharp
MW	174.16	168	250.25	57.1
BP°C	251	213	172	39
MP°C	22	-55	37	-80
Sol H ₂ O	Not Soluble, Reacts Slowly with Water	Not Soluble, Reacts with Water to Liberate CO ₂	0.2g/100g Water at 20°C	6.7g/100g Water 20°C, Reacts Slowly
Specific Gravity	1.22 at 25°C	1.05 at 25°C	1.27 at 25°C	0.96 at 25°C
Vapor Pressure	0.025 mmHg at 25°C	0.05 mmHg at 25°C	0.05 mmHg at 20°C	348 mmHg at 25°C

Table 4-2. Reactivity Data of Isocyanates

	TDI	HDI	MDI	MI
Stability	Stable Material at Standard Temperature and Pressure	Stable at Standard Temperature and Pressure	Stable at Standard Temperature and Pressure	Stable in solutions of acetone for 24 hours.
Hazardous Polymerization	May Occur; May occur if in contact with moisture or other materials which react with isocyanates. Self reaction may occur at temperatures over 170°C or at lower temperatures if sufficient time is involved	May Occur; Contact with moisture or other materials which react with isocyanates or temperatures over 204°C may cause polymerization.	No Information Available	May occur at temperatures above 25°C
Incompatibilities	Water, amines, strong bases, alcohols, will cause some corrosion to copper alloys and aluminum reacts with water to form heat, CO ₂ and insoluble ureas.	Water, amines, strong bases, alcohols, metal compounds and surface active materials.	Strong alkalis, acids and alcohol.	Water causes formation of CO ₂ and methylamine gases. The reaction with water is more rapid in the presence of acids, alkalis and amines. Contact with iron, tin, copper (or salts of these elements) and with certain other catalysts (such as triphenylarsenic oxide, triethyl phosphine and tributyltin oxide may cause violent polymerization. Attacks some forms of plastics and rubber coatings.
Instability Conditions	Temperatures Above 170°C	High Heat and Moisture	Temperatures above 37.8°C	Moisture, mineral acids and bases
Decomposition Products	By high heat and fire: CO, oxides of Nitrogen, traces of HCN, TDI vapors and mist.	By high heat and fire: CO ₂ , CO, oxides of Nitrogen, traces of HCN, HDI	By Fire: CO and oxides of nitrogen.	CO, CO ₂ and HCN

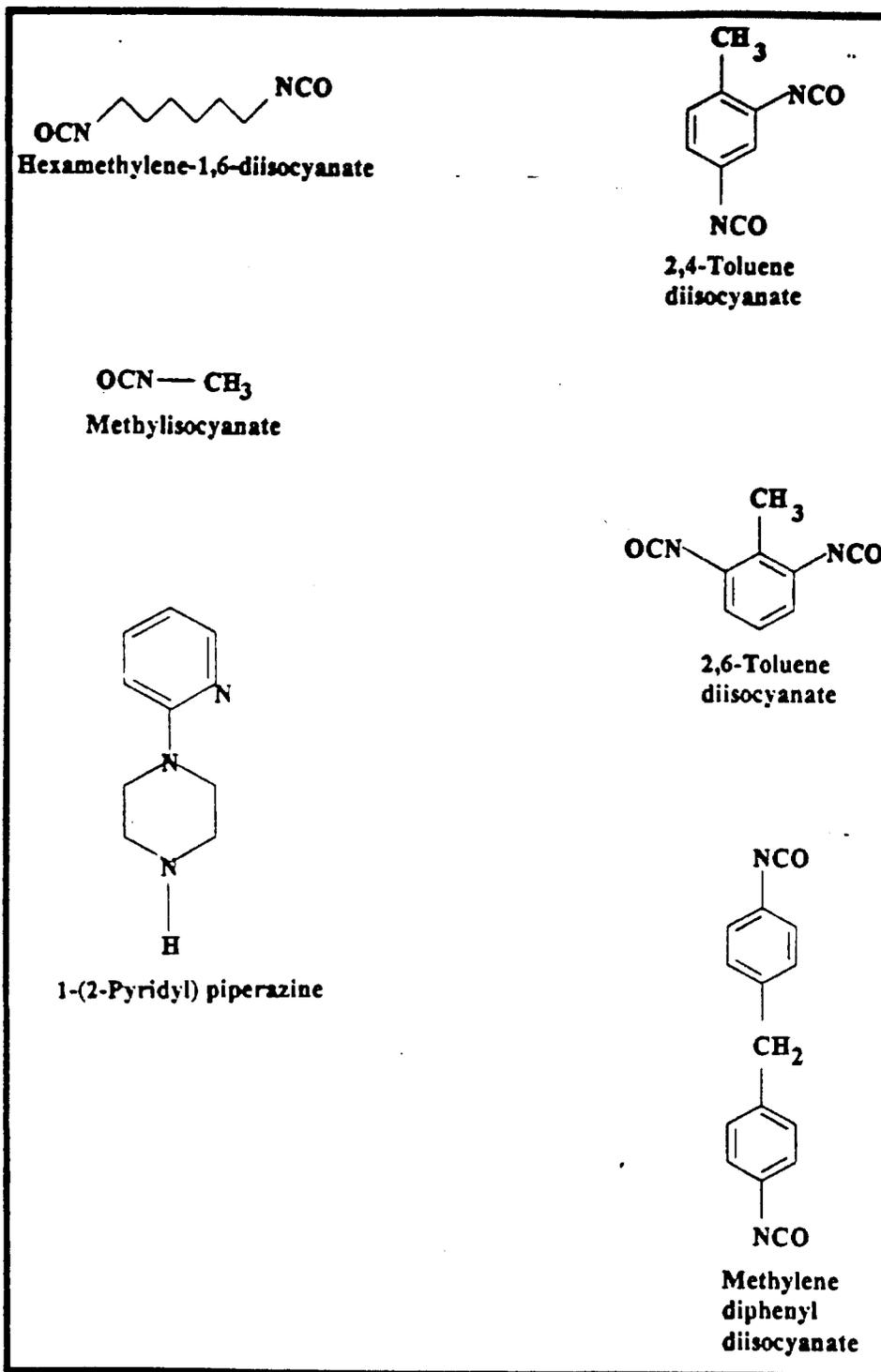


Figure 4-1. Structures of the isocyanates and derivatizing agent.

Isocyanates undergo several different types of reactions. The reaction of an isocyanate with an alcohol produces a urethane. The reaction is a simple alcohol addition mechanism.² The oxygen in the alcohol group combines with the carbon on the cyano group of the isocyanate. The displaced hydrogen from the alcohol combines with the free electron on the nitrogen from the cyano group to form a stable urethane. The article by E.H. Niemine, et al., detailed the potassium ethoxide method for derivatizing aromatic isocyanates with ethanol (EtOH).³ Figure 4-2 shows the reaction of 2,4-TDI with ethanol. This reaction showed promise as a derivatization reaction, because the reagents are readily available and the reaction appeared to be immediate.

A second reaction of isocyanates is the reaction of an isocyanate with an amine which produces an urea. The reaction proceeds as a one-step addition of the isocyanate to the $-NH_2$ group of the amine.² The article by P.A. Goldberg, et al., detailed a method for derivatizing isocyanates with an aromatic amine 1-(2-pyridyl) piperazine (1,2-pp).⁴ Figure 4-3 shows the reaction of methyl isocyanate with 1,2-pp. This method was also promising as a derivatization reaction, because the reagents are readily available and all isocyanates can be detected by ultraviolet (UV) absorption. A paper by V. Dharmarajan, et al., detailed a method for generating isocyanate atmospheres, sampling with mini impingers, and derivatizing the isocyanate with 1,2-pp.

The third reaction that an isocyanate can undergo is with water. Water combines with the isocyanate to form an unstable carbamic acid (Figure 4-4). The carbamic acid decomposes to form an amine and carbon dioxide, and in the presence of an additional isocyanate, a stable polyurethane is formed. The reaction of diisocyanates with water is the basis for the production of polyurethane foams. This reaction as an analytical tool is undesirable for analysis because of the unlimited number of polymers that could be formed in an uncontrolled environment (i.e., stack emissions). The laboratory investigation of these reaction mechanisms as possible approaches to the development of a sampling and analysis method for stationary sources is discussed in the following sections.

4.1.2 Evaluation of Derivatization Techniques

4.1.2.1 Potassium Ethoxide Method

The potassium ethoxide derivatization method was investigated first because the available data showed that there was an immediate reaction with the isocyanates, the reagent was readily available, and the derivatives were stable for long periods of time. The reaction of ethanol with an isocyanate is accomplished by a simple alcohol addition mechanism (Figure 4-2). The oxygen in the alcohol group from the ethanol combines with the carbon on the cyano group of the isocyanate. The displaced hydrogen from the alcohol combines with the free electron on the nitrogen from the cyano group to form a stable urethane.

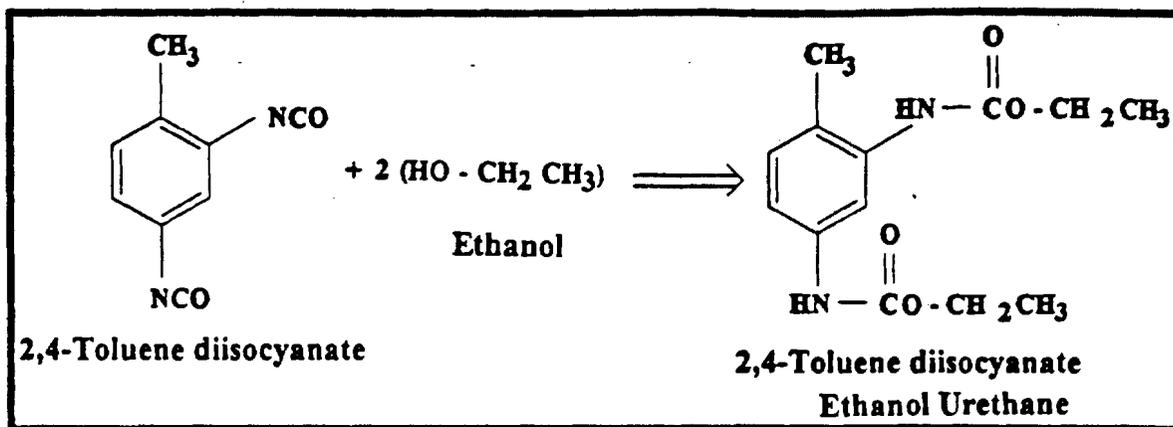


Figure 4-2. Reaction of ethanol with 2,4-TDI.

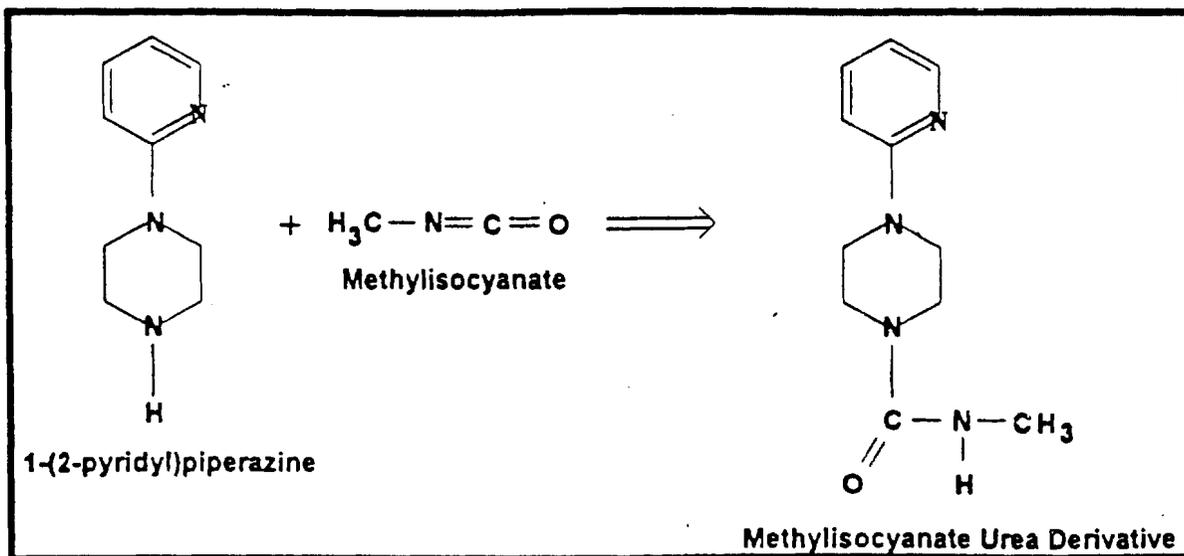


Figure 4-3. Reaction of 1,2-PP with methyl isocyanate.

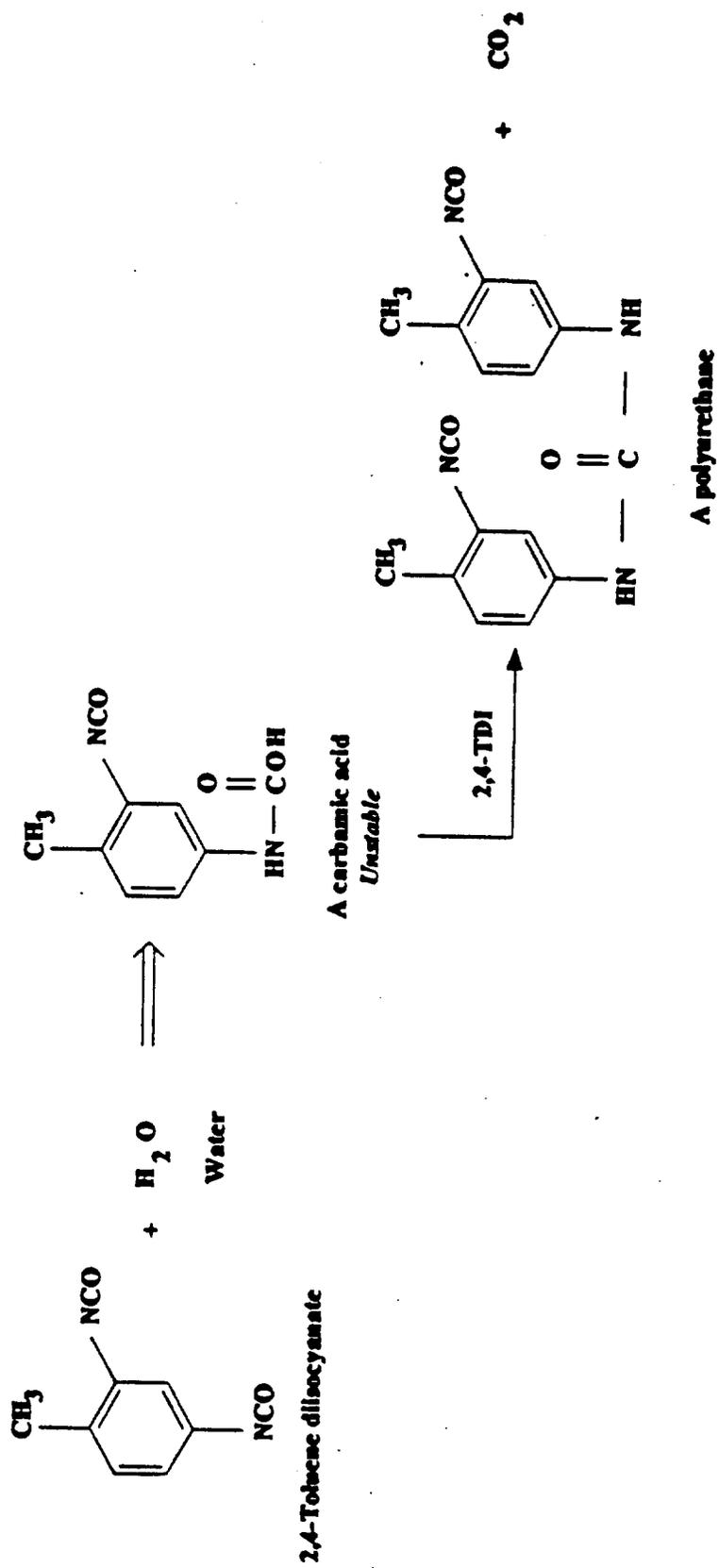


Figure 4-4. Reaction of 2,4-TDI with water.

The evaluation of the method proceeded by first preparing the isocyanate derivatives then analyzing by HPLC. The derivatizing solution was prepared by adding 1 gram of potassium hydroxide (KOH) to 500 mL 99.9% ethanol. Stock solutions of each isocyanate were prepared by dissolving 10 mg of the isocyanate in 50 mL methylene chloride. A 100 μ L aliquot of each solution was added to 20 mL of the absorption solution and the pH adjusted to 5 with hydrochloric acid (37%). The potassium chloride (KCl) precipitate was removed by filtration and washed with ethanol, saving the rinses. The KCl was discarded and the supernatant was evaporated to dryness at 35°C under vacuum. The residue was dissolved in 1 mL of (50:50) ethanol:water and 20 to 50 μ L was injected onto the column of the HPLC.

The derivatives were analyzed as follows:

- Instrument: Waters Model 510 HPLC;
- Valve: Rheodyne 6 port injector with 50 μ L loop;
- Detector: Varian UV-50; 254 nm; 0.02 au/s;
- Solvent: Acetonitrile (ACN):Tetrahydrofuran (THF):H₂O (30:30:40):1 mL/min; and
- Column: Zorbax ODS C18 4.6 mm x 250 mm.

There were no peaks observed for HDI and MI because they have no strong chromophores detectable at 254 nm. Several large peaks were detected for 2,4-TDI and MDI. A positive identification of the derivatives, ideally with the presence of single peak chromatograms, was necessary to evaluate the method.

The derivatization method was, therefore, modified to allow the neat isocyanate to be added directly to the absorption solution. A 30 mg portion of MDI and 10 μ L volumes of MI, HDI, and TDI were transferred to individual vials containing 5 mL of the derivatizing solution prepared as described above. To compare the derivatized isocyanates with the underivatized isocyanates, a 30 mg portion of MDI and 10 μ L volumes of MI, HDI, and TDI were transferred to individual vials without the derivatizing reagent and diluted with hexane. Each of the solutions, derivatized and underivatized, was diluted 1:10 with tetrahydrofuran (THF) before analysis.

The following observations were made for the reaction of EtOH with the isocyanates:

- TDI: Rapid evolution of gas and the formation of a white precipitate.
- MI: Rapid evolution of gas, no precipitate formation was observed.
- HDI: Evolution of gas was not observed. Two layers formed after the THF was added and solidification occurred after 20 minutes. The solid was dissolved in ACN for analysis.
- MDI: Immediate reaction with slow evolution of gas, no precipitate observed.

Each of the solutions was analyzed using the above HPLC conditions. The chromatogram of the underivatized 2,4-TDI and MDI revealed significant peak tailing, but the peak shape was gaussian for the derivatized isocyanate. Underivatized TDI eluted at 5.37 minutes and derivatized TDI eluted at 4.71 minutes. Underivatized MDI eluted at 6.86 minutes and derivatized MDI eluted at 6.36 minutes. No peaks were observed for MI or HDI, derivatized or underivatized. Since MI and HDI could not be analyzed by HPLC with UV detection, gas chromatography (GC) with a nitrogen specific detector (NPD) was employed as an alternate method for analysis of these derivatized isocyanates.

The derivatives were analyzed on a GC under the following conditions:

- Instrument: Varian 6000 with autosampler;
- Detector: NPD, 320°C;
- Injector: 320°C;
- Column: RTX-5, 30m x 0.54 mm; and
- Oven: 40°C for 2 min., ramp at 10° C/min. to 320°C, 320°C for 40 min.

The chromatograms showed multiple peaks for each of the four derivative solutions as well as the blank EtOH. Peaks occurring in the sample chromatogram that were due to background were eliminated by overlaying the blank chromatogram onto each sample chromatogram. Using this approach, a major peak was identified for 2,4-TDI and MI. No peaks specific for HDI and MDI could be identified.

Gas chromatographic/mass spectral (GC/MS) analysis confirmed the presence of a TDI derivative and an MI derivative. The other isocyanate derivatives could not be positively identified through GC/MS analysis. The investigation of the potassium ethoxide reaction was suspended because the HPLC analysis was selective only for the aromatic isocyanates and the GC method was inconclusive.

An alternative approach was the reaction between an isocyanate and the derivatizing compound 1-(2-pyridyl) piperazine (1,2-pp).

4.1.2.2 1-(2-Pyridyl) Piperazine Method

The derivatizing reagent 1,2-pp was chosen because the aromatic ring can be detected by UV spectroscopy. With the addition of the isocyanate, each compound could potentially be separated chromatographically by HPLC with a UV detector. The analytical method would then be responsive to each of the four isocyanates because the derivatizing reagent would provide the chromophore.

The derivatization reaction proceeds as a one-step addition of the isocyanate to the -NH group of 1,2-pp (Figure 4-3). The analytical method described in Reference 2 was evaluated as described in the following paragraphs.

4.1.2.3 Initial Preparation and Evaluation of 1,2-pp Isocyanate Derivatives

Each isocyanate (0.8 mmol of neat material) was dissolved in a separate 10 mL volume of methylene chloride. A 150 μ L volume of neat 1,2-pp was added to each isocyanate standard. Separate solutions of each of the isocyanates were prepared as above, except that 1,2-pp was not added to the solutions. Each of the solutions was diluted 1:10 with methylene chloride. A 10 μ L aliquot was injected on the HPLC system described below:

- Instrument: Varian 5500 with autosampler;
- Data System: Nelson 2600 (1 volt);
- Column: Hypersil BDS C18, 5 micron particle size, 250 mm x 4.6 mm;
- Mobile Phase: Acetonitrile/0.1M Ammonium Acetate Buffer (AAB);
- For TDI and HDI: 31:69 ACN/ (0.1 M AAB, pH 6.2), isocratic;
- For 1,2-pp and MI: 20:80 ACN/ (0.1 M AAB, pH 6.2), isocratic;
- For MDI: From 31:69 ACN/ (0.1 M AAB, pH 6.2) to 90:10 ACN:AAB over 5 mins., gradient;
- Detector: Ultraviolet at 254 nm (0.5 AUFS); and
- Flow Rate: 2 mL/min.

Analysis showed that derivatives formed for all four isocyanates and that these components could be separated and analyzed in the presence of reagents and unreacted isocyanates (Figures 4-5 through 4-12). Based on these findings, crystalline derivatives were prepared, isolated, and purified for each of the isocyanates.

4.1.3 Preparation of Derivatives

4.1.3.1 Dimethyl Sulfoxide as the Solvent (HDI, TDI, MDI)

The crystalline derivatives were prepared by first dissolving 0.8 mmol of the isocyanate in 3 mL of dimethyl sulfoxide (DMSO).⁴ Then 1,2-pp (1.8 mmol) was dissolved in 3 mL of DMSO. The two mixtures were combined, heated to 60°C, and stirred for 15 minutes. The reaction was quenched by adding 200 mL of deionized water, which also caused the derivative to become insoluble and precipitate. The precipitate was removed by filtration, washed with water, and dried at 50°C. All of the isocyanates formed a precipitate except MI. A separate approach was established for MI and is discussed in Section 4.1.3.4.

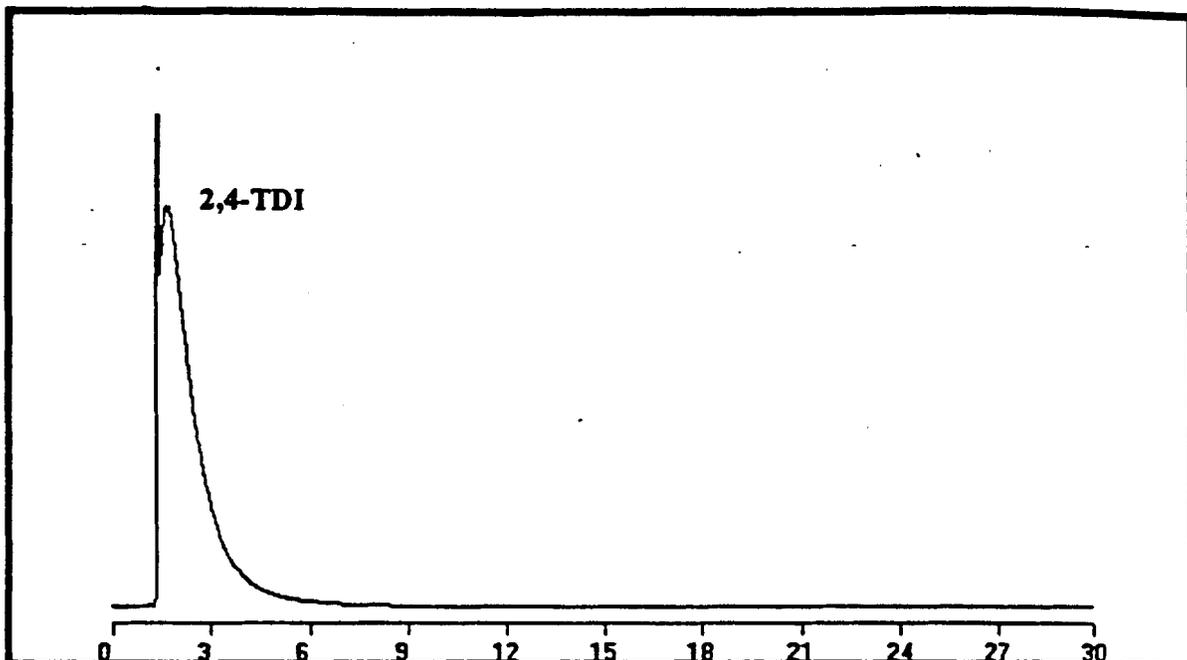


Figure 4-5. HPLC chromatogram of underivatized 2,4-TDI mobile phase - 31:69 ACN:AAB (isocratic).

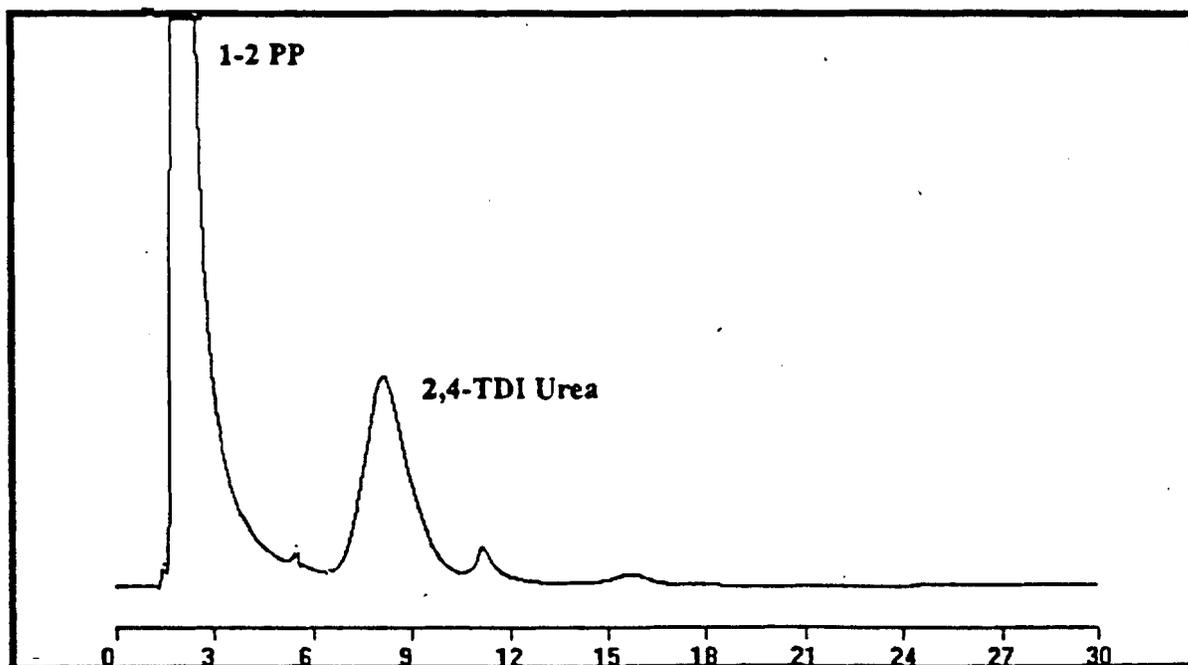


Figure 4-6. HPLC chromatogram of 2,4-TDI urea mobile phase - 31:69 ACN:AAB (isocratic).

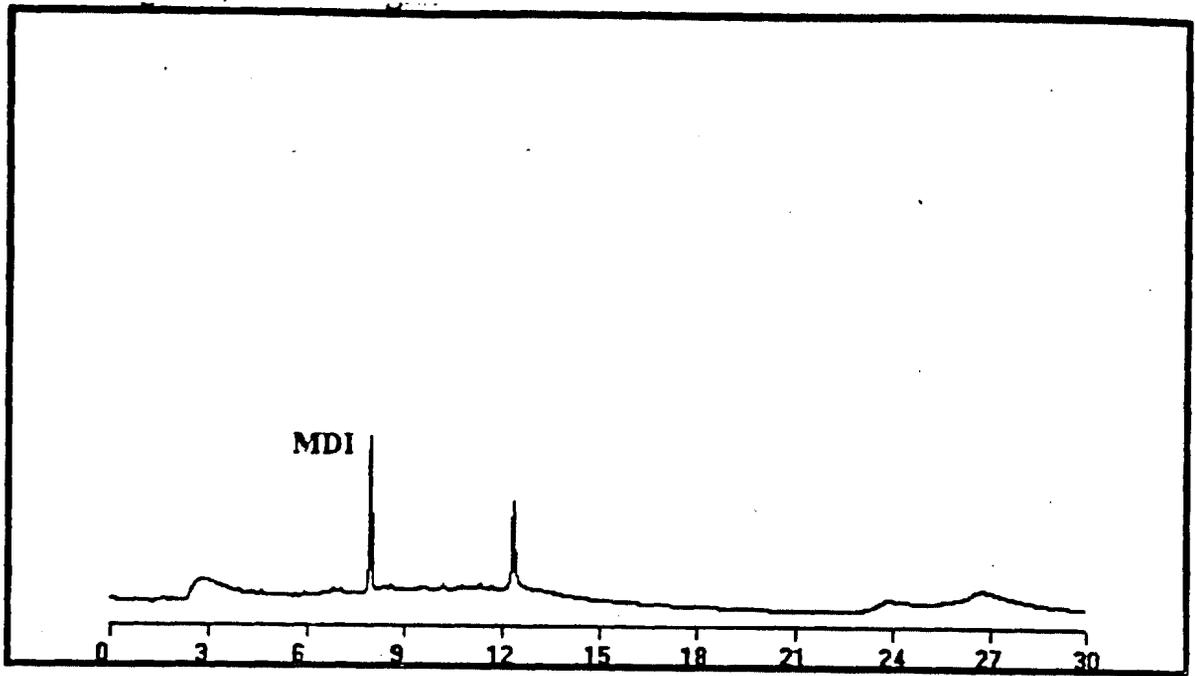


Figure 4-7. HPLC chromatogram of underivatized MDI Gradient Program - 31:69 to 90:10 (ACN:AAB)

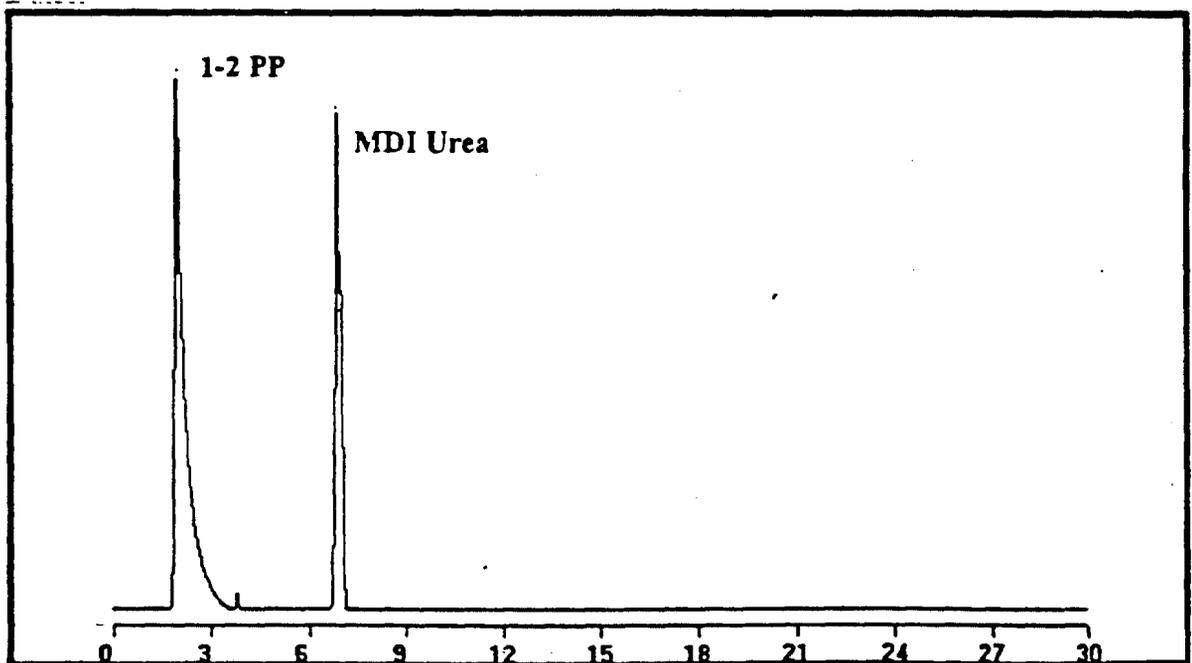


Figure 4-8. HPLC chromatogram of MDI Urea Gradient Program - 31:69 to 90:10 (ACN:AAB).

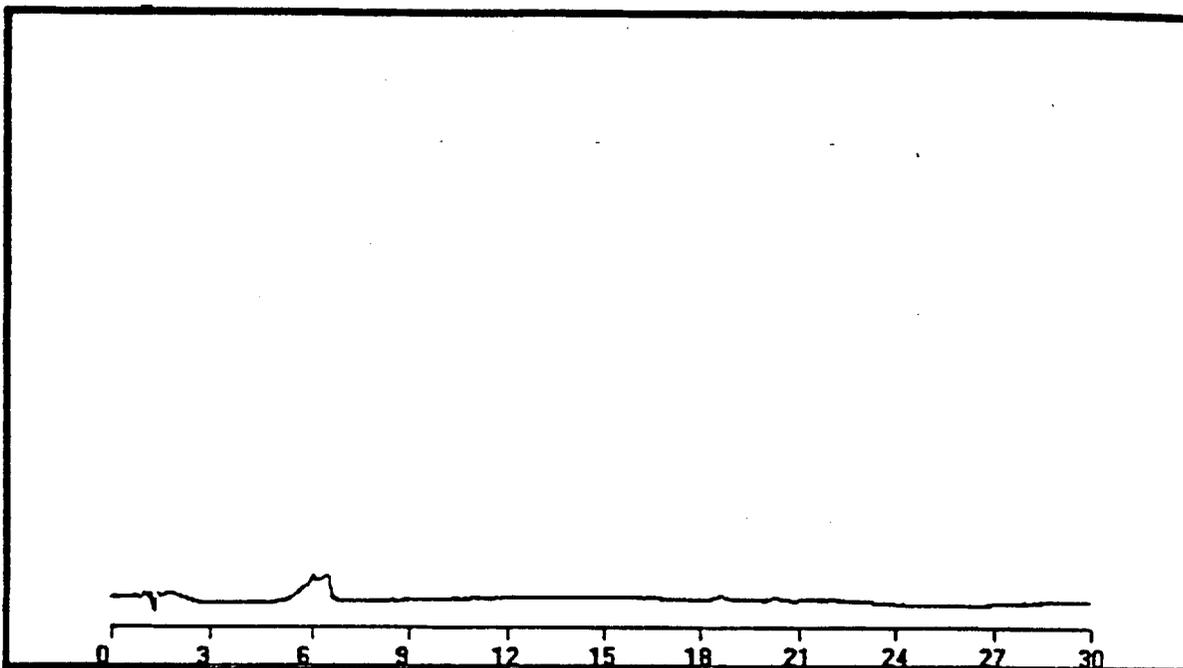


Figure 4-9. HPLC chromatogram of underivatized HDI mobile phase - 31:69 ACN:AAB (Isocratic).

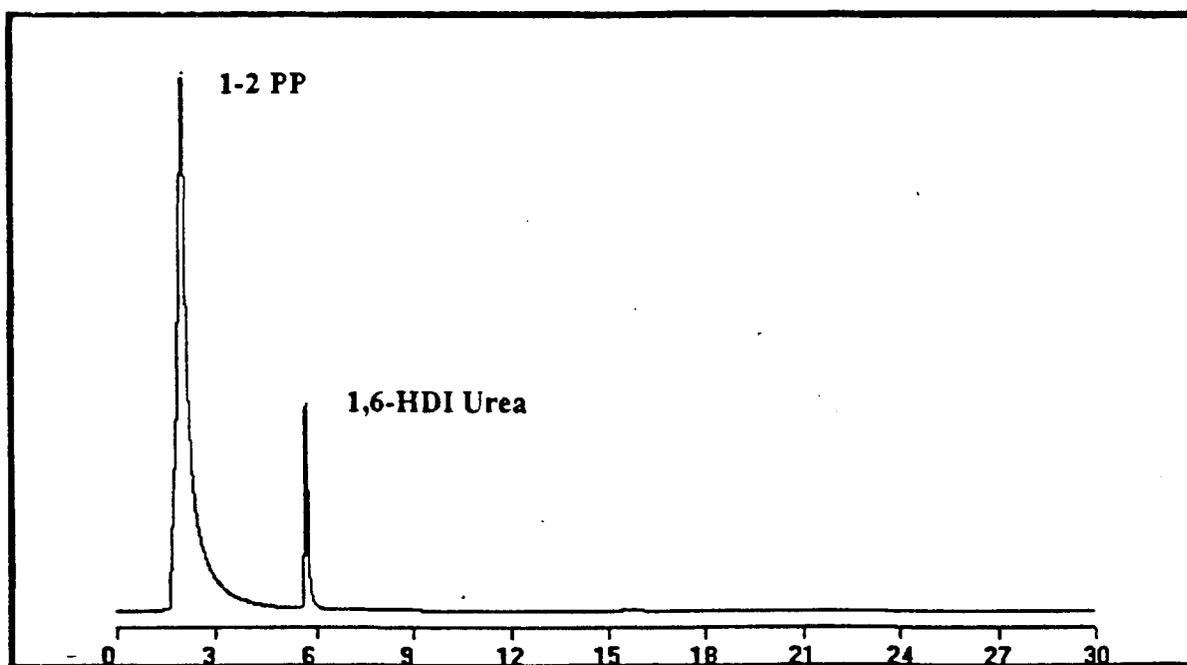


Figure 4-10. HPLC chromatogram of HDI urea Mobile Phase - 31:69 ACN:AAB (isocratic).

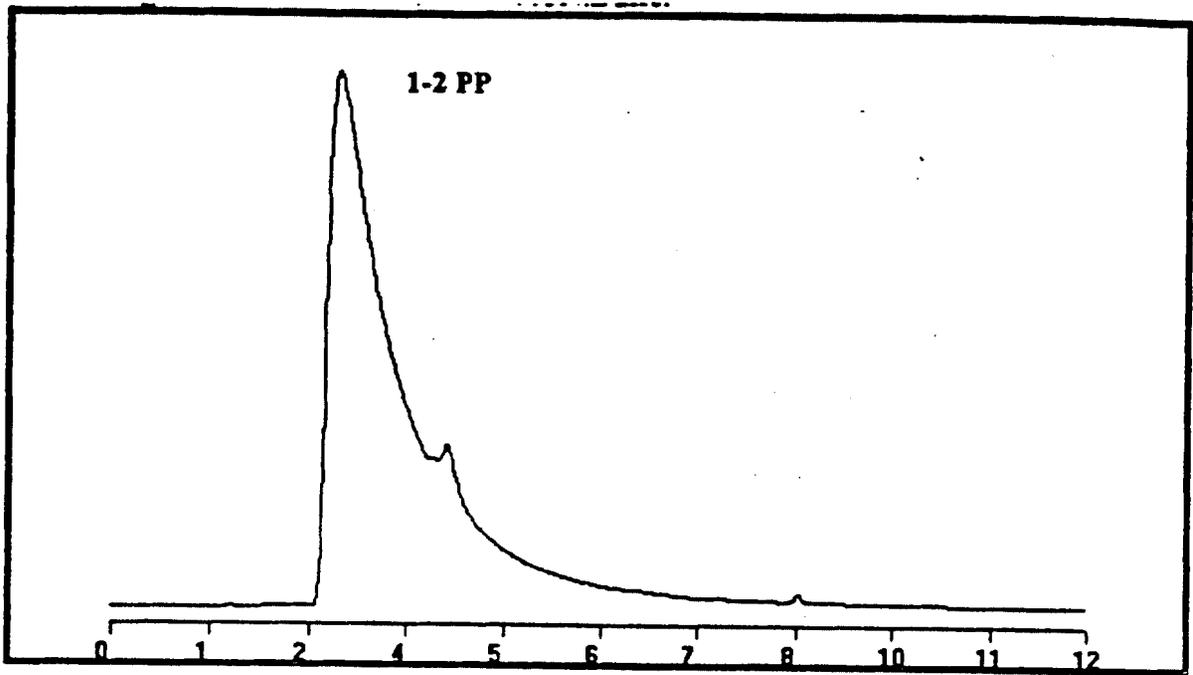


Figure 4-11. HPLC chromatogram of 1,2-PP Mobile Phase - 20:80 ACN:AAB (Isocratic).

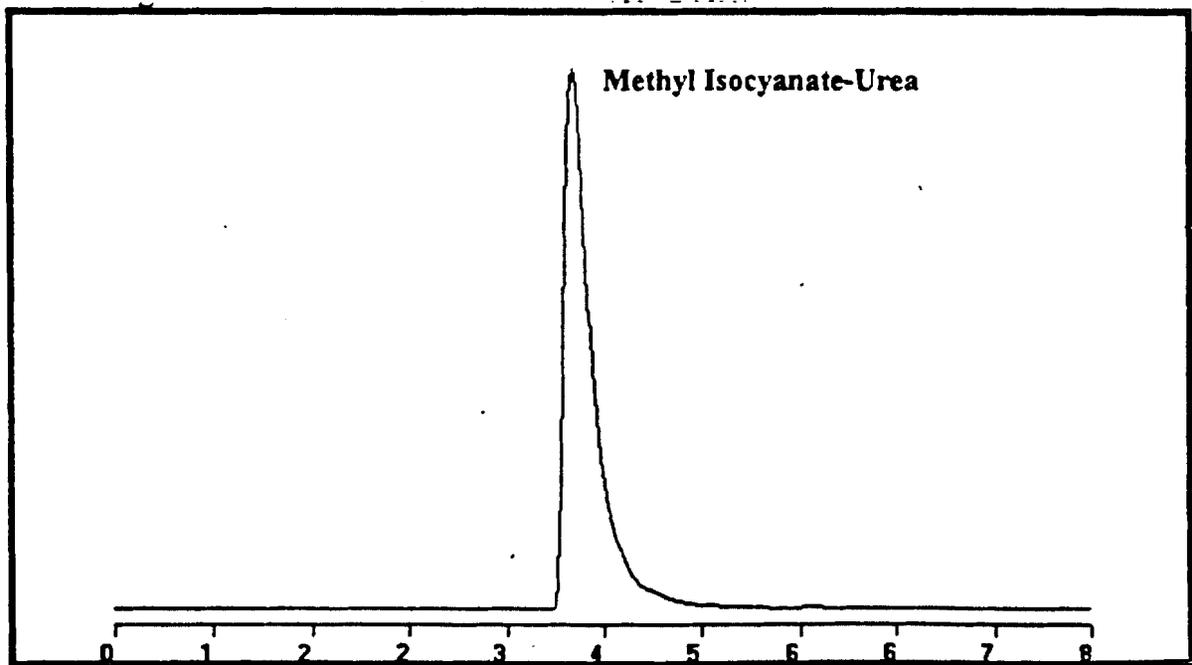


Figure 4-12. HPLC chromatogram of MDI Urea Mobile Phase - 20:80 ACN:AAB (Isocratic).

The HPLC analysis of the 2,4-TDI urea showed several unidentified peaks. Through a personal communication with a representative of a manufacturer of isocyanates, the extra peaks were determined to be the result of a reaction or series of reactions between the solvent DMSO and the neat isocyanate. The resulting solution contained isomers of the isocyanate that contained oxygen substituents. The use of DMSO was abandoned in favor of ACN, a less reactive solvent.

4.1.3.2 Acetonitrile as the Solvent (HDI, TDI, MDI)

Derivatives were prepared by dissolving 150 mg of each isocyanate in individual 5 mL volumes of ACN. The derivatizing solution was prepared by dissolving 300 μ L of 1,2-pp in 5 mL ACN. The two solutions were then mixed. A white precipitate formed for each of the isocyanates. The reactions were quenched by adding 150 mL of water. Each derivative was removed by filtration and air dried. The precipitates were redissolved in a minimum volume of ACN. A 150-mL volume of water was added to precipitate the crystals, which were filtered, air dried, and transferred to 20 mL screw cap vials for subsequent analysis. The HPLC analysis did not show any unidentified peaks, and the process for preparing the derivatives was considered a success. There was a concern that unless the ACN was dry, water may react with the isocyanates forming polymers. The use of ACN for the preparation of the crystals was abandoned in favor of methylene chloride (MeCl_2).

4.1.3.3 Methylene Chloride as the Solvent (HDI, TDI, MDI)

Derivatives were prepared by dissolving 500 mg of each isocyanate in individual 100 mL volumes of MeCl_2 , except for MDI which was dissolved in 250 mL of MeCl_2 . A 5-mL volume of 1,2-pp was added to each of the solutions, stirred and allowed to react overnight. A 150-mL volume of hexane was added to each of the solutions to precipitate the ureas. The precipitate was then filtered and washed with 50 mL of hexane and dissolved in a minimum volume of methylene chloride. A 150-mL volume of hexane was added to precipitate the urea, followed by filtration and a hexane wash. The precipitate was again dissolved in MeCl_2 , precipitated and washed with hexane, filtered, and then dried at 50°C. This process produced white, powdered crystals which showed no impurities when analyzed by HPLC.

4.1.3.4 Derivatization of Methyl Isocyanate

Special attention was paid to the derivatization of MI because it did not form a precipitate when added to a solution containing 1,2-pp. The derivatization approach was modified to verify that MI could be derivatized and analyzed along with the other isocyanates.

The MI derivative was prepared by transferring 100 μ L of neat MI to 1 mL of ACN and adding 300 μ L of neat 1,2-pp. The solution was shaken for 5 minutes and then diluted 1:1000 with ACN for analysis. This solution was prepared so that the 1,2-pp would be in excess due to the toxicity of MI.

The HPLC analytical conditions were changed to: 20:80 ACN:Buffer for 4 min, a gradient from 4 minutes to 20 min to 60:40 ACN:Buffer. Two peaks were observed in the chromatogram, presumably the excess 1,2-pp and the derivatized MI. To determine the identity of these peaks, a 20 μ L volume of MI was then added to the 1:1000 dilution and the solution reanalyzed. The 1,2-pp peak became smaller and the MI peak became larger thus confirming the formation of the MI derivative and establishing the retention time of the MI derivative.

4.1.4 Reaction Kinetics Study

The 1,2-pp was chosen for the derivatization of the isocyanates because all the isocyanates could be derivatized, chromatographically separated, and showed linear response with increasing concentration. A procedure was then developed to determine the completeness of the reaction between 1,2-pp and the isocyanates.

The completeness of the reaction had to be determined under varying conditions. The reaction was studied with the absence of water, the presence of water, the presence of acidic water, and the presence of basic water. In addition, toluene was selected as a candidate for use in the sampling impingers because it is the solvent of choice for many of the studies described in the literature. Toluene has a lower vapor pressure than acetonitrile and would be more likely to be retained in an impinger during sampling. Toluene is not miscible with water and, therefore, the possibility of the reaction of TDI with water is minimized. Toluene is also less toxic than ACN.

A recovery study was performed in ACN and in toluene to determine the best solvent for the impinger solution. Mixtures of known concentrations of TDI and 1,2-pp were prepared in duplicate in ACN and in toluene. The mixtures were prepared dry (no moisture added), with 20% water, with 20% water adjusted to pH 3 using sulfuric acid, and with 20% water adjusted to pH 11.7 using sodium hydroxide. Standards prepared from the purified crystals of the derivatized TDI were used to calibrate the HPLC. The solutions were analyzed under the following HPLC conditions:

- Instrument: Rainin HPXL Delivery system, Waters 710B WISP autosampler;
- Data System: Nelson 2600 (1 volt);
- Column: Zorbax ODS (4.6 mm ID x 25 cm);
- Gradient: 25:75 ACN/0.1 M Ammonium Acetate Buffer, pH 6.2, hold 2 min, then to 60:40 over 19.5 min, then resetting to initial conditions;
- Detector: Rainin Dynamax Dual-Wavelength, 254 nm (0.5 AUFS);
- Flow Rate: 2 mL/min; and
- Injection Volume: 50 μ L.

Table 4-3 summarizes the results of the analysis. The derivatization reaction between 1,2-pp and TDI indicates completion for the ACN solutions with and without water added as demonstrated by recoveries of 90% or better. The same was true for the toluene solutions with and without water added. However, when acidic or basic water was added the percent recoveries from the ACN solutions drop to 0 percent. The recoveries from the toluene mixtures with acidic or basic water added averaged 30% and 86%, respectively. Because there is a single phase system when ACN is the solvent, the neat isocyanate is in constant contact with the acidic or basic water and the reaction between 1,2-pp and TDI is adversely affected. In contrast, when toluene is used as the solvent the isocyanate is not in direct contact with the acidic or basic water in a two-phase system and the derivatization reaction is less affected.

Table 4-3. Recoveries for 2,4-TDI Derivative Under Varying Conditions of Moisture, pH and Solvent

Sample ID	Amount μg	Target μg	% Target
ACN-TDI-(1-2 PP)	111	109	102
	97	109	89
TOL-TDI-(1-2 PP)	103	85	121
	105	85	124
ACN-TDI-(1-2 PP)-H ₂ O	116	109	106
	111	109	102
TOL-TDI-(1-2 PP)-H ₂ O	96	68	141
	95	68	140
ACN-TDI-(1-2 PP)-pH3	0	109	0
	0	109	0
TOL-TDI-(1-2 PP)-pH3	25	68	37
	15	68	22
ACN-TDI-(1-2 PP)-pH 11.7	0	230	0
	0	230	0
TOL-TDI-(1-2 PP)-pH 11.7	240	280	86
	241	280	86

The studies described above indicate that the reaction between 1,2-pp and TDI does go to completion as indicated by the high recoveries. However, the rate at which this reaction occurs was still in question and, therefore, a set of dynamic spiking experiments was designed to test the proposed sampling procedure under conditions that simulated actual source testing for isocyanates (Section 4.1.12).

4.1.5 Stability of Isocyanate Urea Crystals

The stability of the isocyanate urea crystals was evaluated on two separate occasions. The stability of the MDI-Urea crystals was evaluated in November 1993 during the second field test, and the stability of the HDI, TDI, and MDI-Urea crystals was evaluated in May 1994 during the third field test.

4.1.5.1 Stability of MDI-Urea Crystals (14 Months)

Purified MDI-Urea crystals, prepared August 22, 1992, were used to prepare the stock solution used for the second field test spiking and calibration solutions. Purified MDI-Urea crystals, prepared on November 11, 1993, were used to evaluate the stability of the crystals prepared in August of 1992. Two separate working standard solutions were prepared at approximately 30 µg/mL and 20 µg/mL from each of the purified crystal batches in ACN. The solutions were analyzed and the results showed that each solution from the 1992 crystals was within 5% of the target value. These data indicate that the MDI-Urea crystals remain stable at least 14 months when stored at room temperature in a closed container.

4.1.5.2 Stability of HDI, TDI and MDI-Urea Crystals (21 Months)

Purified HDI, TDI, MDI-Urea crystals (collectively as iso-urea crystals), prepared May 3, 1994, were used to prepare the stock solution used for the third field test spiking and calibration solutions. The May 1994 batch of iso-urea crystals was used to check the stability of the August, 1992, batch of iso-urea crystals. A five-point calibration curve of the May, 1994, batch was prepared in the range of 10 µg/mL to 50 µg/mL and analyzed. The correlation coefficient for each isocyanate was greater than 0.99. Five standards, 10 µg/mL to 50 µg/mL were prepared using the August, 1992, batch of iso-urea crystals. The standards were analyzed and compared to the calibration curve. The results of the analysis showed that the HDI and MDI-urea crystals were +5% of the target value, while the TDI-Urea crystals were -27% of the target value. The reason for the low values obtained for the TDI-Urea crystals is that the analysis of the May, 1994, batch did not show a 2,6-TDI peak in the chromatogram, while the August, 1992, batch showed a 2,6-TDI peak that was 17% of the 2,4-TDI peak. The 2,4-TDI that was used to prepare the August, 1992, batch consisted of 80% 2,4-TDI and 20% 2,6-TDI. The 2,4-TDI that was used to prepare the May, 1993, batch was greater than 98% pure. Using the 2,4-TDI calibration curve to calculate the amount of 2,6-TDI in each standard and then correcting the amount of 2,4-TDI the average increases to -18% of the target value. Since the actual purity of the 2,4-TDI crystals was not determined, the actual stability of the crystals is not known. However, there is no evidence to indicate that the 2,4-TDI crystals should not be as stable as the HDI and MDI-urea crystals. These data indicate that the Iso-Urea crystals remain stable at least 21 months when stored at room temperature in a closed container.

4.1.6 Inter-Laboratory Round Robin

An inter-laboratory round robin analysis of aliquots of four of the samples collected during the same field test was organized by Mr. Mark Baker of ICI Polyurethanes Group. Seven laboratories participated in the round robin including Radian Corporation. Two samples in the 1 µg/mL range, two samples in the 10 µg/mL range and a 1-2 PP/ACN blank were sent to each of the laboratories for analysis. The sample identifications are listed below. The samples were shipped to the laboratories the week of November 14, 1993, and the results were compiled by Mark Barker and made known to each laboratory on December 20, 1993. Each laboratory was instructed to analyze the samples using any method they selected. The results from each laboratory are presented in Table 4-4. The results showed close agreement with the average RSD (%) for all laboratories and all analysis being 6.9 percent.

Table 4-4. Results of Round Robin

Laboratory Number	Radian Sample Number									
	1		2		3		4		5	
	ug/mL	Bias ¹ (%)	ug/mL	Bias (%)	ug/mL	Bias (%)	ug/mL	Bias (%)	ug/mL	Bias (%)
1	1.45	12.4	1.41	11.0	8.84	16.6	8.83	12.5	< 0.01	NA
2	1.21	-6.2	1.25	-1.6	7.83	3.3	7.91	0.8	< 0.5	NA
3	1.34	3.9	1.33	4.7	8.04	6.1	8.08	2.9	< 0.5	NA
4	1.12	-13.1	1.13	-11.0	7.91	4.4	8.32	6.0	< 0.2	NA
5	1.29	0.0	1.27	0.0	7.58	0.0	7.85	0.0	< 0.05	NA
6	1.25	-3.1	1.18	-7.1	7.32	-3.4	7.26	-7.5	< 0.05	NA
7	1.30	0.8	1.25	-1.6	7.75	2.2	7.78	-0.9	< 0.05	NA
Average	1.28	-0.8	1.26	-0.8	7.9	4.2	8.00	2.0		
Standard Dev.	0.10		0.09		0.48		0.49			
Range	0.33		0.28		1.52		1.57			
RSD (%)	8.1		7.3		6.1		6.1			

¹Uses Radian value as true value, % Bias = Laboratory Value - Radian Value/Avg Value X 100.

4.1.7 Instrument Conditions

Derivatives were re-prepared by dissolving 150 mg of each isocyanate in individual 5 mL volumes of ACN. The derivatizing solution was prepared by dissolving 300 µL of 1,2-pp in 5 mL ACN. The two solutions were then mixed. A white precipitate formed for HDI, MDI, TDI. The reactions were quenched by adding 150 mL of water. Each derivative was removed by filtration, air dried, and transferred to 20 mL screw cap vials for subsequent analysis. Standards of each derivative were prepared at 80 µg/mL in ACN. The standards were analyzed using the HPLC conditions below:

- Instrument: Varian 5500 with autosampler;
- Data System: Nelson 2600 (1 volt);
- Column: Hypersil BDS C18 5µ particle size, 250 mm x 4.6 mm;
- Mobile Phase: Acetonitrile/0.1 M AAB;
- Detector: Ultraviolet at 254 nm (0.5 AUFS);
- Flow Rate: 2 mL/min; and
- Injection Volume: 10 µL.

The isocyanates 2,4-TDI and HDI were analyzed isocratically at 31:69 ACN:Buffer. Figure 4-13 shows a representative chromatogram for the analysis of the two isomers of TDI. The peaks are gaussian in shape with no tailing. MDI was analyzed using a gradient program starting at 31:69 ACN:Buffer for 10 minutes, then changing to 50:50 ACN:Buffer over the next five minutes. A gradient was used to keep the total run time as short as possible (under 20 minutes) and to maintain good peak shape for MDI.

Next a single solution containing TDI, HDI, and MDI was prepared at 30 $\mu\text{g}/\text{mL}$ each in ACN. This solution was analyzed using the gradient program used for MDI (Figure 4-14) to determine if all isocyanate derivatives developed to this point could be analyzed with one method. The retention times listed below for the isocyanates are specific to the HPLC conditions given above:

- 2,6-TDI: 5.52 min;
- HDI: 6.5 min;
- 2,4-TDI: 7.98 min; and
- MDI: 17.45 min.

Sufficient separation between the isocyanates was observed to allow quantitative analysis. A three-point calibration curve was prepared for 2,4-TDI, HDI, and MDI. A stock solution containing the three isocyanates was prepared by transferring 4.0 mg of each derivative to a single 25 mL volumetric flask and diluting to volume with ACN. A three point curve was prepared by diluting aliquots of the stock to nominal concentrations of 8, 16, and 33 $\mu\text{g}/\text{mL}$ of each isocyanate in ACN. The calibration curve was analyzed using the above analytical conditions. The slope, intercept, and correlation coefficient were calculated for each derivative. The correlation coefficients were 0.999 or greater indicating that the analytical method is linear for three of the isocyanates.

4.1.8 Analysis of MI, HDI, TDI, MDI

A solution containing 1,2-pp, MI, HDI, 2,4-TDI, and MDI (each at a nominal concentration of 20 $\mu\text{g}/\text{mL}$) was prepared and analyzed using the following instrument conditions:

- Instrument: Varian 5500 with autosampler;

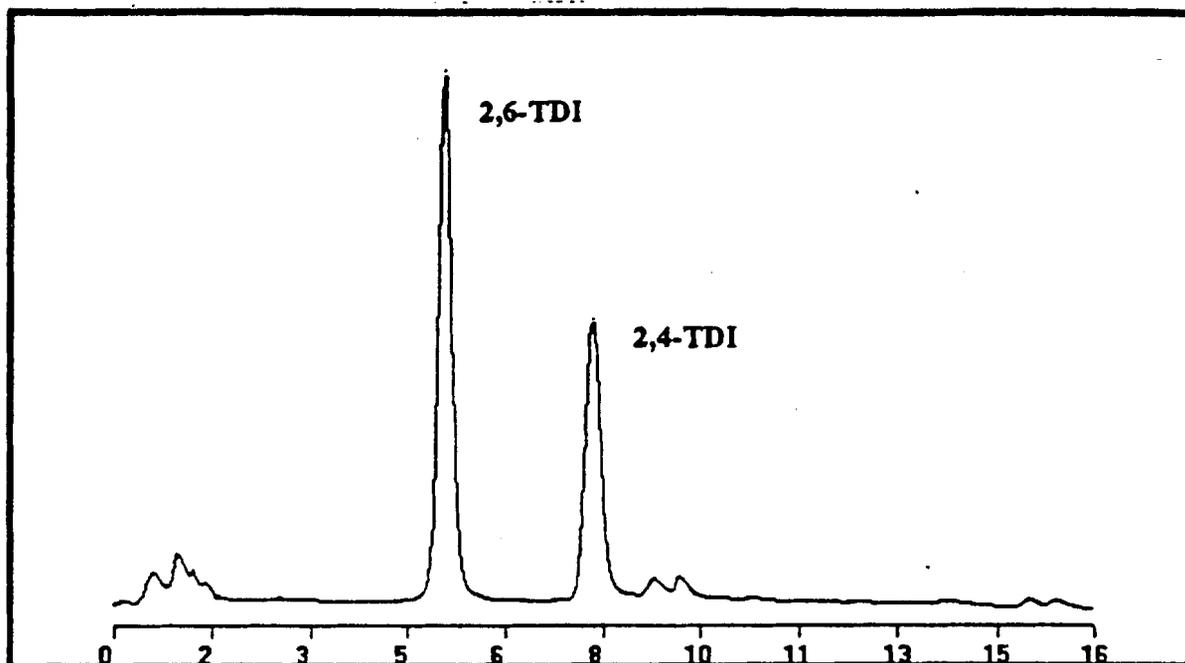


Figure 4-13. HPLC chromatogram of 2,4-TDI and 2,6-TDI (80:20) Mobile Phase - 31:69 ACN:AAB (isocratic)

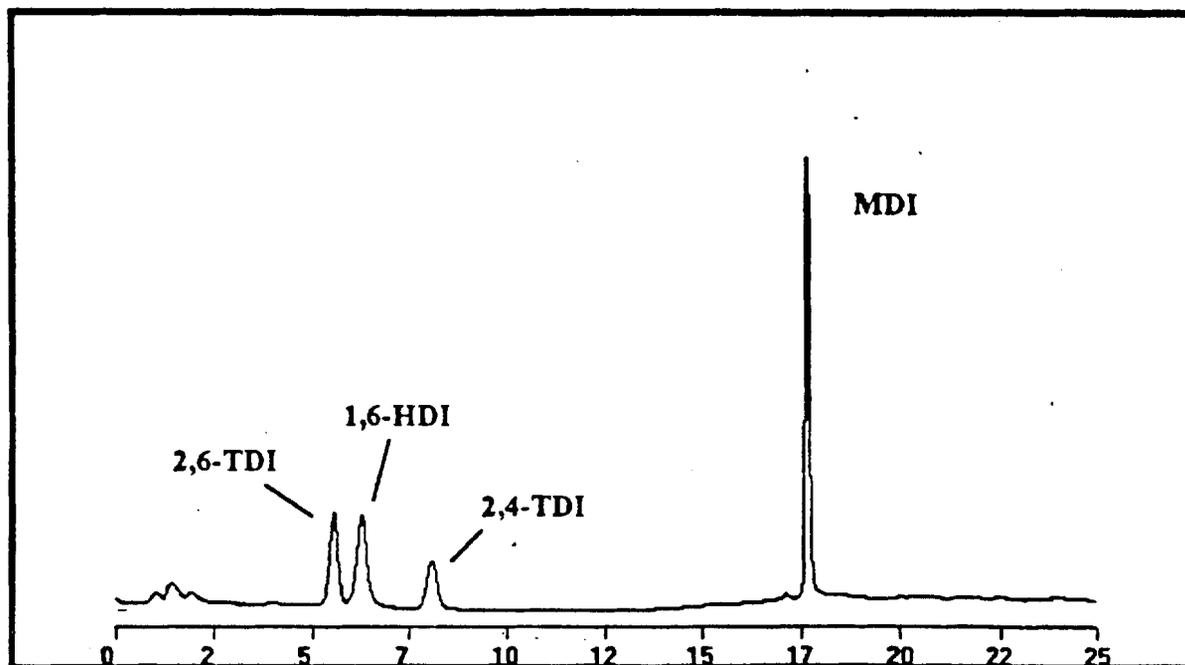


Figure 4-14. HPLC chromatogram of mixture of 2,6-TDI, 2,4-TDI, HDI, and MDI Gradient Program - 31:69 for 10 minutes to 50:50 over 5 minutes.

- Data System: Nelson 2600 (1 volt);
- Column: Hypersil BDS C18 5 micron particle size, 250 mm x 4.6 mm;
- Gradient: 20:80 ACN/(0.1 M AAB, pH 6.2), hold 4 min then changing to 60:40 for 16 min, then resetting to initial conditions;
- Detector: Ultraviolet at 254 nm (0.5 AUFS);
- Flow Rate: 2 mL/min; and
- Injection Volume: 50 μ L.

Adequate separation between all components was observed for quantitation of each derivative (Figure 4-15).

The first two of the three field tests evaluated the method using only one isocyanate at a time (TDI and MDI, respectively). The third field test involved evaluating all four isocyanates of interest. The analytical method used for all four of the isocyanates as described above is successful when the amount of excess 1,2-pp is kept at a minimum or MI is not a compound of interest. The amount of 1,2-pp in the sampling train is at a concentration of 40 mg per 300 mL of impinger solution. The results of the first two field tests showed that a large 1,2-pp peak was present on the chromatograms. There is baseline resolution between 1,2-pp and MI when the concentration of 1,2-pp is less than 20 ppm. The concentration of 1,2-pp in a sample with a 10 mL final volume is approximately 4 mg/mL which is 200 times higher than the minimum needed to obtain baseline resolution using the above instrument conditions. A column was purchased that was more stable with the buffer, and a guard column was added to extend the life of the column. The conditions that produced the best resolution between 1,2-pp and MI, while maintaining good separation between the other isocyanates, were as follows:

- Instrument: Varian 5500 with WISP Autosampler;
- Data System: Turbochrom 4.0 (1 volt);
- Column: Alltech Alltima C18 5 micron particle size, 250 mm x 4.6 mm;
- Gradient: 10:90 ACN/(0.1 M AAB, pH 6.2), changing to 60:40 over 30 minutes, then resetting to initial conditions;
- Detector: Ultraviolet at 254 nm;
- Flow Rate: 2 mL/min; and
- Injection Volume: 50 μ L.

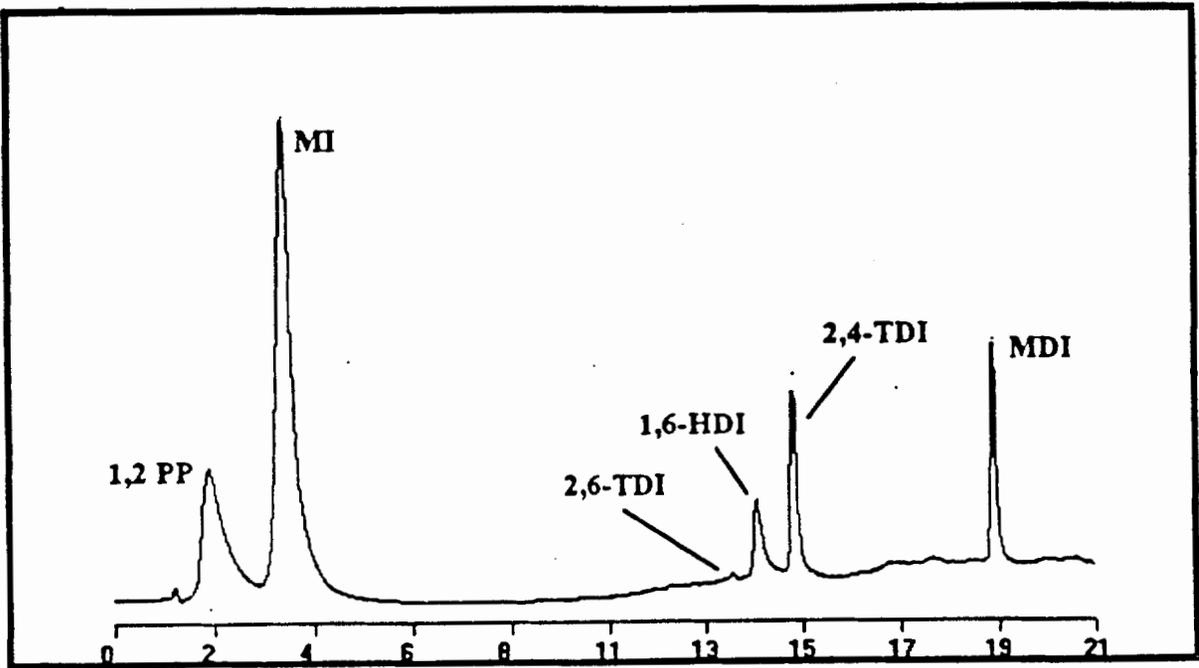


Figure 4-15. HPLC chromatogram of MI, 2,6-TDI, 2,4-TDI, HDI, and MDI gradient program for 4 minutes to 60:40 over 16 minutes.

The retention times, in minutes, were:

1,2-pp: 4.3

MI: 10.2

HDI: 19.9

TDI: 21.1

MDI: 27.3

There was baseline resolution between each of the isocyanates as well as between 1,2-pp and MI, even with samples similar to actual field samples.

4.1.9 Instrument Detection Limit Study

The detection limit was determined for 2,4-TDI, 1,6-HDI, and MDI (MI was not under consideration at this time) using the Federal Register method for instrument detection limits.⁵ A single standard was prepared that contained each of the isocyanates. The standard was subsequently analyzed seven times on the following HPLC system:

- Instrument: Rainin HPXL Delivery system, Waters 710B WISP autosampler;
- Data System: Nelson 2600 (1 volt);
- Column: Zorbax ODS (4.6 mm ID x 25 cm);
- Gradient: 25:75 ACN/0.1 M Ammonium Acetate Buffer, pH 6.2, hold 2 min, then to 60:40 over 19.5 min, then resetting to initial conditions;
- Detector: Rainin Dynamax Dual-Wavelength, 254 nm (0.5 AUFS);
- Flow Rate: 2 mL/min; and
- Injection Volume: 50 μ L.

The Instrument Detection Limit (IDL) was calculated by determining the standard deviation of the area count for seven replicate injections and then multiplying the standard deviation for seven replicate injections by the Student's t-value at the 99% confidence level (3.143). The Instrument Limit of Quantitation (ILOQ) is estimated to be 3 times the IDL (ng on column).

The Estimated Method LOQ was calculated based on a 10 mL final sample volume, a 50 μ l injection and a 1 cubic meter sample collected (Table 4-5). The IDL and the ILOQ are higher for HDI than for TDI or MDI because

HDI has a lower extinction coefficient. This will be matrix and instrument dependent and may vary from laboratory to laboratory.

Table 4-5. Instrument Detection Limit and Limit of Quantitation for 2,4-TDI, HDI and MDI Ureas

	1,6-HDI	2,4-TDI	MDI
Areas	7092	8204	20735
	6930	8584	20504
	6232	8081	20221
	6968	8474	20160
	6787	8483	20132
	6558	8477	21028
	6098	7979	20600
Average Area	6666	8326	20483
Area Std. Dev.	382.8	234.9	334.3
Area RSD	5.7%	2.8%	1.6%
Standard (µg/mL)	0.23	0.12	0.22
ng on Column (50 µl injection)	11.5	6.0	11
IDL ng on column*	1.98	0.53	0.56
MDL ng/m³	396	106	112
ILOQ ng on column**	5.94	1.59	1.7
MLOQ ng/m³***	1188	318	336

The Limit of Quantitation was calculated based on a 10 mL final sample volume, and 35.314667 cubic feet (1 cubic meter) of air collected at sampling time.

$$* \text{IDL ng on Column} = \left[\frac{\text{ng isocyanate injected}}{\text{Average Area}} \times \text{Area Std. Dev.} \right] \times \text{Student's t value}$$

** ILOQ = IDL x 3

*** MLOQ = MDL x 3

4.1.10 Interferants

The identification of all potential interferants is important but the process can be difficult and time consuming. A source can have any number of compounds that could interfere with analysis. Many interferants will not be known before sampling and the type and number of interferants will change from source to source. Two interferants, aqueous solutions of strong acids and bases, have been discussed previously. Phosgene, which is a gas at room temperature and is used in the production of isocyanates, has been identified as a third possible interferant.

The proposed reaction of phosgene with 1,2-pp is a substitution reaction where 1,2-pp replaces the Cl on phosgene and 1,2-pp loses a H⁺ (Figure 4-16). The reaction occurs at a 2:1 molar ratio consisting of 2 moles of 1,2-pp to 1 mole of phosgene. The formation of hydrochloric acid as part of the reaction mechanism could also present problems because the formation of the 1,2-pp isocyanate urea is hindered by acids.

Phosgene was derivatized with 1,2-pp to determine if it would interfere chromatographically with the analysis of the isocyanates. A 1 mL aliquot of a 20% solution of phosgene in toluene [1.93 M by volume] was transferred to a 100 mL flask containing 500 μ L of 1,2-pp and 50 mL of ACN and brought to volume with toluene. A second solution was prepared by transferring 500 μ L of a 20% solution of phosgene to a 100 mL flask containing 500 μ L of 1,2-pp and ACN and brought to volume with toluene. The solutions were filtered with a No. 42 Whatman filter and the precipitate recovered.

Stock standards of the precipitate were prepared at 50 μ g/mL in ACN and the stocks were diluted 1:10 with ACN and analyzed on the HPLC system described previously. Figures 4-17 and 4-18 show chromatograms of the high and low concentration standards. The area of a peak at 8 minutes decreases from the high standard to the low standard and was tentatively identified as the phosgene derivative. All other peaks were present in all of the chromatograms. The chromatogram of the crystals (Figure 4-19), does not show any peaks that were not present in Figures 4-17 and 4-18. The tentatively identified phosgene derivative will interfere chromatographically with the analysis of 2,6-TDI and 1,6-HDI under the current HPLC conditions. Since the presence of phosgene will probably be known before sampling, the analytical conditions can be changed to avoid this problem.

4.1.11 Toluene as an Impurity

During analysis of the samples an unidentified peak with a retention time of 19 minutes was observed and the origin of the impurity was investigated. Three 15 mL volumes of HPLC grade toluene were concentrated to dryness with nitrogen at 65°C and then reconstituted with 4 mL ACN for analysis. Three 15 mL volumes of ACN were prepared in the same manner as the toluene. Neat MDI was transferred to two separate 15 mL volumes of toluene containing 1-(2-pyridyl) piperazine and allowed to derivatize for 2 hours in a sonicator at 40°C. Each was concentrated to dryness with nitrogen at 65°C and then reconstituted to 4 mL with ACN for analysis. Each sample was analyzed on the HPLC system previously described. These results showed no peak at 19 minutes for any of the samples that were prepared. A 20 μ g/mL solution of toluene in ACN was prepared and analyzed. A peak at 19 minutes was observed. These results show that the peak in question observed at 19 minutes was due to small amounts of residual toluene remaining in the sample during preparation for analysis. This residual toluene does not interfere with the analysis, and, therefore, does not pose any problems in positively identifying the isocyanate derivatives.

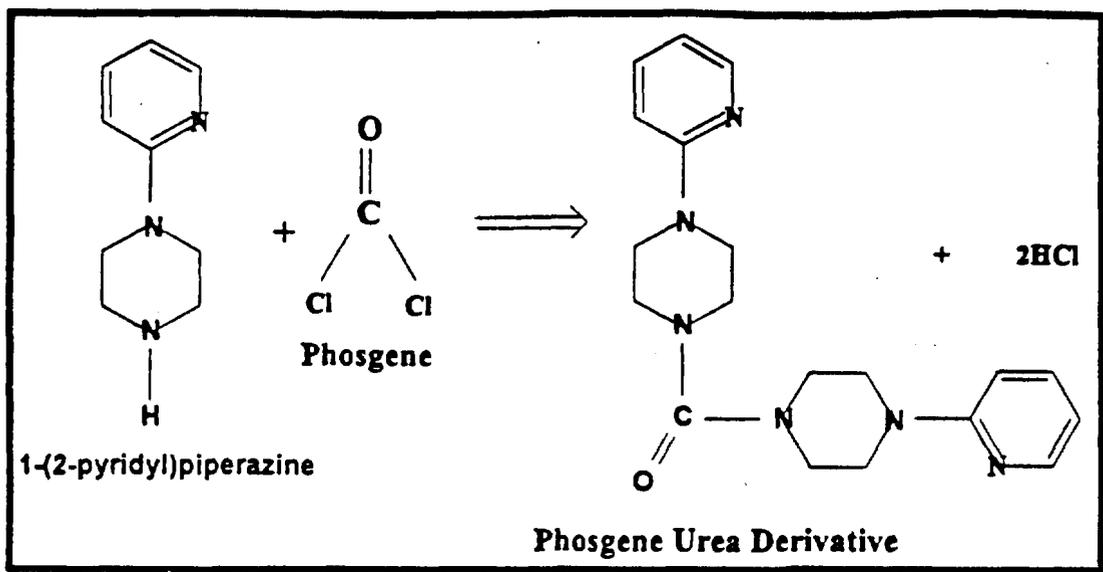


Figure 4-16. Reaction of phosgene with 1-(2-pyridyl) piperazine.

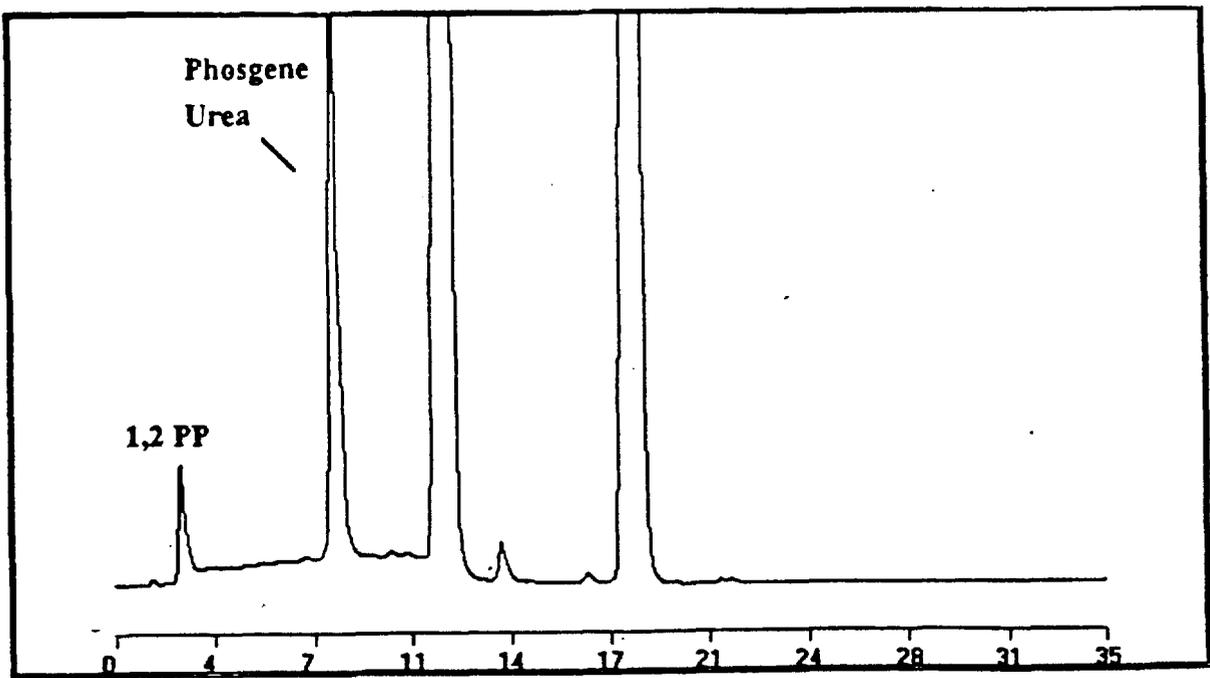


Figure 4-17. HPLC chromatogram of a high level solution of phosgene derivatized with 1,2-pp.

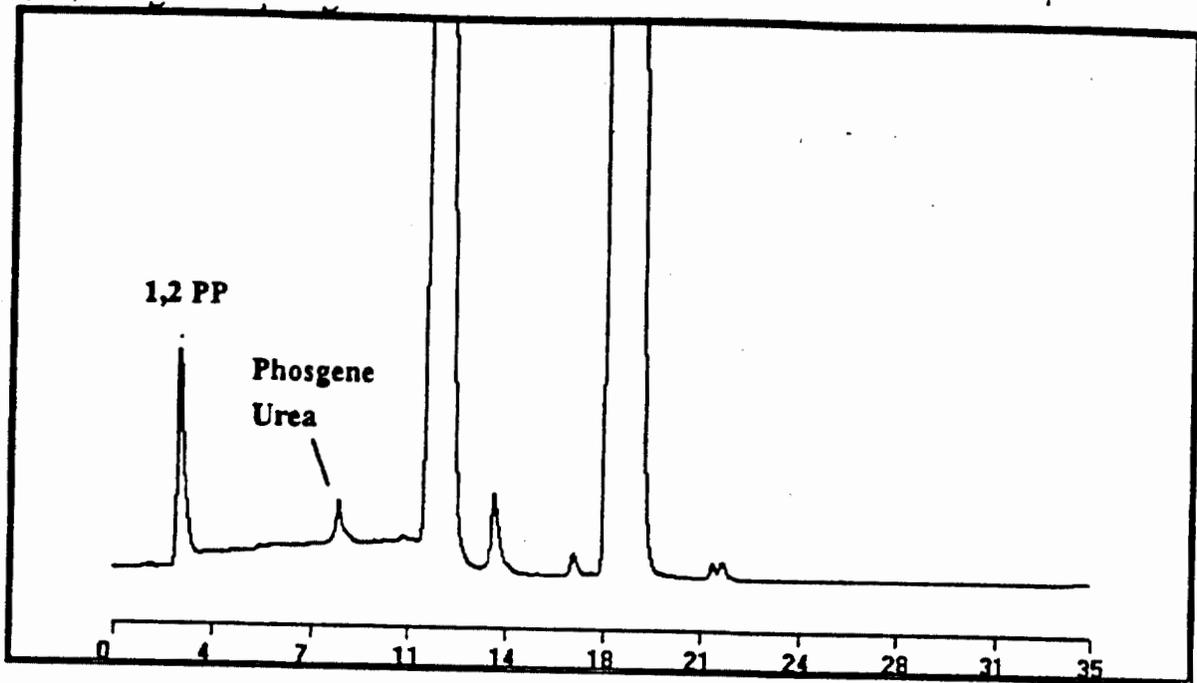


Figure 4-18. HPLC chromatogram of a low level solution of phosgene derivatized with 1,2-pp.

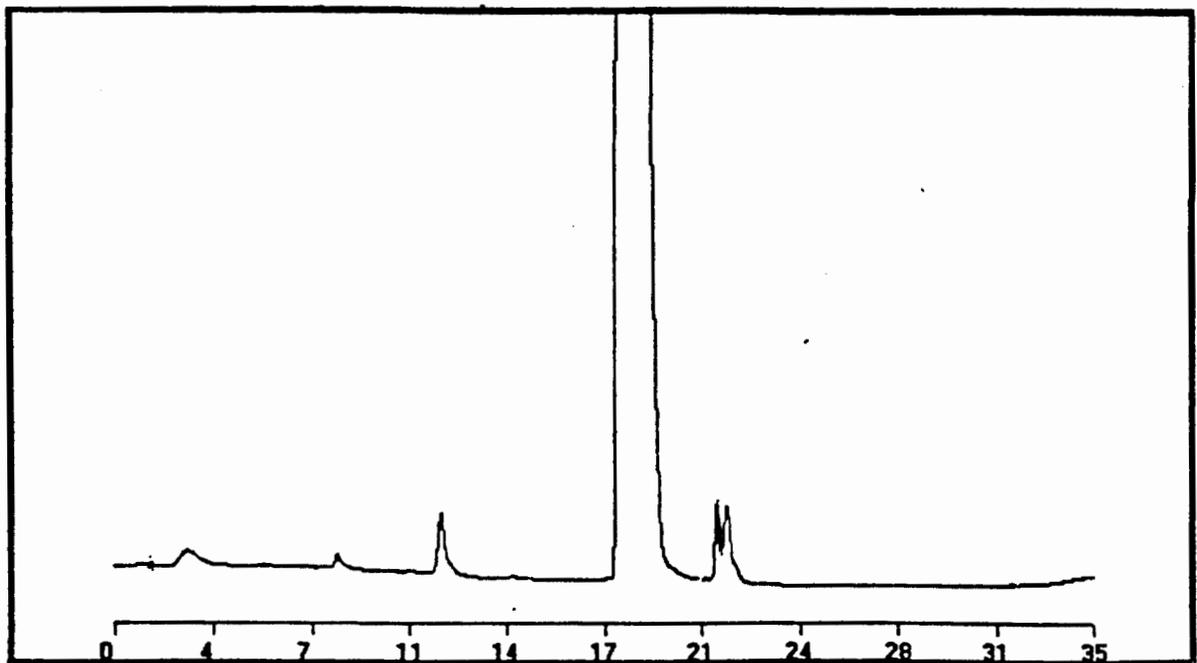


Figure 4-19. HPLC chromatogram of a solution of the precipitate recovered from the derivatization of phosgene with 1,2-pp.

4.1.12 Train Spiking Experiments

Train spiking experiments were conducted to test the proposed method in appropriate apparatus under laboratory controlled conditions. The spiking system used in this study was based on work published in a journal article entitled "Recent Developments in Sampling and Analysis of Isocyanates in Air."⁶ Dynamic spiking was done to develop and test the possibility of using such a system in the field and to simulate stack sampling under conditions similar to clean stack environments.

4.1.12.1 Spiking Configuration Number One

The spiking system, depicted in Figure 4-20, was designed to allow dynamic spiking of the isocyanates, as gases, into the sampling train. A motor driven syringe pump was used to deliver a solution of neat TDI in methylene chloride at a known flow rate into a heated (60°C) nitrogen stream flowing at 3 liters/min. The vaporized TDI was then swept into the main heated nitrogen stream, flowing at 15 L/min and into the sampling train. This system allowed a constant rate of vaporized TDI to be carried into the sampling train. The positive pressure of the spiking apparatus transferred the entire amount of TDI in the syringe into the train.

The sampling train consisted of a glass transfer line (simulating the sampling probe) followed by a series of five impingers. The first impinger (Greenburg-Smith) contained 300 mL of the absorbing solution, 1,2-pp. The remaining four impingers were of the modified Greenburg-Smith design with the second containing 200 mL of absorbing solution, the third being empty, the fourth containing approximately 300 g of silica gel, and the fifth containing approximately 400 g of charcoal. A water jacketed condenser was located between the outlet of the first impinger and the inlet to the second impinger to minimize the loss of toluene from the first impinger into the second. No filter was used to avoid loss of isocyanate through retention on and reaction with the glass filter matrix.

Using this system, five trains containing ACN and 1,2-pp and two trains using toluene and 1,2-pp as the absorbing solution were spiked with known amounts of TDI. Each sampling run was nominally one hour. The first and second impingers were analyzed separately to evaluate the ability of the solution to trap the isocyanate. The impinger solutions for each train were taken to dryness under vacuum at 65°C and the residue then redissolved in 10 mL of ACN. The samples were analyzed under the following conditions:

- Instrument: Rainin HPXL Delivery system, Waters 710B WISP autosampler;
- Data System: Nelson 2600 (1 volt);
- Column: Zorbax ODS (4.6 mm ID x 25 cm);

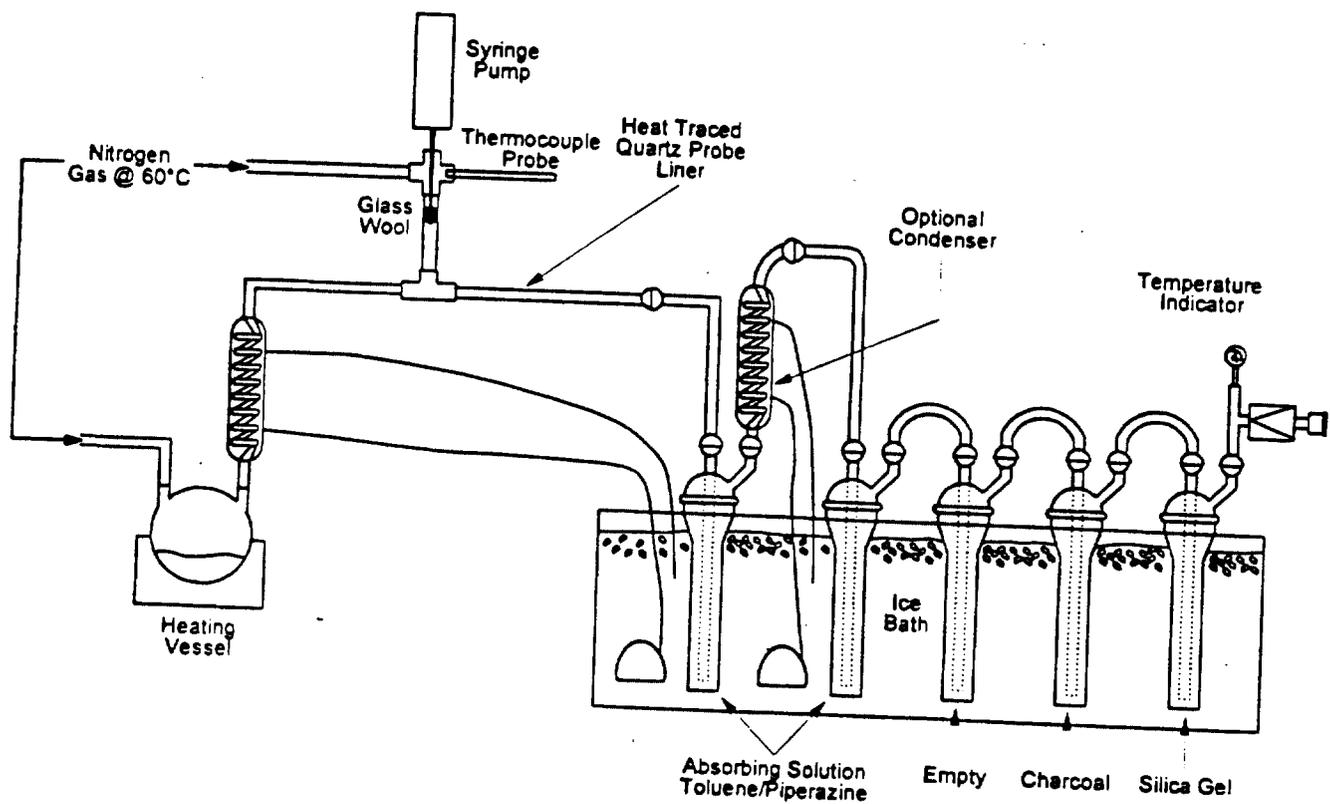


Figure 4-20. Spiking system configuration number one.

- Gradient: 25:75 ACN/0.1 M Ammonium Acetate Buffer, pH 6.2, hold 2 min, then to 60:40 over 19.5 min, then resetting to initial conditions;
- Detector: Rainin Dynamax Dual-Wavelength, 254 nm (0.5 AUFS);
- Flow Rate: 2 mL/min; and
- Injection Volume: 50 μ L.

The TDI recoveries averaged 74% (ranging from 59% to 80%) in ACN and 88% (ranging from 86% to 91%) in toluene (Table 4-6). The average percentage breakthrough from the first to the second impinger was 10% for the ACN train and 6% for the toluene train (Table 4-7). The average percentage of solvent loss from the first and second impingers was 37% for the ACN train and 23% for the toluene train (Table 4-8). Taking into account the volatility of the solvents, toluene was determined to be the best choice for the absorbing solution and all other spikes were performed using toluene.

4.1.12.2 Spiking Configuration Number Two

The system was next modified to more closely simulate actual sampling conditions (Figure 4-21). A 1-meter glass probe heated to 120°C was installed between the spiking system and the impingers. In this configuration, sample was pulled through the train using a standard EPA Method 5 meterbox. Moisture was also introduced into the system by applying heat to a glass reservoir containing water connected in series with the heated sampling probe. Three 1-hour runs were performed at a flow rate of 18 L/min through the impingers. An average of 100 mL of water was collected in the impingers representing 92.6 g/m³ of water (approximately 14% by volume) within the simulated stack gas. The water was removed from the toluene absorbing solution by transferring the sample to a 1000 mL separatory funnel and draining the water into a glass container, which was archived. The toluene absorbing solution was transferred to a 500 mL round bottom flask, taken to dryness under vacuum and then reconstituted with 10 mL of ACN in preparation for analysis. The samples were analyzed by HPLC to determine the average recovery. The average recovery of the spiked TDI was found to be 64% (Table 4-9).

4.1.12.3 Spiking Configuration Number Three

The water bath was removed (Figure 4-22) to test the spiking system for precision and repeatability under the lower humidity conditions (1-3% by volume) routinely found in the field. Seven trains were spiked with 2.5 μ g of 2,4-TDI. The contents of the first and second impingers were concentrated to dryness under a vacuum and reconstituted to 10 mL with ACN. The peaks resulting from the analysis of the first and second impingers of each train were combined for the evaluation of the recoveries. The recoveries ranged from 24% to 122%, with an average recovery of 77% (Table 4-10). The amount collected was approximately 23 times the instrument detection limit and 7 times the limit of quantitation.

Table 4-6. Recoveries of 2,4 TDI Using Spiking Configuration Number One

Train ID	μg Derivative		Total μg	Target μg	% Recovery
	1st Impinger	2nd Impinger			
ACN					
1	1252	96	1348	2299	59
2	1498	258	1756		76
3	1563	240	1803		78
4	1684	150	1834		80
5	1637	97	1734		75
		Average	1695		74
		SD	198		8
		CV	12		11
Toluene					
1	3362	233	3596	3967	91
2	3241	158	3399		86
		Average	3497		88

Table 4-7. 2,4-TDI Breakthrough from First Impinger to Second Impinger Using Spiking Configuration Number One

Train ID	μg Derivative			% of Total Collected	
	1st Impinger	2nd Impinger	Total μg	1st Impinger	2nd Impinger
ACN					
1	1252	96	1348	93	7
2	1498	258	1756	85	15
3	1563	240	1803	87	13
4	1684	150	1834	92	8
5	1637	97	1734	94	6
		Average	1695	90	10
		SD	198	4	4
		CV	12	4	40
Toluene					
1	3362	233	3596	94	6
2	3241	158	3399	95	5
		Average	3497	94	6

Table 4-8. Change in Impinger Volumes from Start of Sampling to End of Sampling Using Spiking Configuration Number One

Train ID	Final Volume, mL		Total mL	Starting Volume, mL	% Loss
	1st Impinger	2nd Impinger			
ACN					
1	86	150	236	400	41
2	70	170	240		40
3	76	175	251		37
4	75	183	258		35
5	88	190	278		30
		Average	253		37
		SD	17		4
		CV	7		12
Toluene					
1	90	220	310	400	22
2	95	210	305		24
		Average	308		23

Table 4-9. Recovery of 2,4-TDI with High Moisture Using Spiking Configuration Number Two

Train ID	mL H ₂ O	Air Vol L	Total µg	Target µg	% Recovery
1	120	1110	7.0	12.5	56
2	80	555	3.8	5	75
3	100	1110	7.5	12.5	60

Table 4-10. Recovery of 2,4-TDI from Seven Replicate Spikes Using Spiking Configuration Number Three

Train ID	Total TDI (µg)*	Target (µg)	% Recovery
1	3.06	2.5	122
2	0.61	2.5	24
3	2.29	2.5	92
4	0.64	2.5	26
5	2.12	2.5	85
6	2.52	2.5	101
7	2.23	2.5	89
		Average	77
		SD	38
		CV	49

*µg TDI for first and second impinger.

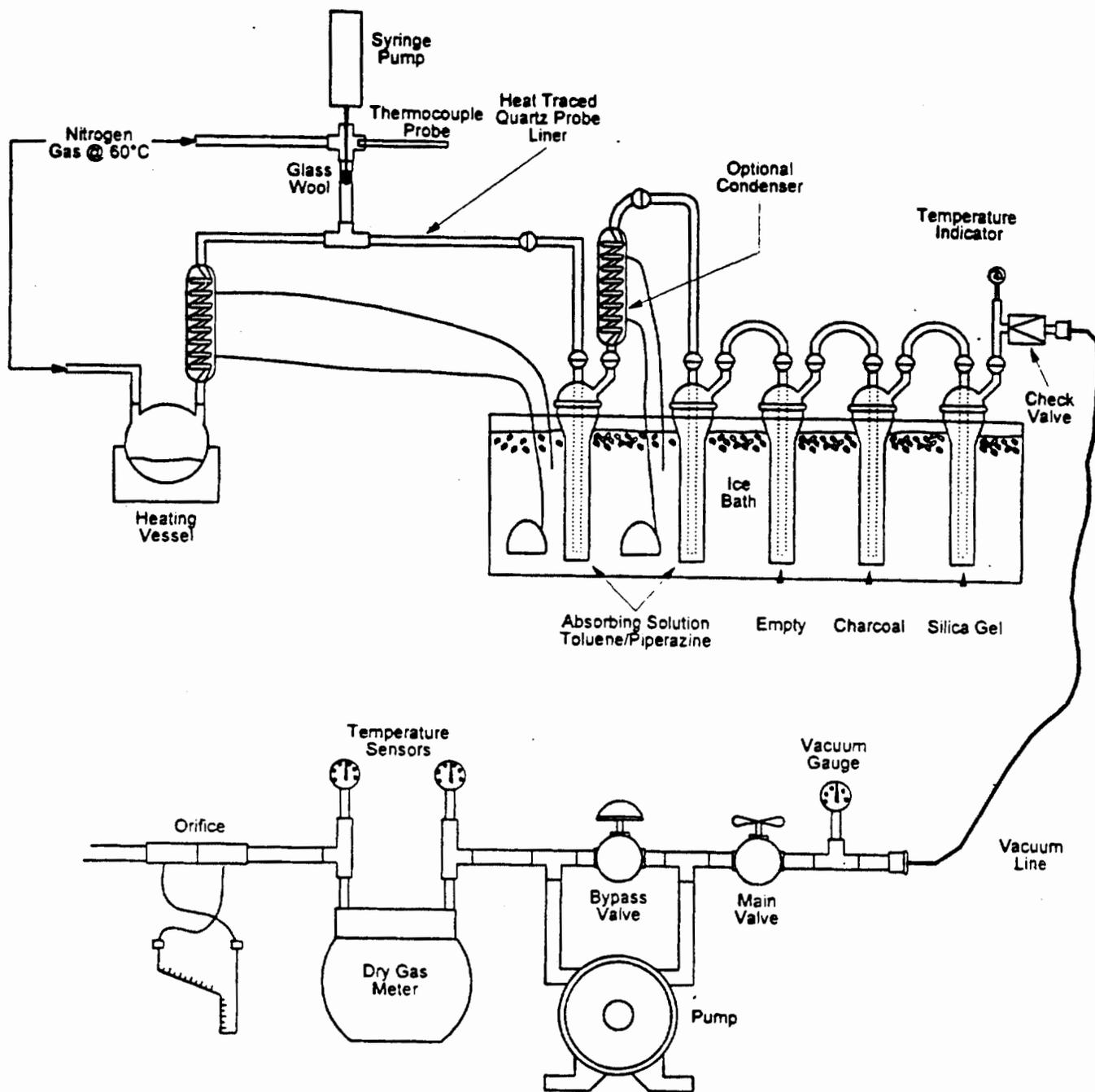


Figure 4-21. Spiking system configuration number two.

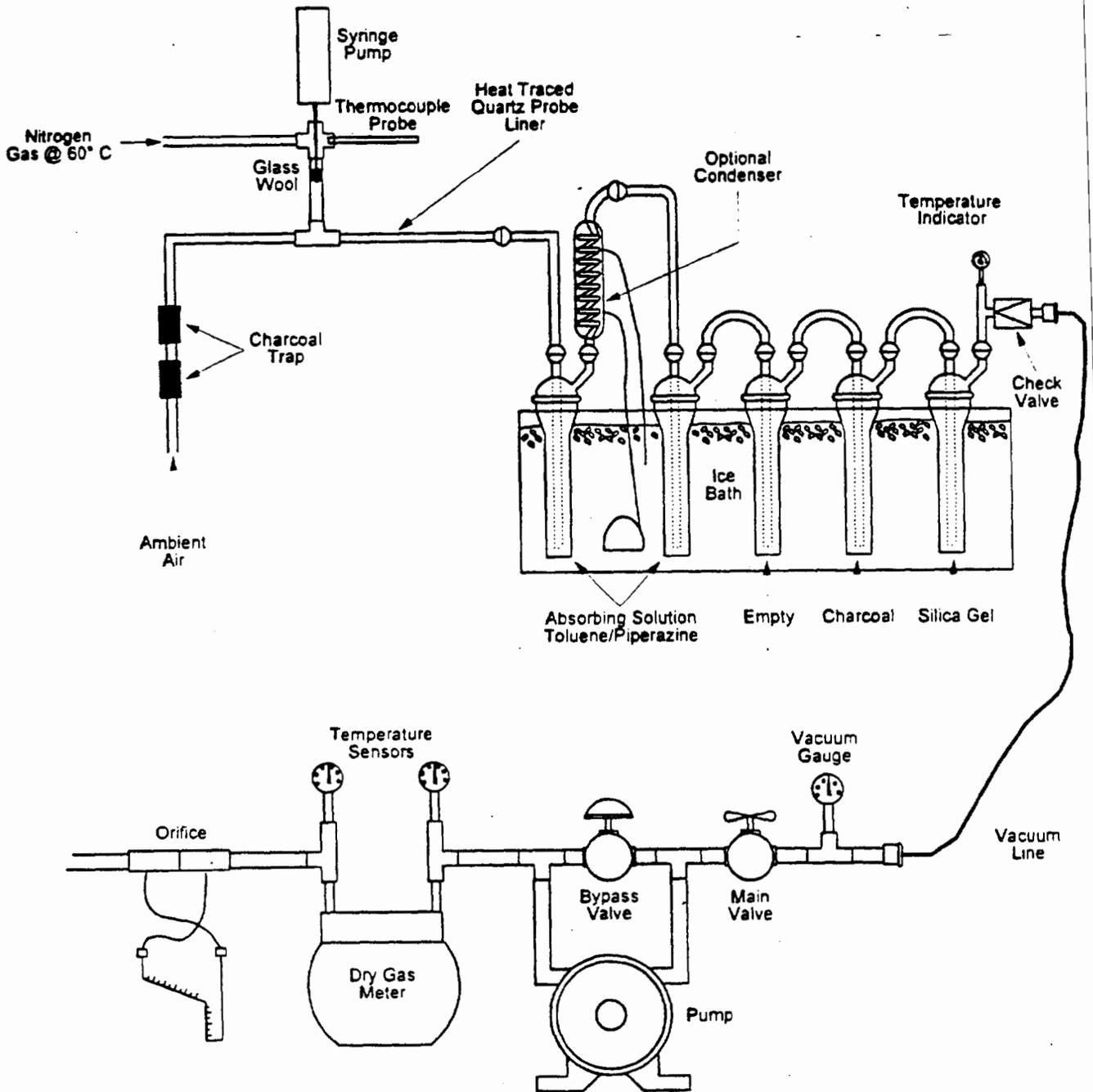


Figure 4-22. Spiking configuration number three.

Figures 4-23 through 4-25 show representative chromatograms of impinger contents from spiked trains. There were several solvent impurities that did not interfere with the analysis of 2,4-TDI. The impurities are present in reagent blanks of toluene and 1,2-pp.

4.2 Field Evaluation

One of the objectives of this program was to perform field tests to establish the bias and precision of a sampling and analysis method for the isocyanate compounds listed in the CAAA of 1990. The bias and precision of the method were statistically determined following the protocol given in EPA Method 301. To achieve the test objectives, manufacturing facilities with known emissions of the specific isocyanates were selected as field test sites. Factors considered in the selection of the test sites were easy access, ample space for the quadruple sampling trains and proximity to Radian's office and laboratory in Research Triangle Park, North Carolina.

Based on the results of samples collected during a presurvey at each host facility, a sampling scheme was designed to ensure the collection of sufficient samples and sample volume to yield statistically valid data, and to determine the level of the spike. Following the EPA Method 301 protocol, quadruplicate (QUAD) trains were operated simultaneously with four co-located sampling probes. The first impinger of two of the trains were statically spiked with the derivative(s) of the isocyanate(s) and two were unspiked. Samples from the QUAD runs (minimum of six valid runs required by Method 301) were returned to the laboratory and analyzed according to the analytical procedures developed in the laboratory. These data were statistically evaluated following Method 301 to determine the performance of the method relative to bias and precision. The method is considered to be a valid method if the precision criteria is met ($\% \text{ RSD} < 50$) and the bias is not significantly different from zero or can be corrected with a correction factor between 0.7 and 1.3.

The sampling procedure used a modification of the EPA stationary source reference Method 5. Gas is extracted from the source duct through a heated glass nozzle/probe system as shown in Figure 4-26. The sample gas stream is passed through a six impinger train. A water cooled condenser is placed between the outlet of the first impinger and the inlet of the second. Following the impingers, the gas is directed through a sample pump, a dry gas meter and an orifice differential pressure meter. For the purpose of this work, the following modifications were made:

- Four co-located sampling trains, referred to as a "quad-train," were used. Four independent samples were collected simultaneously under identical stack conditions with the quad-train. This approach, allowed the collection of data to determine precision of the proposed sampling and analytical method.

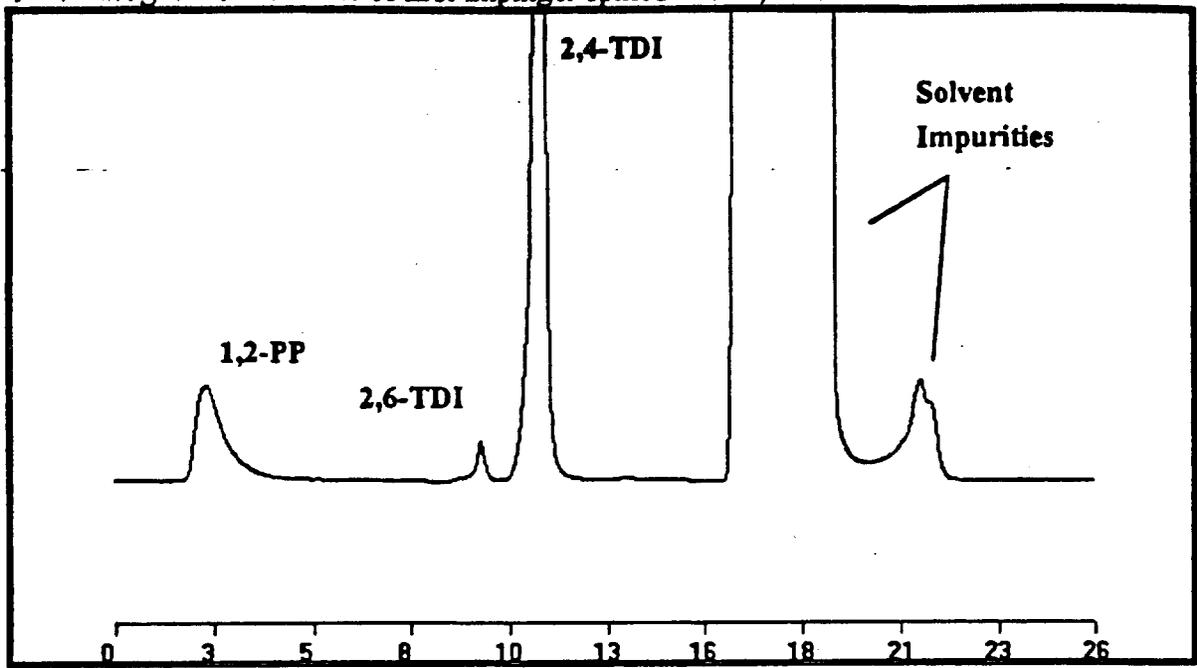


Figure 4-23. HPLC chromatogram of contents of first impinger.

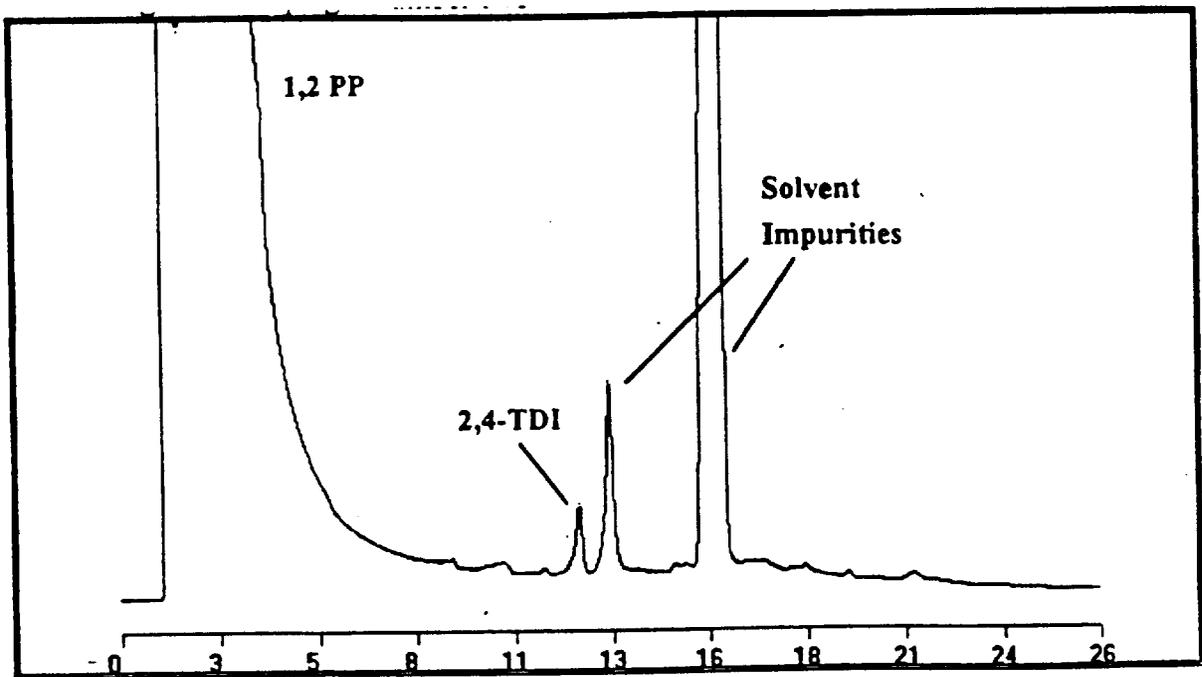


Figure 4-24. HPLC chromatogram of contents of second impinger, spiked train.

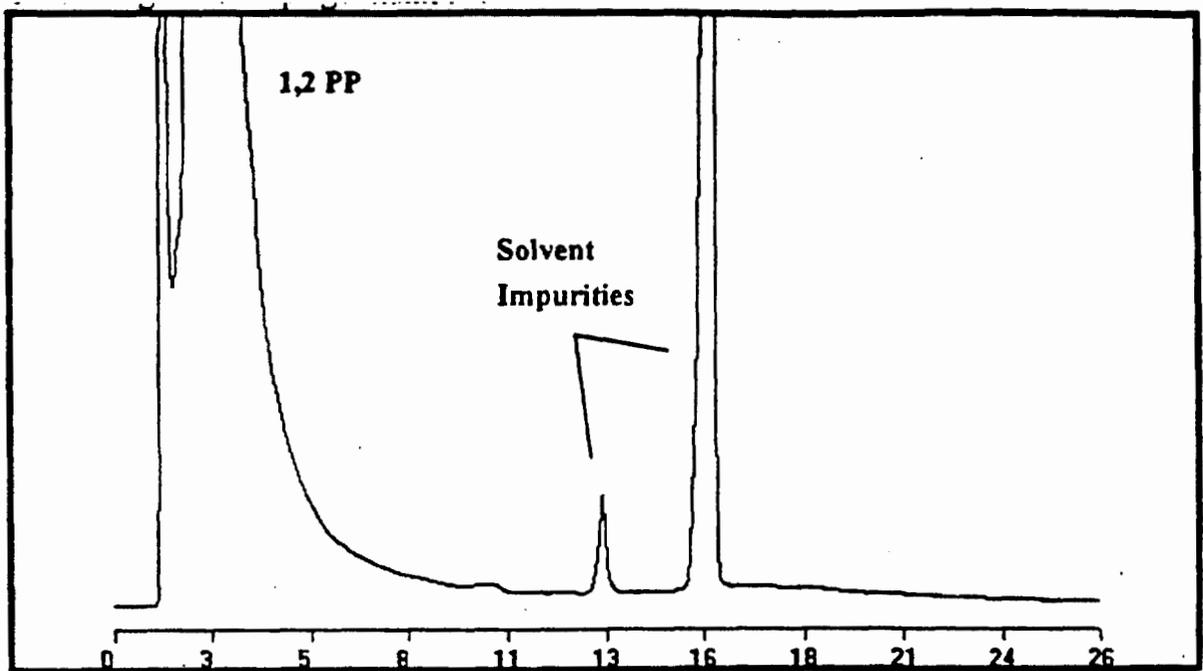


Figure 4-25. HPLC chromatogram of contents of third second impinger.

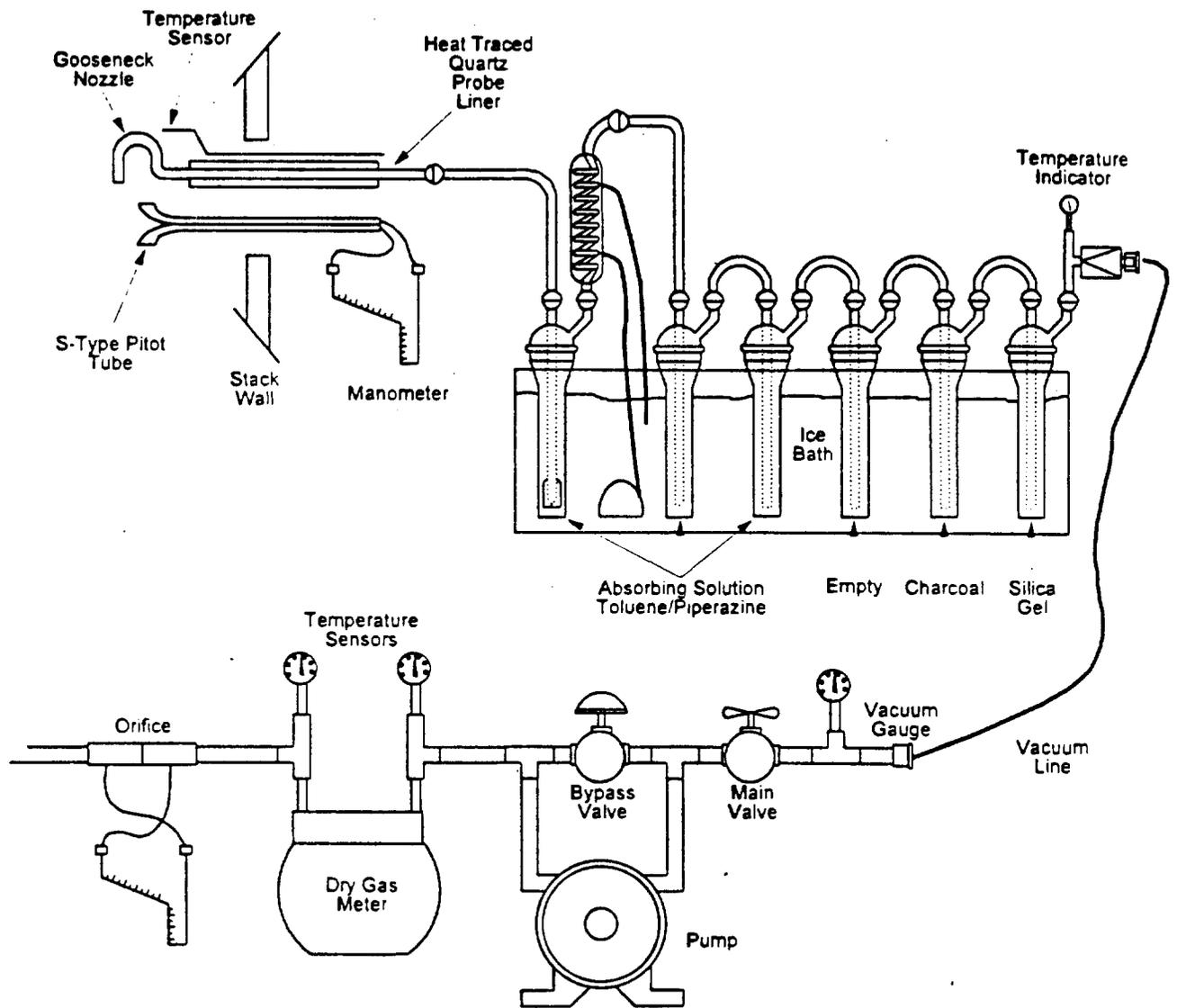
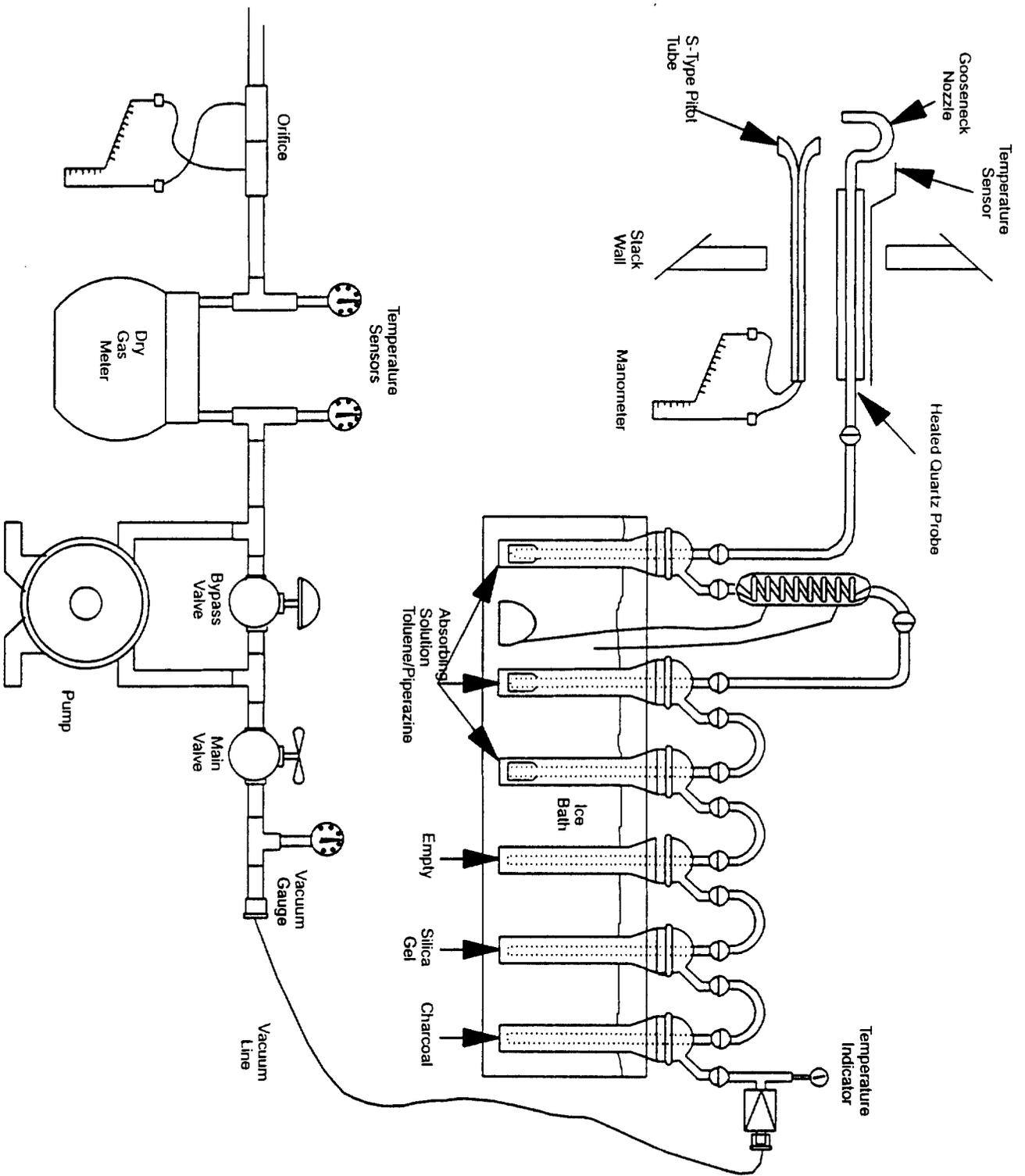


Figure 4-26. Sampling train for isocyanates.



Isocyanate Sampling Train

- The contents of the first impinger in two of each set of four trains was spiked with a standard solution of one or more of the isocyanates derivatized with 1-(2-pyridyl)piperazine. This activity provided information on sampling and analytical recoveries and the bias of the proposed sampling and analytical method.

4.2.1 Quad-Probe

A special probe assembly was required to allow simultaneous sampling from essentially the same point with four independent sampling trains. Variations in the velocity of the stack gas within the area occupied by the four sampling nozzles must be minimized. The quad-probe arrangement described in EPA Method 301 minimizes this variation and has been proven to be a good approximation of multiple-train sampling from a single point.⁷

Figures 4-27 and 4-28 illustrate the configuration of the sampling probe which was used during the isocyanate test program. The two primary considerations in the arrangement of the four sampling probes are:

- The probe inlets should be in the same plane perpendicular to the gas stream; and
- The probe tip openings should be exposed to the same conditions.

The flow at the probe tips can be considered similar if the area encompassed by the probe tip arrangement is less than 5% of the stack cross-sectional area.

4.2.2 Quad-Train Assembly

Four independent sampling trains make up the quad-train assembly. Although four meter boxes were required, the velocity head (ΔP) was determined using only one of the four control boxes. The sampling trains were identified as Train A, B, C, or D. Trains A and B were designated as "spiked" trains for the first run. The spiking compounds were statically spiked into the first impinger of these trains in the field for bias determination. The two spiked trains for each run alternated between Trains A and B and Trains C and D for all subsequent runs.

Static spiking rather than dynamic spiking of neat isocyanates was performed in the field due to health and safety concerns.

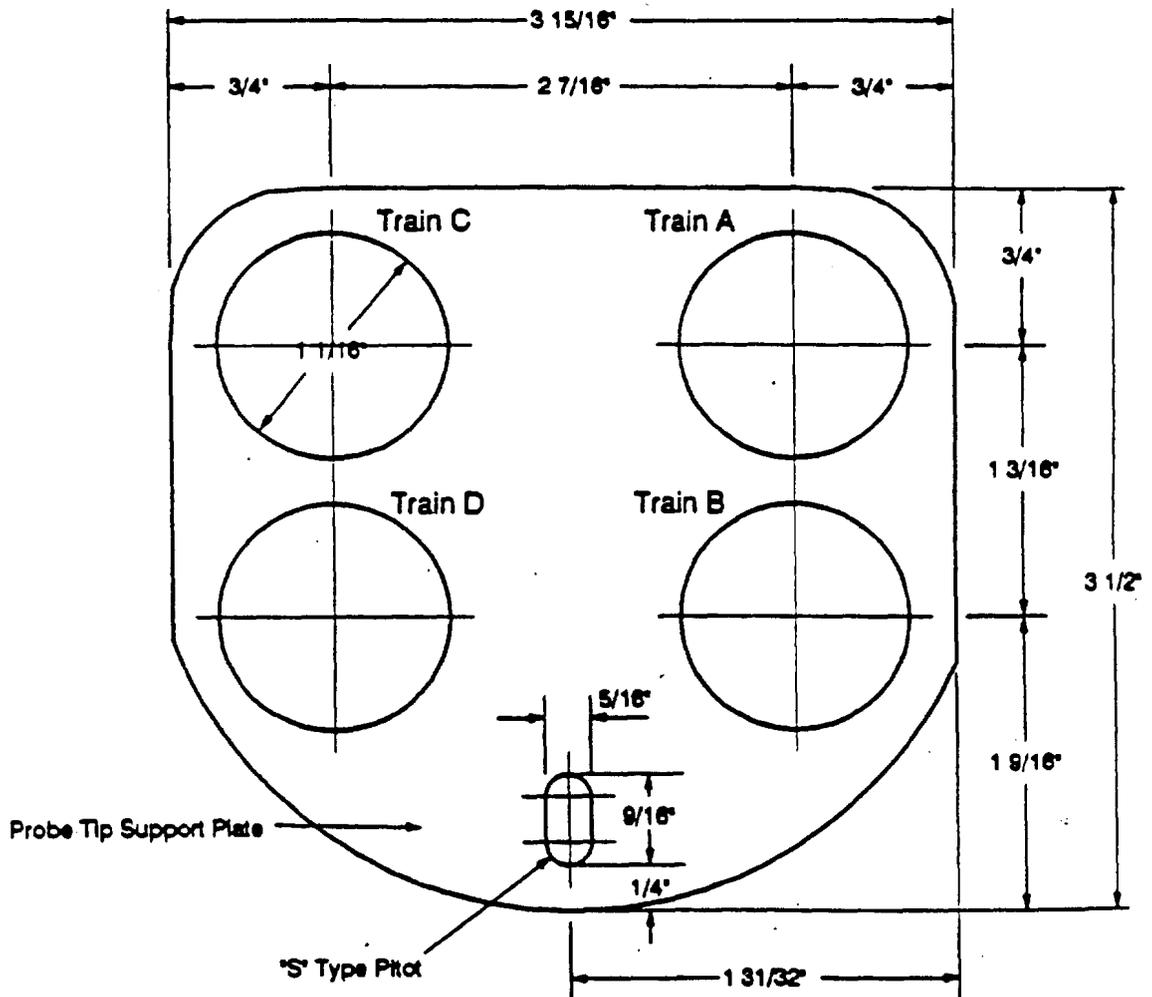
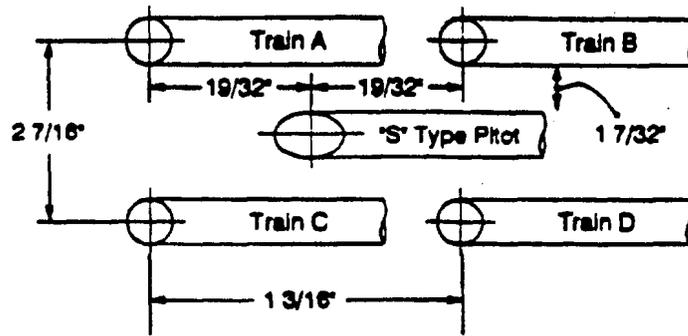
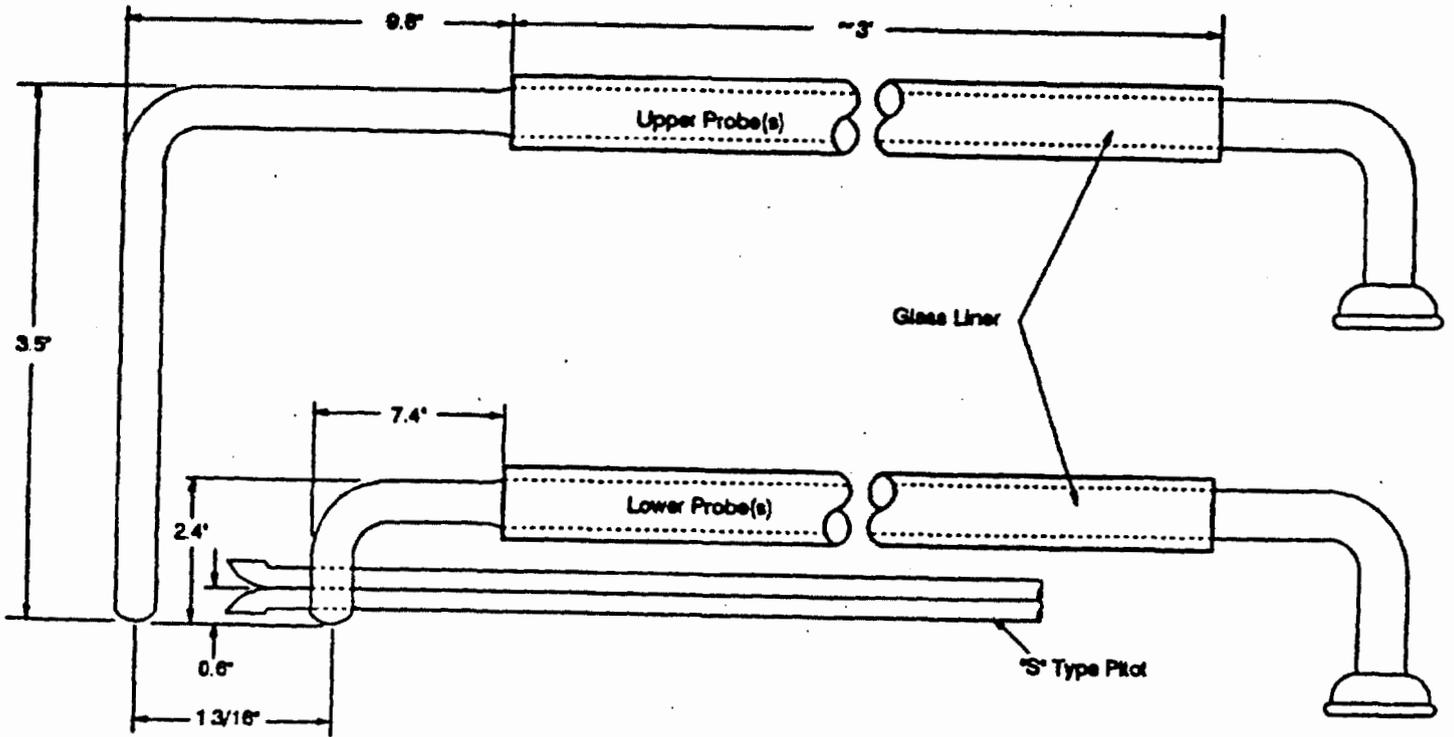


Figure 4-27. Quad-train probe and pitot arrangement.

5510431R



Drawing not to scale. For clarity, probe detail is exaggerated.

Figure 4-28. Upper and lower sampling probes (side view).

4.2.3 Preparation for Sampling

4.2.3.1 Glassware Preparation

All glassware used for sampling was thoroughly cleaned prior to use, including the probe, impingers, all sample bottles and all utensils used during sample recovery. All glassware was washed with hot soapy water, rinsed with hot tap water, rinsed with distilled water and baked in a oven at 300°C for four hours. The glassware was then triple rinsed with HPLC grade acetonitrile followed by triple rinsing with HPLC grade toluene.

4.2.3.2 Preparation of Impinger Absorbing Solution

Data collected by Radian from preliminary samples taken at the test site facility was used to determine the amount of the isocyanate that would be collected in 30 cubic feet of stack gas. Based on the stoichiometric relationship between the derivatizing agent and the isocyanate compound detected (HDI), the minimum concentration of piperazine in toluene for use in the impingers was calculated. The actual concentration of piperazine needs to be in excess of this minimum amount to ensure that the capacity of the absorbing solution is not exceeded due to variations in isocyanate concentration and/or sample volume collected. Therefore, the concentration of piperazine in toluene was prepared at a level four times the calculated minimum needed based upon the analysis of pre-survey samples. This solution was prepared in the laboratory just prior to going into the field and was used within 10 days of preparation.

4.2.3.3 Preparation of Spiking Solutions

Sufficient spiking solution was added to the first impinger so that the amount present in the two spiked trains was at least twice the amount expected in the two unspiked trains. The actual concentration of the spiking solution was determined by the results of the preliminary sampling. The spiking solution was spiked into the first impinger of two of the trains prior to each quad run.

4.2.3.4 Sampling Equipment Preparation

The remaining pre-test preparation included calibration and leak checking of all the train equipment, including meterboxes, thermocouples, nozzles, pitot tubes, and umbilicals. Reference calibration procedures were followed when available, and the results were properly documented and retained. If a referenced calibration technique for a particular piece of apparatus was not available, then a state-of-the-art technique was used. A discussion of the techniques used to calibrate this equipment is presented below.

S-Type Pitot Tube Calibration. The EPA has specified guidelines concerning the construction and geometry of an acceptable S-Type pitot tube. Information pertaining to the design and construction of the Type-S pitot tube is presented in detail in Section 3.1.1 of the EPA's *Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods* (EPA 600/4-77-027b). If the specified design and construction guidelines are met, a pitot tube coefficient of 0.84 can be used. Only S-Type pitot tubes meeting the

required EPA specifications were used. Pitot tubes were inspected and documented as meeting EPA specifications prior to field sampling.

Sampling Nozzle Calibration. Glass nozzles were used for sampling. All nozzles were thoroughly cleaned, visually inspected, and calibrated according to the procedure outlined in Section 3.4.2 of the EPA's Quality Assurance Handbook.

Dry Gas Meter Calibration. Dry gas meters (DGMs) were used in the sample trains to measure the sample volume. The sampling rate was also monitored; however, no exhaust gas volumetric flow rate was reported. All DGMs were calibrated to document the volume correction factor prior to the departure of the equipment to the field.

Prior to calibration, a positive pressure leak check of the system was performed using the procedure outlined in Section 3.3.2 of the EPA's Quality Assurance Handbook. The system was placed under approximately 10 inches of water pressure and a gauge oil manometer was used to determine if a pressure decrease could be detected over a one-minute period. If leaks were detected, they were eliminated before actual calibrations were performed.

After the sampling console was assembled and leak checked, the pump was allowed to run for 15 minutes to allow the pump and DGM to warm up. The valve was then adjusted to obtain the desired flow rate. For the pre-test calibrations, data were collected at the orifice manometer settings (ΔH) of 0.5, 1.0, 1.5, 2.0, 3.0, and 4.0 in H_2O . Gas volumes of 5 ft^3 are used for the two lower orifice settings, and volumes of 10 ft^3 are used for the higher settings. The individual gas meter correction factors (γ) are calculated for each orifice setting and averaged. The method requires that each of the individual correction factors fall within $\pm 2\%$ of the average correction factor or the meter will be cleaned, adjusted, and recalibrated. In addition, Radian requires that the average correction factor be 1.00 ± 1 percent.

Dry gas meter calibrations were performed at Radian's Perimeter Park (PPK) laboratory in Morrisville, N.C. using an American wet test meter as an intermediate standard. The "intermediate standard" is calibrated every six months against the EPA spirometer at EPA's Emission Measurement Laboratory in Research Triangle Park (RTP), North Carolina.

Preparation of Sample Train. The four sample trains for each run were charged and assembled in the recovery trailer. The impinger buckets were clearly marked as Train A, B, C, or D. Tared impingers were used. Approximately 300 mL of the absorbing reagent were transferred to the first impinger and 200 mL to the second and third impingers. (Only two impingers with reagent were used in the first field test for TDI.) The first impinger was a Greenburg-Smith design and all remaining impingers were of the modified Greenburg-Smith design. The fourth impinger remained empty, 200 to 300 g of silica gel was placed in the fifth impinger, and 400 g of charcoal was placed in the sixth impinger. A water jacketed condenser was placed between the outlet of the first impinger and the

inlet to the second impinger. Ten (10) mL of the spiking solution was pipetted into the first impinger of Trains A and B. Openings were covered with Teflon® film or aluminum foil after the assembly of the trains.

Final assembly of the sample trains occurred at the sampling location. Thermocouples were attached to measure the stack temperature and probe outlet and impinger outlet temperatures. Crushed ice was added to each impinger bucket, and the probe heaters turned on and allowed to stabilize at $120^{\circ} \pm 13^{\circ}\text{C}$ ($248^{\circ} \pm 25^{\circ}\text{F}$).

The isocyanate trains were leak checked after sampling was completed as required in EPA Method 5. Leak checks were also performed prior to sampling as a precautionary measure. If a piece of glassware needed to be emptied or replaced, a final leak check was performed before the glassware piece was removed. An initial leak check was performed after the train was re-assembled.

To leak check the assembled train, the nozzle end was capped off and a vacuum of 15 in. Hg was pulled in the system. Once the vacuum had been pulled, the volume of gas flowing through the system was measured for 60 seconds. The leak rate is required to be less than 0.02 acfm (ft^3/min) or 4% of the average sampling rate, whichever is less. After the leak rate was determined, the cap was slowly removed from the nozzle end until the vacuum dropped off, and then the pump was turned off. If the leak rate requirement was not met, the train was systematically checked until the leak was located and corrected.

The leak rates and sampling start and stop times were recorded on the sampling task log. Also, any other events that occurred during sampling were recorded on the task log (such as pitot cleaning, thermocouple malfunctions, heater malfunctions, and any other unusual occurrences).

Sampling train data were recorded every five minutes on standard data forms. With the single-pitot arrangement used in the quad-test, the pitot tube was connected to only one of the four DGM boxes.

4.2.4 Sample Recovery

Recovery of the sample from the probes and nozzles was performed at the sampling location. The sample bottles containing the probe and nozzle washings and each of the sampling trains were moved to the recovery trailer.

Each impinger was carefully removed from the impinger bucket, the outside wiped dry, and the final impinger weight determined and recorded. The isocyanate sample was then collected in the following fractions as separate samples:

- First impinger contents, toluene rinses from the nozzle/probe liner and toluene/acetonitrile rinses of the first impinger and connecting glassware; and

- Contents and toluene/acetonitrile rinses from the second, third, and fourth impingers and the condenser.

Recovery procedures are detailed below. All recovery bottles were wide mouth amber glass with Teflon® lined lids.

4.2.4.1 Container 1 - Probe and First Impinger Contents

The contents of each of the first impingers and first impinger connectors were included with the appropriate probe/nozzle washing solution. The entire contents of the first impinger were recovered as a single sample even if two phases were present. A small portion of toluene was used to rinse the first impinger and connector three times. A final rinse of the impinger with acetonitrile was also necessary to remove any water left on the impinger wall and to recover any remaining derivatized isocyanates.

4.2.4.2 Container 2 - Second, Third, and Fourth Impinger Contents/Condenser Rinse

The contents and toluene/acetonitrile rinses of the second, third, and fourth impingers and the condenser of each train were collected in the same manner described above. The contents of these impingers were analyzed separately from the contents collected in the first impinger to check for breakthrough; therefore, care was taken to avoid physical carryover from the first impinger to the second. Any carryover would invalidate the breakthrough assessment and would be noted on the recovery documentation. The contents of the fifth and sixth impingers were weighed as previously described and then discarded.

4.2.4.3 Sample Storage and Shipping

Sample containers were checked to insure that complete labels had been affixed. The labels identified Trains A, B, C, or D as appropriate. Teflon® lids were tightened and secured with Teflon® tape. The sample bottles were placed in a cooler, packed with ice, and returned to Radian's laboratory at the end of the field test.

4.2.5 *Blanks*

4.2.5.1 Field Blanks

Two sets of four complete trains were used for sampling during this test. Quad trains not in use for a particular run were available for preparing field blanks. A total of four field blanks were prepared and recovered. The four field blanks were prepared by systematically using Trains A, B, C, and D from each set (A-1, B-2, C-1, D-2). A field blank was prepared by assembling a sampling train in the staging area, taking it to the sampling location, and performing a leak-check. The probe of the blank train was heated during the sample test, but no gaseous sample passed through the sampling train. The sampling train was recovered in the same manner previously described.

4.2.5.2 Reagent Blanks

Aliquots of each lot of toluene, acetonitrile and absorbing reagent were collected daily.

4.2.6 Results of Field Tests

Three host facilities were identified which agreed to allow the use of their facility for the evaluation of the method under actual test conditions. Each of these facilities is discussed below in chronological order, along with the results of the field test.

4.2.6.1 Flexible Foam Manufacturing (TDI)

Vent gas samples containing TDI were collected at a foam production plant located in Central NC during the period February 22, 1993 to February 26, 1993. In the manufacturing process starting materials (TDI, water, a polyether resin, methylene chloride, an amine catalyst, and coloring additives) are blended in specific proportions and continuously fed onto a conveyer belt. The TDI reacts with H₂O releasing CO₂ which causes the foaming action to occur in the resin material. Methylene chloride (MeCl₂) can be added as a supplemental "blowing" or foaming agent. The heat from the reaction of TDI and water causes the MeCl₂ to vaporize, resulting in increased foaming. The degree of foaming (i.e., the density of the foam) is controlled by the amount of TDI and MeCl₂ added. The foaming action continues as the material proceeds down the conveyer belt. Each continuous length of finished product (or "Bun"), is then allowed to cure and degas for 24 to 48 hours.

Two production runs were performed each day Monday through Friday, one in the morning and one in the afternoon. Each continuous production run is one to two hours in length and may result in as many as ten different types of foam based on foam density, hardness, color, and width. The production of each foam type will consume approximately 15 minutes of the continuous production run. The composition of the starting materials is changed to produce the different types of foam. The lower the density of a particular foam, the greater the amount of TDI and/or MeCl₂ that is required in the starting formulation.

Three exhaust vents are used to remove the TDI and MeCl₂ vapors from over the production line.

Figure 4-29 presents a schematic view of the sampling location. Three induction (ID) fans are used to exhaust vapors from the production process through three separate uninsulated sheet metal ducts that extend through the roof. Two of the ducts are connected by a 30' horizontal length of duct, 34" in diameter, which then extends vertically to a height of 25' above the roof top. A 6" diameter sampling port is located in the horizontal duct midway between the vertical ducts #2 and #3, approximately 5' feet above the roof level. The roof level is approximately 15' above the ground.

Eight QUAD runs were collected (two per day for four days). This number of runs allowed for two extra runs above the required six in the event of sample loss during recovery, transport, or sample analysis.

Bias and Precision. Table 4-11 is a summary table which presents the results of the statistical evaluation of the test data following the EPA Method 301 criteria showing the method precision and bias for 2-4 TDI. Method 301 requires valid data from a minimum of six QUAD runs. Table 4-11 presents data from all eight runs. Precision is shown as the percent relative standard deviation of the measured amounts of TDI in the samples. Results for precision of both the spiked and unspiked samples were less than 5 percent RSD, which is well within the limits of acceptable precision (upper limit of 50%) given in EPA Method 301.

Table 4-11. Summary of Method 301 Statistical Calculations for TDI

Parameter	Spiked Trains		Unspiked Trains	
	7 Runs	8 Runs	7 Runs	8 Runs
Spiked Amount ¹	7828	7828	--	--
RSD, %	3.6	3.4	4.7	5.2
Average Bias ¹	-295	-395	--	--
Bias Significant?	No	Yes	--	--
Correction Factor	1.0	1.053	--	--

¹Values are presented as μg of underivatized TDI

Using the data from all eight QUAD runs, method bias was measured at -395 micrograms. This value was determined to be statistically significant at the 95% confidence level, using the t-statistic calculated for the analytical data. A correction factor of 1.053 was calculated for use with the method to compensate for the bias should the method be used to measure TDI emissions from similar sources.

Using the data from only seven QUAD runs (eliminating run 8 because this run had the lowest average % recovery and the final leak check for one of the trains was questionable), the method bias was -295 micrograms. This bias was not statistically significant and therefore no correction factor was calculated. In either case, the criteria for an acceptable method were met (i.e., a correction factor between 0.7 and 1.3).

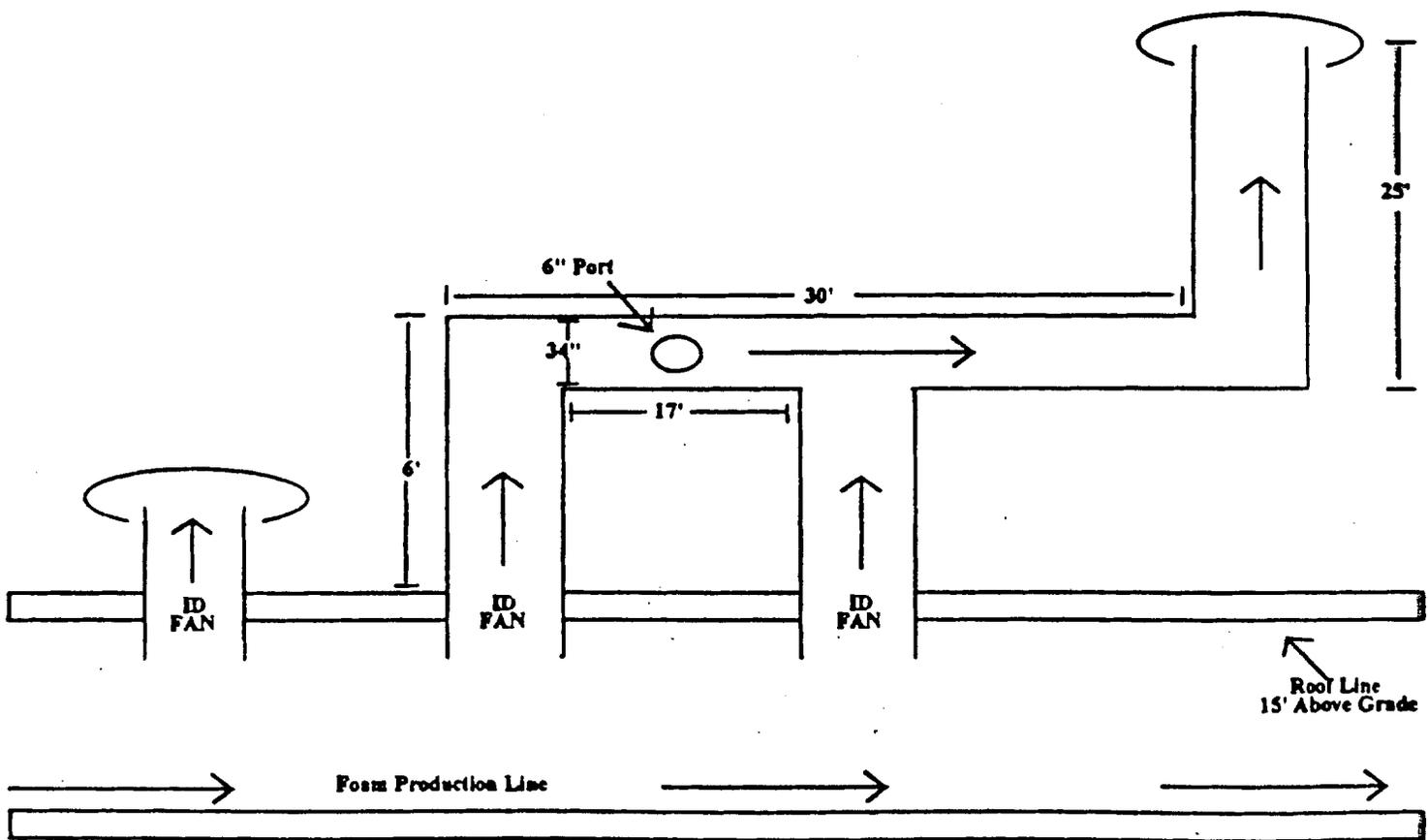


Figure 4-29. Sample location for TDI.

Breakthrough and Recovery. This section presents details of the breakthrough and recovery results for the field samples, as well as recovery information for the spiked compound (2,4-TDI).

Breakthrough. Table 4-12 provides a summary of the combined total mass of 2,4-TDI collected in the probe/first impinger and second/third impinger samples for the unspiked and spiked trains, respectively. These totals are used as a basis for calculating breakthrough of the TDI from the first impinger to the second impinger. The mass of compound found in the probe/first impinger fraction and in the second impinger fraction was divided by the total mass of TDI for that train and then multiplied by 100 to yield the percent of the total TDI found in the separate train sections. The results are presented in Table 4-13.

Table 4-12. 2,4-TDI Detected in Each Train, μg

Quad Run	Train 1	Train 2	Train 3	Train 4
1	12,263	11,520	4,735	4,811
2	6,287	6,270	13,258	13,733
3	11,625	12,078	3,466	3,166
4	2,132	2,139	9,694	9,805
5	12,233	12,717	4,947	5,522
6	8,042	7,608	15,741	15,610
7	10,450	9,290	2,558	2,616
8	4,086	4,579	11,197	10,770

Table 4-13. Percent 2,4-TDI Recovered from 2nd Impinger

Quad Run	Train 1 %	Train 2 %	Train 3 %	Train 4 %
1	1.41	0.61	0.41	1.89
2	1.19	0.76	0.69	0.97
3	1.12	1.14	0.96	1.06
4	0.86	1.24	3.09	1.42
5	0.88	0.73	0.36	0.82
6	1.31	1.17	1.15	1.29
7	1.99	1.68	1.07	1.62
8	1.49	1.29	1.21	1.13

The average breakthrough for the spiked trains was 1.5% and for the unspiked trains 1.1 percent. More than 98% of the TDI was collected in the first impinger under the sampling conditions used in this study.

The amount of the toluene contained in the first impingers of each of the trains was reduced by approximately 25% (by weight) during the sampling run due to evaporation. The second impingers showed, on the average, a net gain of approximately 5 percent. The remainder was collected in the silica gel and the charcoal, both of which showed net weight gains. The total weight gained in the train components following the first impinger more than compensates for losses from the first impinger, probably due to the collection of a small amount of moisture. The loss of toluene from the first impinger was minimized by keeping the impingers in an ice bath and placing a water cooled condenser between the outlet of the first impinger and the inlet of the second impinger.

Recovery. One of the objectives of this test program was to obtain bias and precision data to validate the proposed test method for isocyanates. Samples from two of the four trains of each quad assembly were spiked with TDI before each sampling run. The estimation of method bias is based on the percentage of the TDI spikes recovered. Analytical results used for this calculation are the averages of the triplicate analysis results for each spiked sample. A summary of the spiked TDI recovery percentages is presented in Table 4-14.

Table 4-14. Percent Recovery of the Spiked 2,4-TDI

Train ¹	QUAD Run No.							
	1	2	3	4	5	6	7	8
A	96 ²	--	106	--	89	--	100	--
B	86	--	112	--	96	--	86	--
C	--	89	--	97	--	98	--	88
D	--	95	--	98	--	99	--	83
Average	95							
% RSD	8.2							

¹Spiked Trains alternated from run to run, A and B, then C and D.

²Values are a percentage based upon a spiked amount of 7827.8 µg as 2,4-TDI.

The percent recovery was calculated for each spiked train for each run following the example calculation procedures outlined in steps 1-3 of Section 6.0. The value obtained at step 3, the amount of spike recovered, is divided by the actual amount of TDI spiked, 7827 µg, multiplied by 100. An average recovery was determined by averaging the 16 individual run recoveries.

The recovery for TDI ranged between 83 and 112 percent and averaged 95 percent with a %RSD of 8.2.

4.2.6.2 Pressed Board Manufacturing (MDI)

Vent gas samples containing MDI were collected at a pressed board manufacturing plant located in western Virginia during the period September 22, 1993 through September 26, 1993. In the manufacturing process, the board product is made from combining wood materials under pressure with an adhesive. The adhesive formulation includes MDI and phenyl formaldehyde.

The process begins as whole logs are de-barked and pass through a chipper, where the logs are reduced to wood chips that are approximately 4 square inches. The chips are dried to a specific moisture content in a rotary kiln and then passed to a rotary mixer where the binder material is added. The chips are then fed onto a conveyor belt in sections that are approximately 4' x 8' x 3". Each section is then heated under high pressure for approximately one minute. The resulting sheets are then trimmed to size and packaged for shipment.

Figure 4-30 presents a schematic view of the sampling location. Two 48-inch axial fans are used to exhaust vapors from the pressing process through a stack on the roof. The inside diameter of the stack is 59.5 inches. There is a stack divider in the section where the ducts from the two fans intersect the stack, which extends approximately 5 feet downstream past the junction. Sampling ports are located approximately 20 feet downstream of the stack divider. The four 6-inch diameter sampling ports are located equidistantly around the stack, five feet above a circular platform. The platform is located approximately 38 feet above the roof and is accessible by ladder from the rooftop. The roof level is approximately 40 feet above the ground.

A total of eleven quad runs were collected over the test period, allowing approximately 3 hours turnaround/recovery time between runs.

Bias and Precision. Table 4-15 is a summary table which presents the results of the statistical evaluation of the test data following the EPA Method 301 criteria showing the method precision and bias for MDI. Method 301 requires valid data from a minimum of six QUAD runs. Table 4-15 presents data from all eleven runs. Precision is shown as the percent relative standard deviation of the measured amounts of MDI in the samples. The precision of the spiked samples was less than 5% RSD, and less than 30% RSD for the unspiked samples, which is within the limits of acceptable precision (upper limit of 50%) given in EPA Method 301.

Using the data from eleven QUAD runs, method bias was measured at -50.6 micrograms. This value was determined to be statistically significant at the 95% confidence level, using the t-statistic calculated for the analytical data. A correction factor of 1.084 was calculated for use with the method to compensate for the bias should the method be used to measure MDI emissions from similar sources.

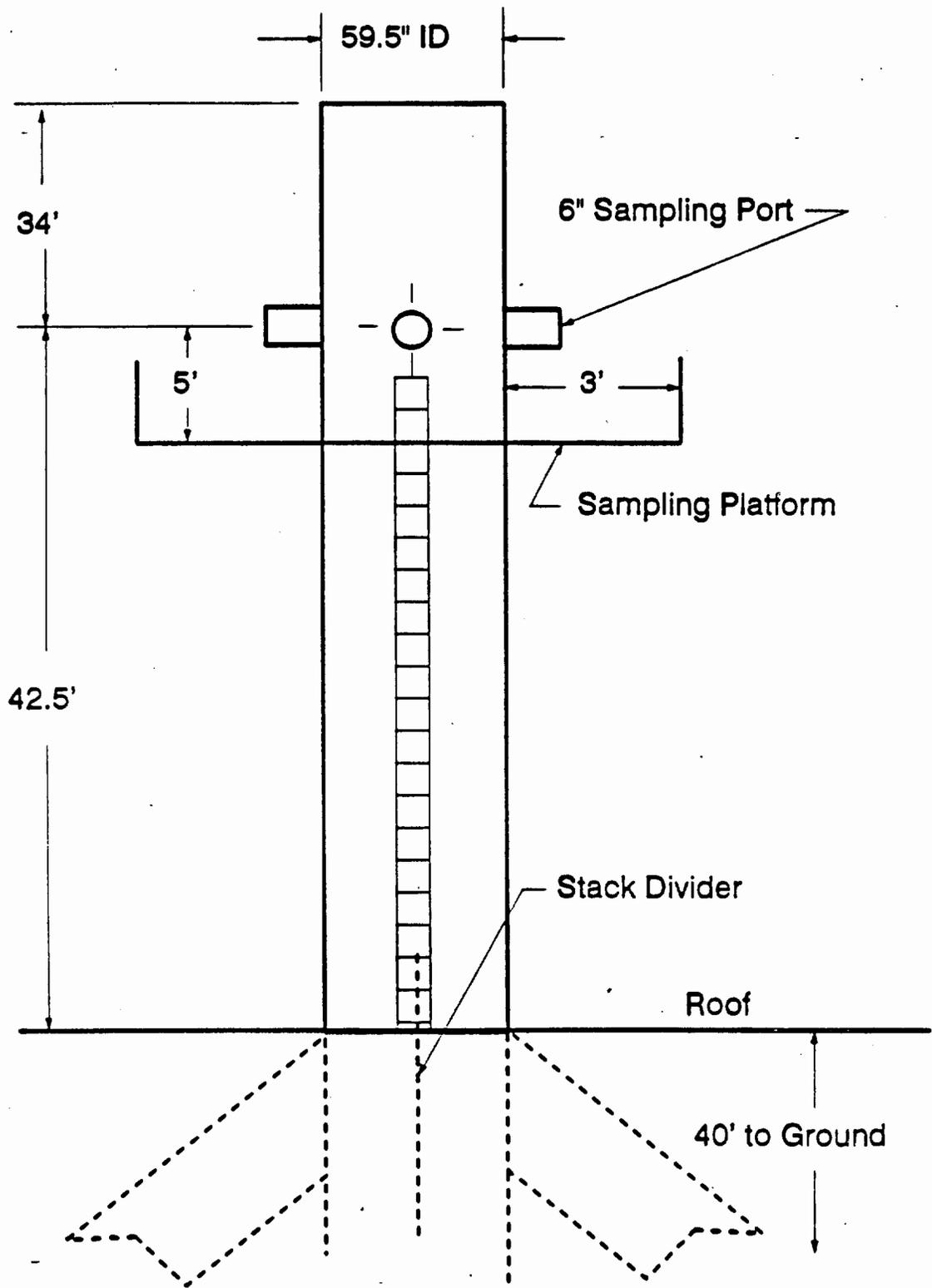


Figure 4-30. Sample location for MDI.

Table 4-15. Summary of Method 301 Statistical Calculations for MDI

Parameter	Spiked Trains			Unspiked Trains		
	Runs 1 to 4 ¹	Runs 7 to 12 ²	Runs 1 to 12 ³	Runs 1 to 4 ¹	Runs 7 to 12 ²	Runs 1 to 12 ³
Spiked Amount ⁴	651	651	651	-	-	-
RSD, %	6.01	2.96	4.25	11.96	33.43	28.18
Average Bias ⁴	-30.7	-52.6	-50.6	-	-	-
Bias Significant?	Yes	Yes	Yes	-	-	-
Correction Factor	1.049	1.088	1.084	-	-	-

¹Samples were collected at a Flow Rate of 0.75 cfm.

²Samples were collected at a Flow Rate of 0.50 cfm.

³Data is a combination of samples collected at both flow rates. Run 5 was statistically excluded as an outlier.

⁴Values are presented as ug of underivatized MDI.

Using the data from QUAD Runs 1 to 4 (Sampling flow rate of 0.75 cfm; isokinetic, and eliminating Run 5 because the data from Train A were statistically found to be outliers), method bias was measured at -30.7 micrograms. This value was determined to be statistically significant at the 95% confidence level, using the t-statistic calculated for the analytical data. A correction factor of 1.049 was calculated for use with the method to compensate for the bias should the method be used to measure MDI emissions from similar sources using a flow rate of 0.75 cfm.

Using the data from QUAD Runs 7 to 12 (Sampling flow rate of 0.5 cfm; non-isokinetic, and eliminating Run 6 because the spike recoveries were significantly lower at 81% and 82% for the two spiked trains), method bias was measured at -52.6 micrograms. This value was determined to be statistically significant at the 95% confidence level, using the t-statistic calculated for the analytical data. A correction factor of 1.088 was calculated for use with the method to compensate for the bias should the method be used to measure MDI emissions from similar sources using a flow rate of 0.5 cfm. In any case, the criteria for an acceptable method were met (i.e., a correction factor between 0.7 and 1.3).

Breakthrough and Recovery. The extent of breakthrough of MDI from the first impinger to the second during sampling was determined by dividing the amount found in the second impinger of each train by the total amount found in the entire train less the amount due to the spike. The results are presented in Table 4-16.

Table 4-16. Percent of MDI Recovered from 2nd Impinger

Quad Run	Train				Averages		
	A	B	C	D	Spiked ¹	Unspiked ¹	All
1	4.2	2.7	8.2	2.6	3.5	5.4	4.4
2	2.9	10.4	12.0	28.7	20.4	6.7	13.5
3	7.5	7.1	6.3	10.4	7.3	8.4	7.8
4	5.8	18.2	10.4	8.6	9.5	12.0	10.8
5	5.9	5.1	11.6	7.0	5.5	9.3	7.4
6	7.0	9.1	12.2	8.3	10.3	8.0	9.1
7	4.0	4.1	4.2	7.1	4.0	5.6	4.9
8	3.0	5.6	3.3	3.9	3.6	4.3	3.9
9	6.4	6.1	6.4	6.9	6.2	6.6	6.5
10	5.6	4.2	5.8	5.4	5.6	4.9	5.3
11	4.1	7.2	5.0	5.0	5.6	5.0	5.3
12	6.4	6.9	7.6	7.9	6.6	6.6	7.2

¹Spiked Trains alternate from run to run, A and B, then C and D.

The average breakthrough for the spiked trains (Flow rate at 0.75 cfm Runs 1 through 5) was 9.2% with an %RSD of 72, and 8.3% for the unspiked trains with a %RSD of 30. The average breakthrough for the spiked trains (Flow rate at 0.5 cfm, Runs 6 through 12) was 6.0% with a %RSD of 37, and 5.9% for the unspiked trains with a %RSD of 22. The average breakthrough for all spiked trains was 7.3% with an %RSD of 63, and for all unspiked trains 6.9% with an %RSD of 32.

One of the objectives of this test program was to obtain bias and precision data to validate the proposed test method for isocyanates. Samples from two of the four trains of each quad assembly were spiked with MDI before each sampling run. An estimation of method bias can be shown by percent recovery of the MDI spikes. Analytical results used for this calculation are the averages of the triplicate analysis results for each spiked sample. A summary of the spiked MDI recovery percentages is presented in Table 4-17 and the total amount of MDI detected is summarized in Table 4-18.

The recovery for MDI ranged between 55 and 105% for those trains collected at 0.75 cfm and averaged 91 percent with an %RSD of 15.3. The seven trains that had a collection flow rate of 0.5 cfm had recoveries that ranged between 81 and 101% and averaged 91% with an %RSD of 7.0. The recovery for MDI for all trains collected ranged from 55 to 105% and averaged 91% with an %RSD of 11.

Table 4-17. Percent Recovery of the Spiked MDI

Quad Run	Train			
	A	B	C	D
1	101	96	--	--
2	--	--	105	88
3	83	94	--	--
4	--	--	93	99
5	55	93	--	--
6	--	--	81	82
7	96	90	--	--
8	--	--	85	83
9	92	85	--	--
10	--	--	87	101
11	95	91	--	--
12	--	--	96	93

Table 4-18. MDI Detected in Each Train, μg

Quad Run	Train 1	Train 2	Train 3	Train 4
1	775	744	113	119
2	63	77	751	664
3	627	698	81	87
4	99	127	717	754
5	483	735	146	111
6	117	122	650	656
7	807	768	223	152
8	254	122	739	728
9	669	622	64	72
10	145	145	775	805
11	746	722	122	133
12	64	67	689	674

4.2.6.3 Paint Spray Booth (HDI, MI, TDI, and MDI)

Vent gas samples containing HDI were collected from the paint spraying operation at an automobile manufacturing facility located in the Eastern one-half of the United States during the period May 24, 1994 through May 27, 1994. In the manufacturing process automobile bumpers are sprayed with an undercoating, a color coating and finally a clear top coating. The process is continuous from the time the untreated bumpers are loaded onto traveling spray racks until they are transported to the assembly area. The first step is the application of the undercoat after which the bumpers pass through a drying oven before the remaining two coats are applied. The bumpers then

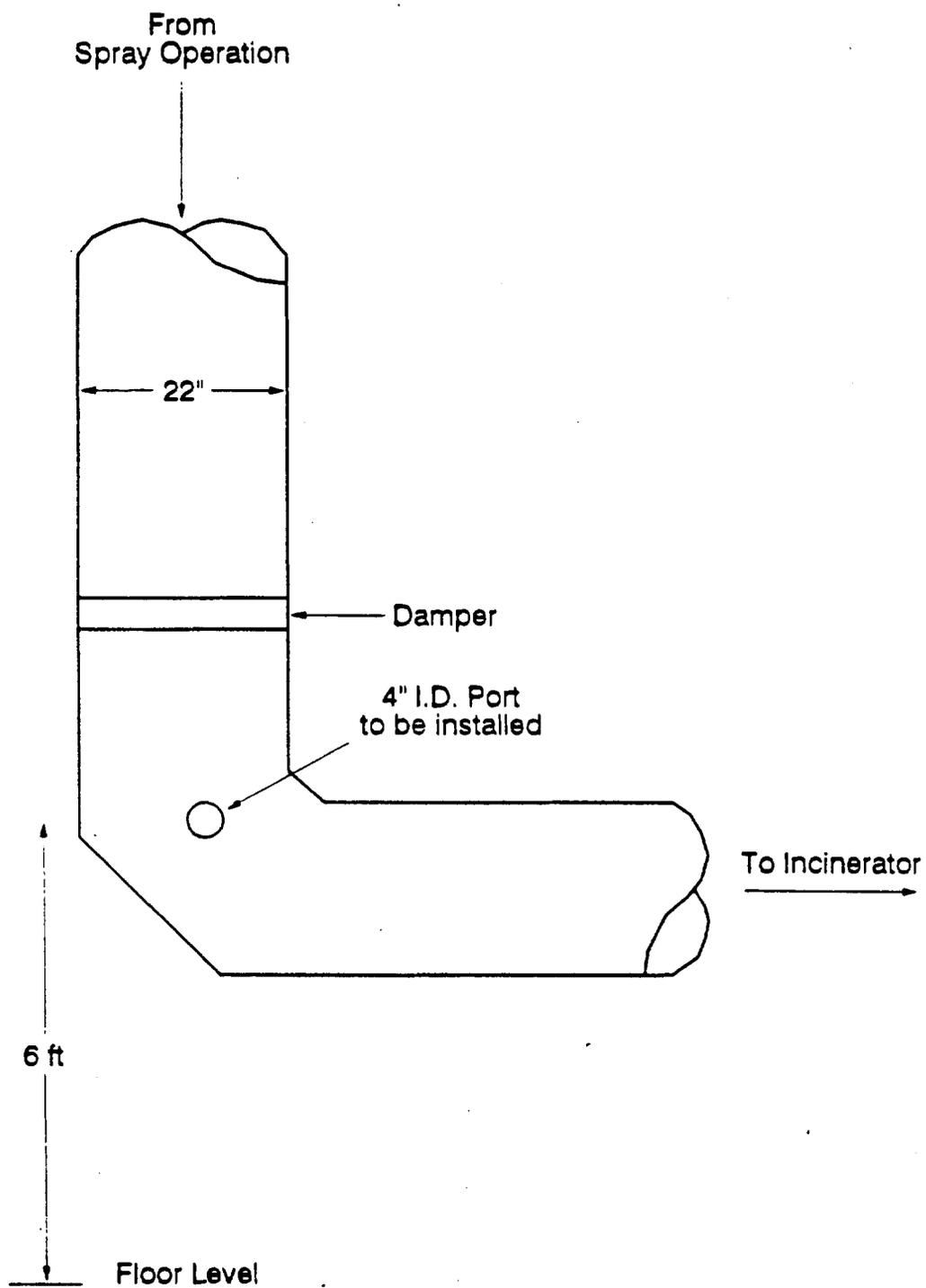


Figure 4-31. Schematic view of the sampling location for HDI.

have the color coat applied, pass through a "flash zone" where the paint begins to dry and then travel to a third spray booth where a clear top coat is applied. The bumpers then travel through the final drying oven and on to the assembly area.

The plant operates three shifts per day, Monday through Friday with scheduled breaks during each shift. Sampling was completed prior to any breaks.

Exhaust vents from the spray booths, "flash zones" and drying ovens converge into a single duct that leads to an incinerator. Samples were collected from this duct. Figure 4-31 presents a schematic view of the sampling location. The uninsulated duct is 24 inches by 24 inches with several 2 inch ports located 107 inches above the floor level. A new 4 inch port was installed at the location indicated in Figure 4-31 by the facility prior to the sampling date.

Bias and Precision. Table 4-19 is a summary table which presents the results of the statistical evaluation of the test data following the EPA Method 301 criteria showing the method precision and bias for HDI, MDI MI, and TDI, with HDI being the only isocyanate in the stack gas. Method 301 requires valid data from a minimum of six QUAD runs. Table 4-19 presents data from all twelve runs. Precision is shown as the percent relative standard deviation of the measured amounts of isocyanates in the samples. The precision of the spiked samples was less than 5% RSD for all four isocyanates, which is within the limits of acceptable precision (upper limit of 50%) given in EPA Method 301. The precision for the unspiked trains for HDI was less than 10% RSD, while the precision values for TDI and MI were less than 30% RSD. The precision for MDI in the unspiked trains was 56.1% RSD. The poorer precision values for the three compounds not present in the stack gas can be explained by the fact that the observed values are most likely due to trace contamination that was detected near the detection limit where values are inherently less precise.

Table 4-19. Summary of 301 Statistical Calculations for Twelve Runs

Parameter	MI		HDI		TDI		MDI	
	Spiked	Unspiked	Spiked	Unspiked	Spiked	Unspiked	Spiked	Unspiked
Spiked amount, μg	10,060	--	161.4	--	171.2	--	164.9	--
RSD, %	3.7	--	3.3	--	2.0	--	2.8	--
Average bias	304	--	3.325	--	1.788	--	-1.4	--
Bias significant	Yes	--	Yes	--	No	--	No	--
Correction factor	0.9706	--	0.9798	--	--	--	--	--

Using the data from twelve QUAD runs, method bias was measured at 3.33, -1.4, 304 and 1.79 micrograms, respectively, for HDI, MDI, MI and TDI. The values for HDI and MI were determined to be statistically significant at the 95% confidence level, using the t-statistic calculated for the analytical data. Therefore, a correction factor was calculated for use with the method to compensate for the bias should the method be used to measure HDI or MI

emissions from similar sources. The calculated correction factor for HDI is 0.9798 and for MI is 0.9706. The biases for MDI and TDI were not significant and therefore do not require a correction factor. The criteria for an acceptable method were met (i.e., a correction factor between 0.7 and 1.3 and a %RSD <50).

Breakthrough and Recovery. The extent of breakthrough of HDI from the first impinger to the second/third impinger during sampling was determined by dividing the total amount found in the second/third impingers of each train by the total amount found in the entire train less the amount due to the spike. Any breakthrough for MDI, MI and TDI would not be due to sampling as these compounds were not in the stack gas but would be the result of impinger solution carry over. The results are presented in Table 4-20 through 4-23.

Table 4-20. Percent MI Recovered From 2nd Impinger

Quad Run	Methyl isocyanate			
	2,606 µg Spiked			
	Train A %	Train B %	Train C %	Train D %
1	41	38	39	36
2	38	37	38	36
3	37	39	37	37
4	33	27	35	34
5	44	44	40	42
6	35	35	37	35
7	38	38	28	32
8	35	25	30	28
9	21	19	17	32
10	33	36	46	32
11	19	25	20	21
12	23	42	31	30

Table 4-21. Percent HDI Recovered From 2nd Impinger

Quad Run	Hexamethyl diisocyanate			
	161.4 µg Spiked			
	Train A %	Train B %	Train C %	Train D %
1	1.8	0.0	0.4	0.0
2	1.2	0.0	0.3	1.1
3	0.3	0.8	0.7	1.0
4	0.0	0.0	0.0	0.9
5	0.0	0.0	0.0	0.0
6	0.5	0.0	0.0	2.4
7	0.7	0.7	2.5	0.4
8	0.5	0.0	0.3	0.0
9	0.0	0.0	0.0	0.0
10	0.6	1.2	0.6	0.5
11	0.0	0.0	0.0	0.0
12	48.9	21.1	15.1	5.4

Table 4-22. Percent TDI Recovered From 2nd Impinger

Quad Run	Hexamethyl diisocyanate			
	161.4 µg Spiked			
	Train A %	Train B %	Train C %	Train D %
1	0.0	0.0	0.0	0.0
2	0.0	0.0	0.0	0.0
3	0.0	0.0	0.0	0.0
4	0.0	5.0	0.0	0.0
5	0.0	0.0	0.0	3.7
6	0.0	0.0	0.0	0.0
7	0.0	2.2	0.0	0.0
8	8.0	0.0	0.0	0.0
9	0.0	0.0	0.0	0.0
10	2.2	0.0	0.0	0.0
11	4.0	0.0	0.0	0.0
12	17.6	15.6	0.0	0.0

Table 4-23. Percent MDI Recovered From 2nd Impinger

Methylene diphenyl diisocyanate		161.4 μg Spiked			
Quad Run	Train A %	Train B %	Train C %	Train D %	
1	0.0	0.0	0.0	56.3	
2	0.0	0.0	0.0	0.0	
3	0.0	0.0	0.0	0.0	
4	0.0	0.0	0.0	0.0	
5	0.0	0.0	0.0	0.0	
6	0.0	0.0	0.0	0.0	
7	0.0	0.0	0.0	0.0	
8	0.0	0.0	0.0	0.0	
9	0.0	0.0	0.0	0.0	
10	0.0	0.0	4.2	0.0	
11	0.0	0.0	0.0	0.0	
12	0.0	0.0	0.0	4.8	

The average breakthrough for the spiked trains for HDI, MDI and TDI was 1.3%, 0.38% and 0.26%, respectively and 3.3%, 2.3%, and 2.2% for the unspiked trains. The average "apparent" breakthrough for MI was 34 percent. This "apparent" breakthrough was due to an impurity present in the 1,2pp that presented a peak in the chromatogram with a retention time similar to that of MI. The area of this peak could not be accurately removed as background due to small variations in the volume of the 1,2pp solution added to the sampling train impingers at the time of sample collection. Therefore, it can be assumed that if any breakthrough was present, the value would be considerably less than the 30% reported.

One of the objectives of this test program was to obtain bias and precision data to validate the proposed test method for isocyanates. Samples from two of the four trains of each quad assembly were spiked with HDI, MDI, MI and TDI before each sampling run. An estimation of method bias can be shown by percent recovery of these spikes. Analytical results used for this calculation are the averages of the triplicate analysis results for each spiked sample. A summary of the recovery percentages is presented in Tables 4-24 through 4-27. The total μg found in each train is shown in Tables 4-28 through 4-31.

The recoveries for all compounds ranged between 90 and 114%. The average recovery for HDI, MDI, MI and TDI was 100%, 99%, 103% and 101%, respectively

Table 4-24. Percent Recovery of the Spiked MI

Methyl isocyanate		2606 μg Spiked		
Quad Run	Train A %	Train B %	Train C %	Train D %
1	103	104	0	0
2	0	0	104	103
3	105	106	0	0
4	0	0	107	96
5	102	106	0	0
6	0	0	105	96
7	103	104	0	0
8	0	0	103	102
9	101	105	0	0
10	0	0	94	102
11	102	100	0	0
12	0	0	113	105

Table 4-25. Percent Recovery of the Spiked HDI

Hexamethyl Diisocyanate		161.4 μg Spiked		
Quad Run	Train A %	Train B %	Train C %	Train D %
1	100	98	0	0
2	0	0	105	101
3	100	105	0	0
4	0	0	97	101
5	101	100	0	0
6	0	0	103	95
7	102	99	0	0
8	0	0	103	96
9	104	95	0	0
10	0	0	90	101
11	98	94	0	0
12	0	0	111	114

Table 4-26. Percent Recovery of the Spiked TDI

Toluene Diisocyanate		171.2 μ g Spiked			
Quad Run	Train A %	Train B %	Train C %	Train D %	
1	100	99	0	0	
2	0	0	103	102	
3	105	106	0	0	
4	0	0	99	104	
5	104	102	0	0	
6	0	0	100	99	
7	101	97	0	0	
8	0	0	102	95	
9	103	96	0	0	
10	0	0	96	103	
11	100	97	0	0	
12	0	0	105	109	

Table 4-27. Percent Recovery of the Spiked MDI

Methylene diphenyl Diisocyanate		161.4 μ g Spiked			
Quad Run	Train A %	Train B %	Train C %	Train D %	
1	97	97	0	0	
2	0	0	103	101	
3	102	103	0	0	
4	0	0	96	101	
5	100	99	0	0	
6	0	0	103	97	
7	100	97	0	0	
8	0	0	102	96	
9	102	94	0	0	
10	0	0	97	101	
11	96	95	0	0	
12	0	0	100	104	

Table 4-28. MI Detected in Each Train, μg

Quad Run	Train A	Train B	Train C	Train D
1	10,86.21	10,721.36	296.98	269.33
2	303.68	311.76	10,783.20	10,616.89
3	10,891.70	10,962.76	316.13	288.66
4	341.25	295.11	11,093.66	9,959.34
5	10,524.07	10,935.88	296.93	217.34
6	310.75	322.03	10,899.79	9,920.60
7	10,752.78	10,754.89	275.15	343.84
8	291.83	428.84	10,716.60	10,642.57
9	10,672.83	11,057.59	673.41	373.07
10	390.77	327.61	9,908.45	10,599.38
11	10,730.82	10,562.45	474.91	410.60
12	526.69	344.44	11,793.18	11,017.68

Table 4-29. HDI Detected in Each Train, μg

Quad Run	Train A	Train B	Train C	Train D
1	175.00	170.94	13.53	12.64
2	66.71	66.68	236.52	230.31
3	248.75	257.56	88.66	86.53
4	10.22	11.52	166.99	173.57
5	186.60	183.77	23.72	21.94
6	48.19	49.54	214.69	203.17
7	205.07	199.93	42.29	38.73
8	15.22	15.83	182.29	169.65
9	178.03	164.32	12.43	8.95
10	121.23	118.13	264.69	282.41
11	184.28	178.05	26.74	26.00
12	8.50	20.73	190/74	195.20

Table 4-30. 2,4-TDI Detected in Each Train, μg

Quad Run	Train A	Train B	Train C	Train D
1	172.35	171.24	1.70	2.25
2	2.01	2.17	178.81	176.33
3	181.01	182.69	2.11	1.94
4	0.54	0.97	169.61	177.98
5	180.38	177.61	2.49	2.15
6	1.32	1.75	172.67	171.04
7	174.20	168.11	2.54	1.53
8	2.09	1.90	176.04	165.39
9	178.36	166.53	2.73	0.65
10	2.15	2.98	167.54	179.66
11	173.98	169.15	2.85	2.55
12	1.46	2.01	180.37	187.51

Table 4-31. MDI Detected in Each Train, μg

Quad Run	Train A	Train B	Train C	Train D
1	161.81	161.69	2.72	4.15
2	0.00	0.00	169.21	166.94
3	169.09	170.48	0.00	0.69
4	0.00	0.00	158.84	166.60
5	166.24	164.28	1.22	0.00
6	0.26	0.00	169.25	160.38
7	165.98	160.55	0.08	1.87
8	0.04	0.00	167.46	157.68
9	168.34	156.70	1.75	0.00
10	1.93	1.32	161.21	168.25
11	162.60	160.75	3.68	5.05
12	5.07	5.18	169.67	176.14

Section 5 Analytical Instrument Performance and Quality Control

The laboratory QA program for this project includes proper handling, logging and tracking of incoming samples, procedure validations including HPLC column efficiency, calibration curves, daily QC checks and replicate analyses, and collection and/or analysis of sample, field and reagent blanks, and method spikes as well as field and laboratory spikes. A summary of the laboratory QC procedures detailed in this section is provided in Table 5-1.

Table 5-1. Laboratory Quality Control Procedures

Parameter	Analytical Method	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Linearity Check	HPLC	Run 6-point curve	At setup or when check std. is out-of-range	Correl. coeff. ≥ 0.995	Check integ., reinteg. if necessary, recalibrate
Retention Time	HPLC	Analyze Check Standard	1/6-8 injections	$\pm 15\%$ day-to-day; $\pm 5\%$ within one day	Check instr. funct. for plug, etc. Heat column; Adjust gradient
Calibration Check	HPLC	Analyze Check Standard	1/6-8 injections min. 2/set	$\pm 10\%$ of calibration curve	Check integ., remake std. or recalib.
System Blank	HPLC	Analyze Acetonitrile	1/day	≤ 0.1 level of expected analyte	Locate source of contam.; reanalyze
Replicate Analyses	HPLC	Re-inject Sample	1/10 samples or 1/set	$\pm 10\%$ of first inj.	Check integ., check instr. function, reanalyze
Method Spikes	HPLC	Analyze Spikes	1/10 samples	$\pm 20\%$	Check integ. check instr. function, reanalyze, re-prepare if possible

As a part of the testing for Work Assignments No. 55, 66, and 71, Radian designed and implemented a quality assurance/quality control (QA/QC) effort tailored to meet the specific needs of this project. The testing was conducted in accordance with QA/QC procedures described in the Quality Assurance Project Plan (QAPjP) prepared for each field test. The results of the QA/QC effort demonstrate that the data are reliable and meet project objectives for completeness and representativeness. The data met the QA objectives for precision and accuracy and there are no data quality issues that effect conclusions regarding the objectives of this project.

A summary of analysis results for QA/QC samples, which includes measures of precision and accuracy and limitations in the use of these data is presented in this section.

5.1 Overview of Data Quality

The QAPjP established specific QA objectives for precision (15% RSD), accuracy ($\pm 30\%$), and completeness (100%) for the determination of isocyanate emissions. The statistical results presented in Tables 4-11, 4-15 and 4-19 and the % recovery values given in Tables 4-14, 4-17 and 4-24 through 4-27 show that the objectives were met. The data quality acceptance criteria and the experimental results for each field test are summarized in Tables 5-2 through 5-4. Results for spike/spike duplicates and triplicate analyses were compared with the criteria. In all cases the criteria were met. Other data quality indicators for each type of analysis are also presented throughout the remainder of this section.

There are no cases where data quality issues impair the study's conclusions with respect to the validity of the sampling and analytical test method procedures. With exception of a limited number of samples, the quality of measurement data generated for the test parameters fully meets the data quality objectives outlined in the QAPjP.

Table 5-2. Data Quality Acceptance Criteria and Results Field Test #1

Parameter	Criteria	Results
TDI Spike Recovery	70 - 130%	83 - 112%
TDI Analysis Results QUAD Train, % RSD	15%	5%
Individual DGM Correction Factor Agreement	$\pm 2\%$ of Avg	<2%
Analytical Balance	≤ 0.1 g of Class S Weights	<0.1 g
HPLC Linearity Correlation Coeff.	>0.995	0.9995
HPLC Retention Time Variation	$\pm 15\%$	$\pm 10\%$
HPLC Calibration Check	$\pm 10\%$ of Curve	$\pm 9\%$
HPLC System Blank	<0.1% Analyte level	<0.1%
HPLC Replicate Analyses	$\pm 10\%$ of 1st injection	$\pm 2\%$
HPLC Method Spikes	$\pm 20\%$ of theoretical	$\pm 5\%$

Table 5-3. Data Quality Acceptance Criteria and Results Field Test #2

Parameter	Criteria	Results
MDI Spike Recovery	70 - 130%	82 - 105%
MDI Analysis Results QUAD Train, % RSD	15%	7.9%
Analytical Balance	≤0.1 g of Class S Weights	<0.1 g
HPLC Linearity Correlation Coeff.	>0.995	0.9995
HPLC Retention Time Variation	± 15%	± 1.2%
HPLC Calibration Check	± 10% of Curve	± 8%
HPLC System Blank	<0.1% Analyte level	<0.1%
HPLC Replicate Analyses	± 10% of 1st Injection	± 2%
HPLC Method Spikes	± 20% of theoretical	± 5%

Table 5-4. Data Quality Acceptance Criteria and Results Field Test #3

Parameter	Criteria	Results
HDI Spike Recovery	70 - 130%	90 - 114%
MDI Spike Recovery	70 - 130%	94 - 104%
MI Spike Recovery	70 - 130%	94 - 113%
TDI Spike Recovery	70 - 130%	95 - 109%
HDI Analysis Results, %RSD	15%	5%
MDI Analysis Results, %RSD	15%	3%
MI Analysis Results, %RSD	15%	4%
TDI Analysis Results, %RSD	15%	3%
Analytical Balance	≤0.1 g of Class S Weights	<0.1 g
HPLC Linearity Correlation Coeff.	>0.995	0.9995
HPLC Retention Time Variation	± 15%	± 2%
HPLC Calibration Check	± 10% of Curve	± 7%
HPLC System Blank	<0.1% Analyte level	<0.1%
HPLC Replicate Analyses	± 10% of 1st injection	± 2%
HPLC Method Spikes	± 20% of theoretical	± 5%

5.2 Sample Storage and Holding Time

Sample hold times specified in the QAPJP were met for all samples. All samples were prepared within 30 days of collection and analyzed within 30 days of preparation.

5.3 Analytical Quality Control

Results for method spikes, field spikes, field blanks, reagent blanks and method blanks are summarized in Table 5-5 through 5-7. These samples served the dual purpose of controlling and assessing measurement data quality, and providing the basis for precision and accuracy estimates. The QC acceptance criteria for each of these types of samples were met as shown in Table 5-2 through 5-4. Field blanks were collected by assembling a sampling train as if to collect a sample, transporting to the sampling location, leak checking and returning the train to the onsite laboratory for recovery. Field spikes and method spikes were prepared by spiking approximately 300 mL of the toluene 1,2-pp solution with 15 mL of the field spiking solution. Method and reagent blanks were prepared by evaporating approximately 300 mL of solvent to dryness and dissolving any residue with 10 mL of ACN. All spikes and blanks met the data acceptance criteria listed in Table 5-5.

No blank contamination problems were identified during the analysis of field and laboratory blanks and no blank corrections were performed for the reported data. All blank analysis data are presented along with other QC and field sample results in Appendices A, B, and C.

Table 5-5. Summary of Analytical Quality Control Results for Field Test #1

Sample ID	Total Detected μg	Theoretical μg	Percent Recovery %
Field Blank A	2.5	NA ⁴	NA
Field Blank B	8.3	NA	NA
Field Blank C	6.4	NA	NA
Field Spike 1	7570	7828	96.7
Field Spike 2	7686	7828	98.2
Method Spike 1	8120	7828	104
Method Spike 2	7838	7828	100
Method Spike 3	7890	7828	101
Method Spike 4	7945	7828	101
Toluene Reagent Blank ¹	0.5	NA	NA
ACN Reagent Blank ²	0.4	NA	NA
Method Blank ³	10.2	NA	NA

¹Average of four, ranging from 0.1 to 1.2 μg

²Average of four, ranging from 0.1 to 0.8 μg

³Average of three, ranging from 0.3 to 20.7 μg

⁴NA, Not Applicable

Table 5-6. Summary of Analytical Quality Control Results for Field Test #2

Sample ID	Total Detected μg	Theoretical μg	Percent Recovery %
Field Blank A	2.2	NA ⁴	NA
Field Blank B	ND	NA	NA
Field Blank C	2.2	NA	NA
Field Blank D	ND	NA	NA
Field Spike 1	627	651	96.0
Field Spike 2	630	651	97.0
Method Spike ⁵	628	651	96.0
Toluene Reagent Blank ¹	ND	NA	NA
ACN Reagent Blank ²	ND	NA	NA
Method Blank ³	0.17	NA	NA

¹Average of four.

²Average of four.

³Average of eleven, ranging from 0.3 to 20.7 μg .

⁴NA, Not Applicable.

⁵Average of ten.

Table 5-7. Summary of Analytical Quality Control Results for Field Test #3

Sample ID	Total Detected μg				Percent Recovery ⁵			
	HDI	MDI	MI	TDI	HDI	MDI	MI	TDI
Field Blank A	ND	ND	0.6	ND	NA	NA	NA	NA
Field Blank B	ND	ND	1.1	ND	NA	NA	NA	NA
Field Blank C	ND	ND	0.7	ND	NA	NA	NA	NA
Field Spike 1	163	170	2740	177	101	103	105	103
Method Spike ⁴	158	163	2736	170	98	99	105	99
Toluene Reagent Blank ¹	ND	ND	1.5	ND	NA	NA	NA	NA
ACN Reagent Blank ²	ND	ND	0.3	ND	NA	NA	NA	NA
Method Blank ²	ND	ND	2.5	ND	NA	NA	NA	NA

¹Average of three, ranging from 0.1 to 1.2 μg .

²Average of three, ranging from 0.1 to 0.8 μg .

³Average of twelve, ranging from 0.3 to 20.7 μg .

⁴NA = Not Applicable.

⁵Theoretical values HDI = 161

MDI = 165

MI = 2606

TDI = 171

ND = Not Detected

NA = Not Applicable

⁶Average of 6.

Section 6

Method Quality Control and Method 301 Statistical Procedures

6.1 Quality Control

The quality control procedures for field and laboratory activities not discussed in previous sections are described below.

6.1.1 Sampling QC Procedures

The sampling QA/QC program for this project included data quality objectives, manual method sampling performance criteria, field equipment calibrations, consistency of field spiking, sampling, and recovery procedures, representative sampling, complete documentation of field data and abnormalities, and adequate field sample custody procedures.

6.1.1.1 Field Equipment Calibrations

Meter boxes, temperature gauges and probe nozzles were calibrated as described in Section 4.2. Only S-Type pitot tubes meeting the requirements specified in the EPA's Quality Assurance Handbook were used during the sampling program. Pitot tubes were inspected and documented as meeting EPA specifications prior to sampling.

6.1.1.2 Sampling Operation/Recovery Procedures

To ensure consistency between trains/runs, specified individuals conducted the manual sampling, and one person was assigned to clean up, recover, and reassemble the glassware. This protocol serves to eliminate propagation of multiple operator variance. All team members were familiar with the procedures detailed in the test plan for each field test.

6.1.1.3 Representative Sampling

Each of the four independent trains in the quad assembly was sampling essentially the same stack gas. Parameters such as flow rates and flue gas temperature were compared to assess the variability in stack gas conditions for different test runs. (Flow rates were used for comparison purposes only and are provided in the test report for reasons of confidentiality.) Any discrepancies were noted. Subsequent evaluation of analytical results for questionable runs was used to determine whether results from inconsistent runs are acceptable.

Communication was maintained between Radian sampling personnel and line operators. Radian was to be notified immediately of any incident which could have affected the steady operation of the process. The field task leader also met daily with appropriate production personnel to coordinate testing around possible product changes. It was desirable to minimize production changes during the week-long test period. Such events were, however, documented.

6.1.1.4 Documentation

Field data sheets were completed and thoroughly checked after each test run. Velocity head (ΔP) determinations were required on only one of the four data sheets.

Any abnormalities observed during the test run or during subsequent recovery was recorded on the appropriate field sheets. Any known variation from steady state (production) operations occurring during run periods was documented. Documentation of pre- and post- test calibrations and inspections were maintained.

6.1.1.5 Sample Custody

Sample custody procedures for this program were based on EPA-recommended procedures. The custody procedures emphasize careful documentation of sample collection and field analytical data and the use of chain-of-custody records for samples being transferred. These procedures are discussed below.

The sample recovery leader was responsible for ensuring that all samples taken were accounted for and that proper custody and documentation procedures were followed for the field sampling efforts. A master sample logbook was maintained by the recovery task leader to provide a hardcopy of all sample collection activities. Manual flue gas sampling data was also maintained by the recovery task leader.

Following sample collection, each sample was given a unique alphanumeric sample identification code. Sample labels and integrity seals were completed and affixed to the sample container. The sample volumes were determined and recorded and the liquid levels marked on each bottle. The sample identification code was recorded on the sample label and in the sample logbook. Sample bottle lids were sealed on the outside with Teflon® tape to prevent leakage. The samples were stored in a secure area until they were packed on ice for shipment to the laboratory.

As the samples were packed for travel, chain-of-custody forms were completed for each shipment container. The chain-of-custody forms and written instructions specifying the treatment of each sample was also enclosed in the sample shipment container. Shipping containers were labelled with arrows to clearly indicate the upright position of sample bottles.

6.1.2 Laboratory QA/QC Procedures

The laboratory QA program for this project included proper handling, logging and tracking of incoming samples, procedure validations including HPLC column efficiency, calibration curves, daily QC checks and replicate analyses, and collection and/or analysis of sample, field and reagent blanks, and method spikes as well as field and laboratory spikes.

6.1.2.1 Sample Custody/Tracking

Upon receipt of samples in the laboratory, the chain-of-custody forms and sample bottle labels were recorded to verify receipt of samples. Any discrepancies or abnormalities (leakage, etc.) were noted. The samples were stored at 4°C to minimize decomposition of derivatives.

6.1.2.2 Calibration Curve

A six-point calibration curve was prepared and analyzed after initially setting up the instrument and whenever the calibration check standard did not fall within the $\pm 5\%$ window. If the correlation coefficient was less than 0.995, the cause was identified and corrected.

6.1.2.3 Daily QC Checks

A check standard was prepared and was used to check instrument response and the calibration curve. The check standard was analyzed before and after all sample analyses and after each sixth to eighth sample. If the calibration check response was not within $\pm 10\%$ of the expected response, the cause was determined.

6.1.2.4 Blanks

Neat acetonitrile (system blank) was analyzed at least once per day to ensure that the system was not contaminated. If a response was obtained that is ≥ 0.1 of the level of the expected analyte concentration, the source of contamination was located and eliminated before analyzing samples.

6.1.2.5 Replicate Analyses

All samples were analyzed in triplicate. The triplicate analyses should have a coefficient of variation (% CV) of $\pm 10\%$ at concentrations greater than 1 $\mu\text{g/mL}$ and $\pm 25\%$ at concentrations less than 1 $\mu\text{g/mL}$. If the replicate analyses were outside of these limits, the following items were checked:

- The peaks are integrated properly;
- There is no interference from other components in the sample; and
- The instrument is working properly.

6.1.2.6 Method Spikes

One method spike for every 10 samples was prepared. The recoveries for method spikes must be ± 20 percent. If the method spike recoveries were outside of this range, the cause was identified and corrected.

6.1.2.7 Field and Reagent Blanks

Field blanks were collected as described in Section 4.2.5. These blanks were collected and processed in the same manner as collected samples.

Reagent blanks of recovery solvents were also collected and shipped to Radian's Morrisville, NC., laboratory. Field and reagent blank analytical results serve as indicators of preparation and recovery contamination.

6.2 Method 301 Statistical Procedures

6.2.1 Calculation of the Amount of Isocyanate Collected

A least squares linear regression analysis of the calibration data was used to calculate a correlation coefficient, slope, and intercept. Concentration was used as the independent or X-variable and response was used as the dependent or Y-variable.

The concentration of isocyanate (as the derivative) in the concentrated samples was then calculated as follows:

$$\text{Concentration} = \frac{(\text{Sample Response} - \text{Intercept})}{\text{Slope}} \quad 6-1$$

The total amount (μg) collected in a sample was then calculated by multiplying the concentration ($\mu\text{g}/\text{mL}$) times the final volume (10 mL) of ACN used to redissolve the concentrated sample.

$$\text{Amount TDI derivative} = \frac{\text{Concentration } (\mu\text{g}/\text{mL}) \times \text{Final Volume (10 mL)}}{\quad} \quad (6-2)$$

Using TDI as an example, the equivalent amount of TDI required to generate this much derivative was calculated by multiplying the ratio of the molecular weights of TDI (174) and the TDI derivative (501) times the amount of TDI derivative (determined by using equation 6-2).

6.2.2 Normalization of the Amount of Isocyanate Collected

In order to simplify the comparison of the analytical results of the four trains in each QUAD run for subsequent calculations of bias and precision, the test plans called for the collection of 30 ft³ of sample in each train. Due to operational variabilities inherent to each train, accurate but slightly differing sample volumes resulted. Therefore, it was necessary to normalize the amount of isocyanate detected to a common sample volume. The following step-wise calculations were used to normalize the data. The data from QUAD Run Number 1 field test #1 for TDI are used as an example, where Trains A and B were dynamically spiked and Trains C and D were unspiked.

Step 1 Normalize unspiked Trains C and D first impinger amounts (μg) to the sample volume collected (cubic feet) in spiked Train A;

$$\text{Train C} \quad \frac{33.42 \text{ ft}^3}{33.02 \text{ ft}^3} \times 4409 \mu\text{g} = 4462 \mu\text{g} \quad 6-3$$

$$\text{Train D} \quad \frac{33.42 \text{ ft}^3}{33.04 \text{ ft}^3} \times 4416 \mu\text{g} = 4467 \mu\text{g} \quad 6-4$$

Step 2 Average the normalized, unspiked train amounts from step 1 above. Assuming the collection efficiency of all trains to be the same, this value would also be the amount of TDI that would be collected by Train A due to sampling the stack gas;

$$\frac{4462 \mu\text{g} + 4467 \mu\text{g}}{2} = 4465 \mu\text{g} \quad 6-5$$

Step 3 Subtract the average value (step 2) from the uncorrected amount (sampled amount plus spike) for spiked Train A, first impinger, to get recovered spike amount;

$$11943 \mu\text{g} - 4465 \mu\text{g} = 7478 \mu\text{g} \quad 6-6$$

Step 4 Normalize the amount collected in spiked Train A, first impinger to 35.31 ft³ (35.31 ft³ which is equivalent to 1m³ was selected for convenience only) using the sample volume for Train A and the value obtained in step 2;

$$\frac{35.31 \text{ ft}^3}{33.42 \text{ ft}^3} \times 4465 \mu\text{g} = 4718 \mu\text{g} \quad 6-7$$

Step 5 Normalize the amount collected in the second impinger of spiked Train A to 35.31 ft³ using the sample volume for Train A and the amount determined by HPLC;

$$\frac{35.31 \text{ ft}^3}{33.42 \text{ ft}^3} \times 63.9 \text{ } \mu\text{g} = 67.5 \text{ } \mu\text{g} \quad 6-8$$

Step 6 Sum the values determined from steps 3, 4 and 5 to get the total amount of TDI found in spiked Train A, normalized to 35.31 ft³;

$$7478 \text{ } \mu\text{g} + 4718 \text{ } \mu\text{g} + 67.5 \mu\text{g} = 12264 \text{ } \mu\text{g} \quad 6-9$$

Steps 1-6 can be repeated for similar calculations for spiked Train B. The total amount of isocyanate collected in each of the unspiked trains can be determined by first normalizing the amounts found in the two impingers of each train to 35.31 ft³ (i.e., lm³) and then summing the two values. The raw and normalized data for all analysis results are presented in Appendix A.

6.2.3 Precision of Spiked Samples

Precision of the spiked compounds was calculated using the difference between the measured normalized concentrations, d_i , of the spiked compound for each spiked train. For this calculation of precision to be valid, the variances of the measured concentrations for each of the 6 runs must be the same. If the variances were determined to be unequal, a review of the experimental data was performed to determine if there were any transcription errors or any irregular experimental procedures. If not, the "unequal" variance was flagged and pooled with the rest of the variances according to Equation 6-10. Precision is reported as the standard deviation of the difference of spiked compounds, SD_d , given by the following equation:

$$SD_d = \sqrt{\frac{\sum d_i^2}{2n}} \quad (6-10)$$

where

n = the number of sampling runs used in the calculation
($n = 6$); and

d_i = the difference of paired sampling train measurements.

The standard deviation of the mean difference, SD_m , was calculated as follows:

$$SD_m = \frac{SD_d}{\sqrt{n}} \quad (6-11)$$

where

n = the number of sampling runs ($n = 6$).

The percent relative standard deviation (or percent coefficient of variation) was calculated as follows:

$$RSD = \frac{SD_s}{S_m} \times 100 \quad (6-12)$$

where

SD_s = standard deviation of the difference of the spiked compounds; and

S_m = mean of the spiked samples.

6.2.4 Precision of Unspiked Samples

Under the assumption of equal variances for the 6 quad runs, the precision of the 12 unspiked samples was determined by calculating the difference, d_i , between the pairs of the unspiked samples for each of the QUAD runs. The standard deviation of the unspiked values, SD_u , was calculated by:

$$SD_u = \sqrt{\frac{\sum d_i^2}{2n}} \quad (6-13)$$

where

n = the number of sampling runs used in calculation ($n = 6$).

The percent relative standard deviation (or percent coefficient of variation) was calculated as follows:

$$RSD = \frac{SD_u}{S_u} \times 100 \quad (6-14)$$

where

S_u = the mean of the unspiked samples.

6.2.5 Bias

Bias was calculated using the data from the analysis of the 12 spiked field samples and 12 unspiked field samples (assuming 6 QUAD Runs).

Bias of the spike compound is defined as:

$$B = S_m - M_m - CS \quad (6-15)$$

where

B = bias for the spiked compound;

S_m = mean of the spiked samples;

M_m = mean of the unspiked samples; and

CS = calculated value of the spike compound.

The pooled standard deviation, SD_p , of the spiked and unspiked trains was calculated as follows:

$$SD_p = \sqrt{\frac{SD_s^2 + SD_u^2}{2}} \quad (6-16)$$

where

SD_s = standard deviation of the spiked sample values; and

SD_u = standard deviation of the unspiked sample values.

Note that this equation overestimates the standard deviation of the mean by a factor of the square root of 2. This is the approach recommended in Method 301, therefore it will be used for this validation procedure.

The bias, B , calculated from Equation (6-15) was tested to determine if it is statistically different from zero. A t -test was used to make this determination. The t test compared the calculated t -statistic of the test data to the critical t value for the specified degrees of freedom and level of significance. For the test matrix in this plan, there are 6 data points, which will be tested using a two-tailed t distribution at the 95% confidence level. The t -statistic was calculated as shown in equation (6-17):

$$t = \frac{|B - 0.0|}{SDM} \quad (6-17)$$

where

B = bias; and

SDM = pooled standard deviation of the mean (i.e., SD_p/\sqrt{n}).

This t test evaluates the hypothesis that the bias is greater than zero. If the calculated absolute value of the t -statistic is greater than the two-tailed critical value for the specified degrees of freedom and level of significance, then there is a 95% probability that the bias calculated for the paired trains is significant. If the calculated absolute value of the t -statistic is less than the critical value for the specified degrees of freedom and level of significance, then the average difference of the concentration between paired sampling trains is assumed to be zero and the measured concentrations can be pooled for statistical tests. The critical value of the t statistic for the two tailed t -distribution at 0.05 level of significance (95% confidence level) with 5 degrees of freedom is 2.571. If the bias was found to be significant, then a correction factor can be calculated to compensate for the bias. If the correction factor value falls between 0.7 and 1.3 the method is still acceptable.

Section 7 References

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5. Appendix B to Part 136. "Definition and Procedure for the Determination of the Method Detection Limit." Revision 1.11. *Federal Register*. Volume 49, No. 209. October 26, 1984, 198-199.
6. "Recent Developments in the Sampling and Analysis of Isocyanates in Air", V. Dharmarajan, R.D. Lingg, K.S. Booth and D.R. Hackathorn, American Society for Testing and Materials, Special Technical Publication 957, 1987.
7. Mitchell, William J., Midgett, M. Rodney, Means to Evaluate Performance of Stationary Source Test Methods, *Environmental Science and Technology*, Vol. 10, Page 85, January 1976.

APPENDIX A

FIELD TEST #1 DATA

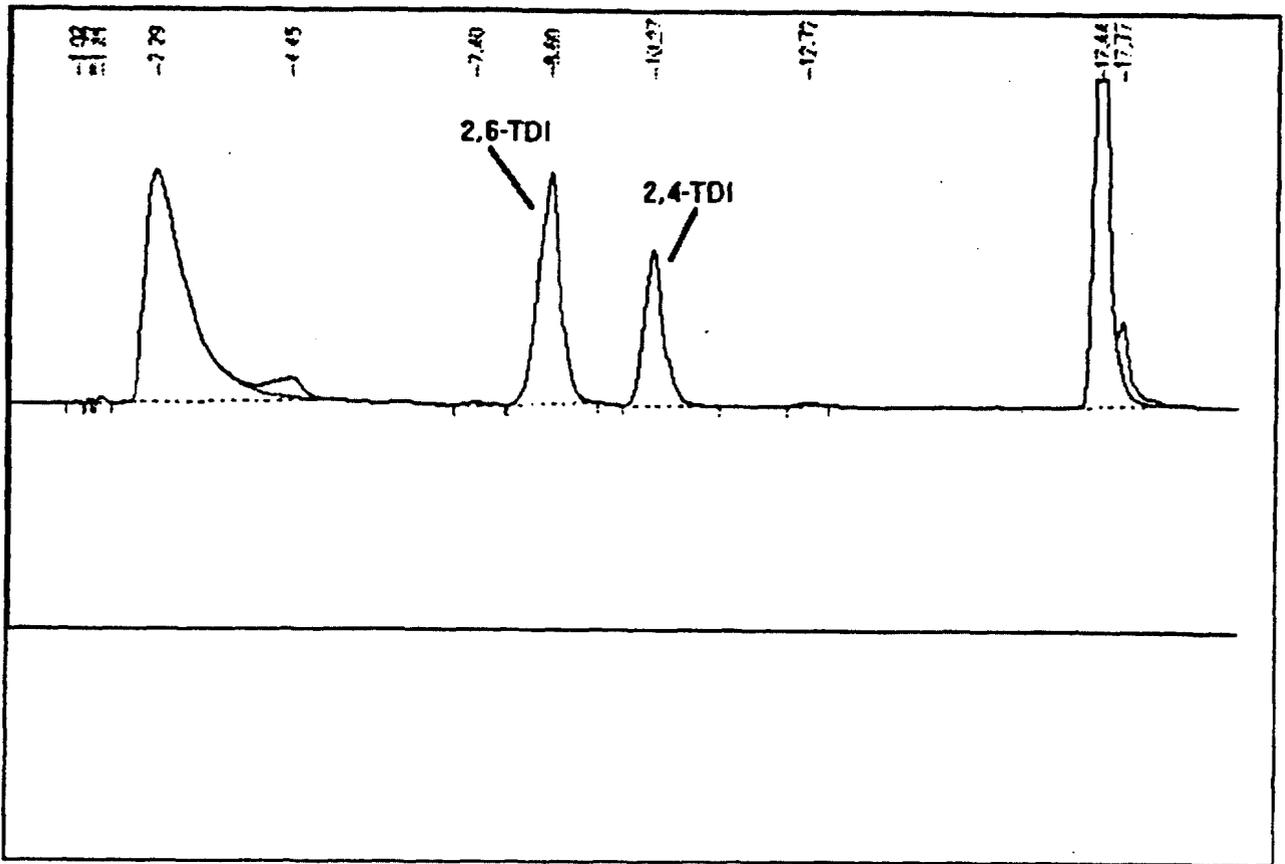


Figure 1 First Impinger, Unspiked Train

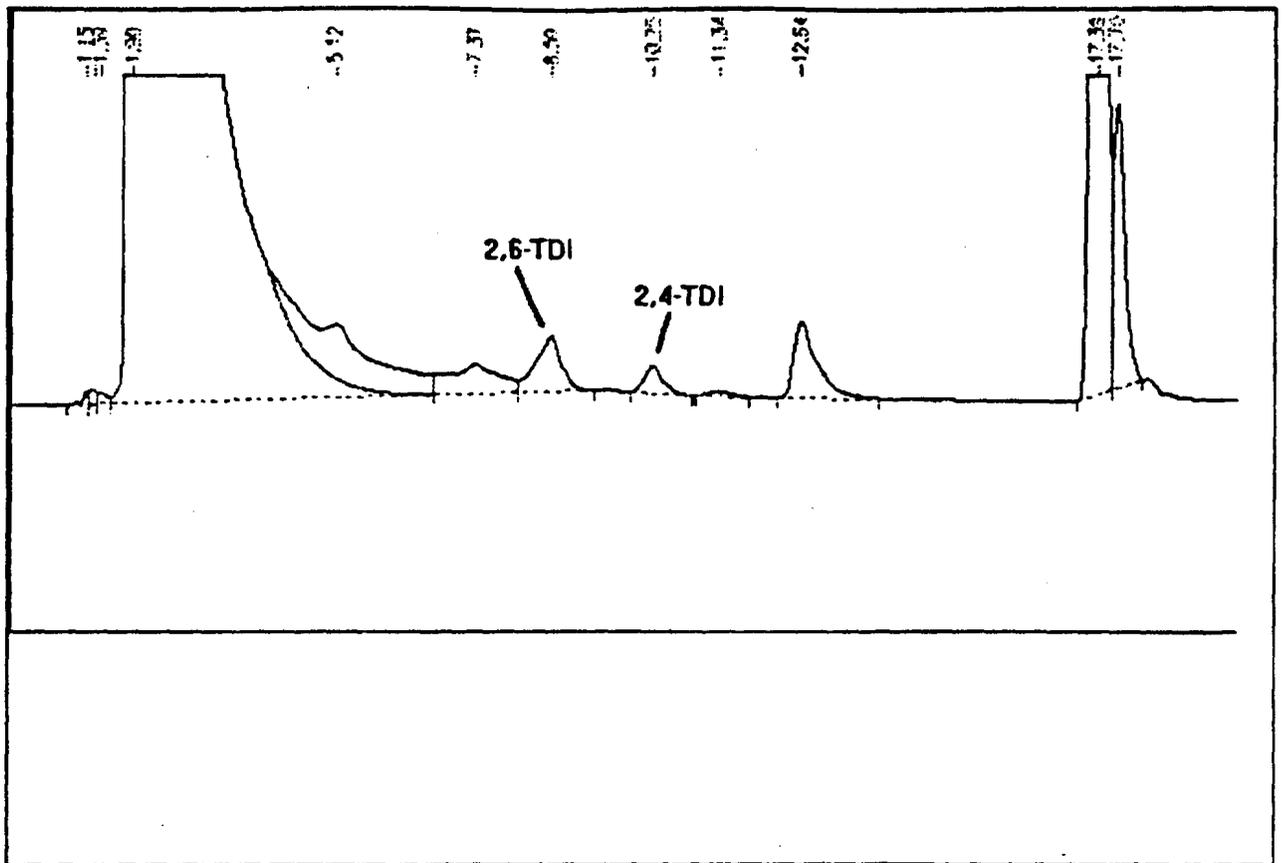


Figure 2 Second Impinger, Unspiked Train

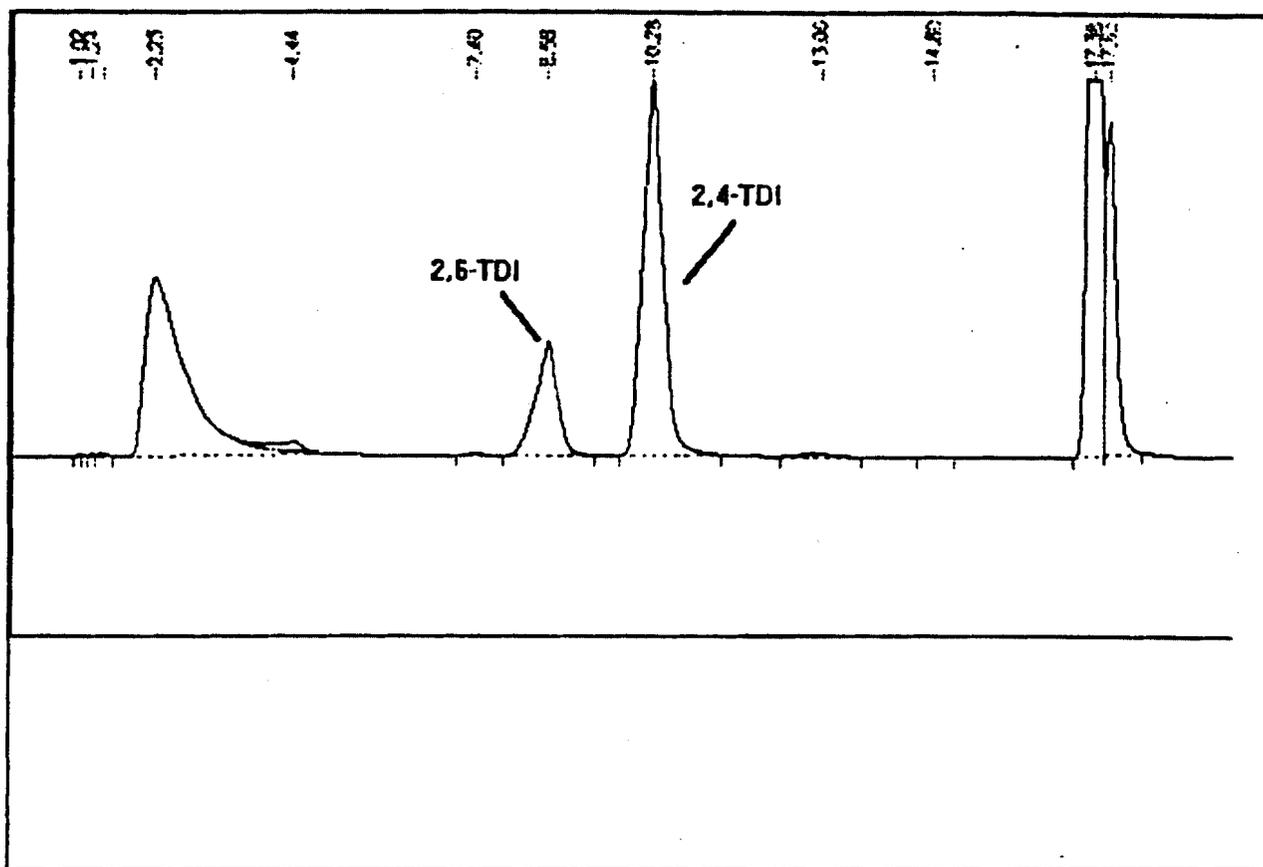


Figure 3 First Impinger, Spiked Train

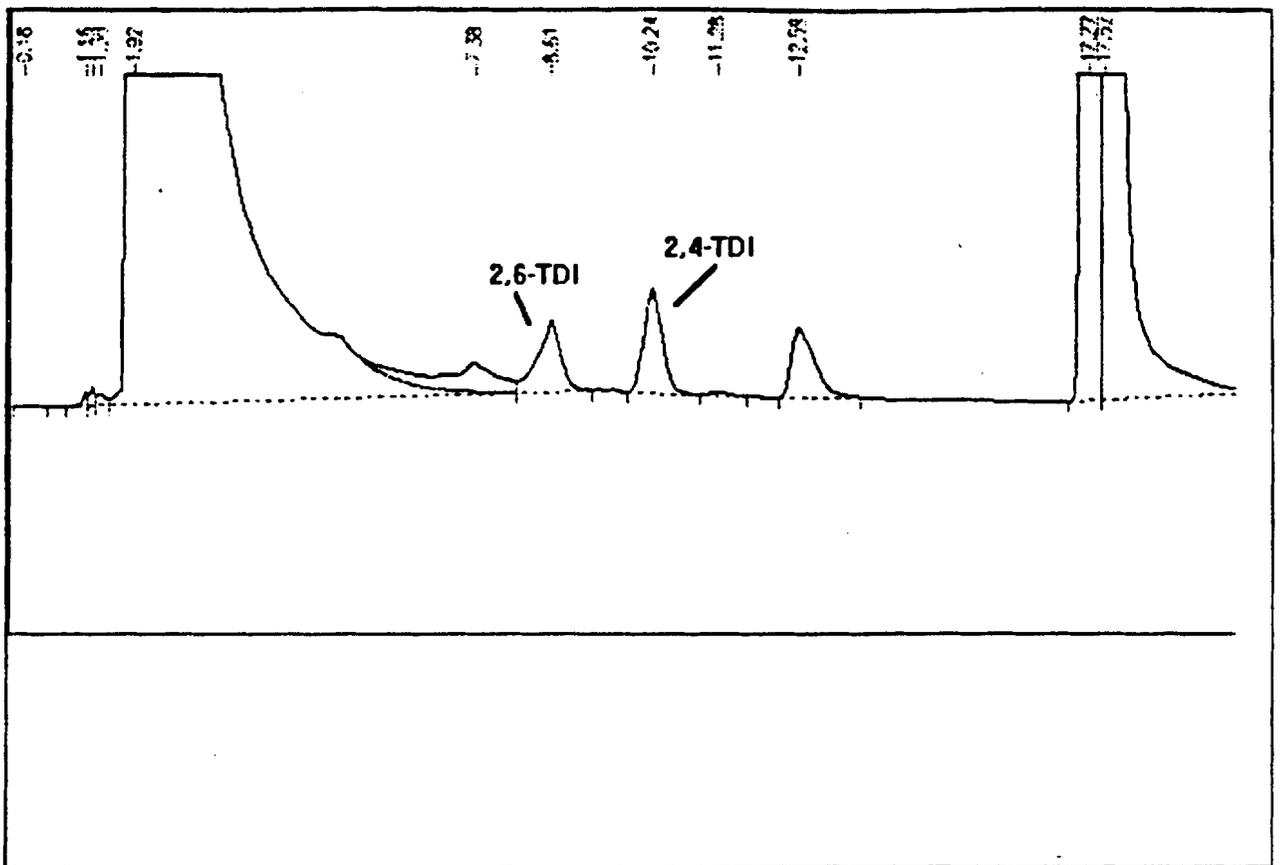
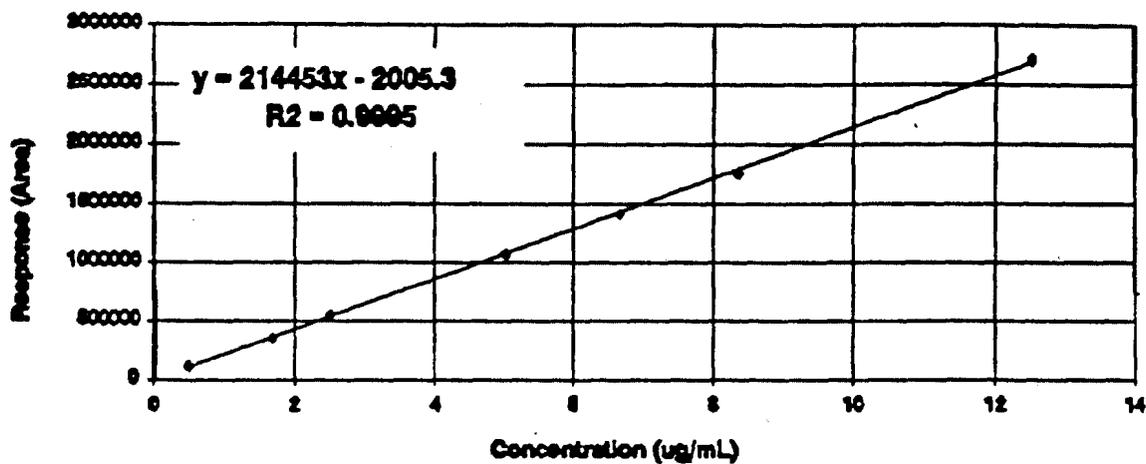


Figure 4 Second Impinger, Spiked Train

2,4-Toluene Diisocyanate Calibration



Calibration Level	Concentration	Response
Level 1	0.50	120958
Level 1	0.50	114900
Level 1	0.50	114013
Level 2	1.67	354848
Level 2	1.67	355366
Level 2	1.67	349382
Level 3	2.50	545246
Level 3	2.50	548441
Level 3	2.50	548605
Level 4	5.01	1069909
Level 4	5.01	1067146
Level 4	5.01	1066865
Level 5	6.68	1417384
Level 5	6.68	1409013
Level 5	6.68	1415648
Level 6	8.35	1763385
Level 6	8.35	1764761
Level 6	8.35	1759671
Level 7	12.52	2691345
Level 7	12.52	2732793
Level 7	12.52	2700490

AI	Date Analyze	Sample Name	AREA	TDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 7827.81 ug
03	03/24/93	ARL-01-I-A-	127707	11932	11943	0.17%	0.946	4465	7478	4718	12263	1.4%	96%
03	03/24/93	ARL-01-I-A-	127691	11930									
03	03/24/93	ARL-01-I-A-	128085	11967									
03	03/24/93	ARL-02-I-A-	135291	64	64	1.06%				67			
03	03/24/93	ARL-02-I-A-	135913	64									
03	03/24/93	ARL-02-I-A-	133152	63									
03	03/24/93	ARL-03-I-B-1	119635	11179	11301	0.94%	0.960	4528	6773	4718	11520	0.6%	86%
03	03/24/93	ARL-03-I-B-1	121453	11348									
03	03/24/93	ARL-03-I-B-1	121742	11375									
03	03/24/93	ARL-04-I-B-2	59159	29	28	2.53%				29			
03	03/24/93	ARL-04-I-B-2	57134	28									
03	03/24/93	ARL-04-I-B-2	56201	27									
03	03/24/93	ARL-05-I-C-1	471546	4418	4409	0.23%	0.935			4716	4735	0.4%	
03	03/24/93	ARL-05-I-C-1	470785	4411									
03	03/24/93	ARL-05-I-C-1	469380	4398									
03	03/24/93	ARL-06-I-C-2	35898	18	18	1.60%				19			
03	03/24/93	ARL-06-I-C-2	37029	18									
03	03/24/93	ARL-06-I-C-2	36906	18									
03	03/24/93	ARL-07-I-D-	469526	4400	4416	2.29%	0.936			4720	4811	1.9%	
03	03/24/93	ARL-07-I-D-	461467	4324									
03	03/24/93	ARL-07-I-D-	482909	4524									
03	03/24/93	ARL-08-I-D-	180144	85	85	0.39%				91			
03	03/24/93	ARL-08-I-D-	179633	85									
03	03/24/93	ARL-08-I-D-	181047	85									

R Results of Quad Run 1, 2,4-Toluene Diisocyanate

Date Analyze	Sample Name	AREA	TDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 7827.81 ug
03/25/93	ARL-09-2-A-	544346	5097	5114	0.35%	0.823			6213	6287	1.2%	
03/25/93	ARL-09-2-A-	548157	5133									
03/25/93	ARL-09-2-A-	545954	5112									
03/25/93	ARL-10-2-A-	130306	62	61	1.55%				75			
03/25/93	ARL-10-2-A-	130940	62									
03/25/93	ARL-10-2-A-	127140	60									
03/25/93	ARL-11-2-B-1	567669	5315	5224	2.38%	0.840			6223	6270	0.8%	
03/25/93	ARL-11-2-B-1	563460	5276									
03/25/93	ARL-11-2-B-1	542754	5083									
03/25/93	ARL-12-2-B-2	83414	40	40	0.88%				47			
03/25/93	ARL-12-2-B-2	83620	40									
03/25/93	ARL-12-2-B-2	82237	39									
03/25/93	ARL-13-2-C-1	128786	12032	12045	0.13%	0.812	5048	6997	6218	13258	0.7%	89%
03/25/93	ARL-13-2-C-1	128887	12042									
03/25/93	ARL-13-2-C-1	129104	12062									
03/25/93	ARL-14-2-C-2	71522	34	35	1.50%				43			
03/25/93	ARL-14-2-C-2	73423	35									
03/25/93	ARL-14-2-C-2	73513	35									
03/25/93	ARL-15-2-D-	133529	12475	12454	0.25%	0.804	5000	7454	6218	13733	1.0%	95%
03/25/93	ARL-15-2-D-	133470	12469									
03/25/93	ARL-15-2-D-	132928	12419									
03/25/93	ARL-16-2-D-	103190	49	49	0.71%				61			
03/25/93	ARL-16-2-D-	103848	49									
03/25/93	ARL-16-2-D-	102349	49									

Results of Quad Run 2, 2,4-Toluene Diisocyanate

Date Analyze	Sample Name	AREA	TDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 7827.81 ug
03/26/93	ARL-17-3-A-	122999	11492	11488	1.23%	0.970	3183	8305	3283	11625	1.1%	106%
03/26/93	ARL-17-3-A-	121406	11344									
03/26/93	ARL-17-3-A-	124445	11627									
03/26/93	ARL-18-3-A-	75825	36	36	1.40%				37			
03/26/93	ARL-18-3-A-	74917	36									
03/26/93	ARL-18-3-A-	73672	35									
03/26/93	ARL-19-3-B-1	128283	11985	12024	0.28%	0.995	3267	8757	3283	12078	1.1%	112%
03/26/93	ARL-19-3-B-1	128951	12048									
03/26/93	ARL-19-3-B-1	128872	12040									
03/26/93	ARL-20-3-B-2	79007	38	38	0.21%				38			
03/26/93	ARL-20-3-B-2	78713	38									
03/26/93	ARL-20-3-B-2	79021	38									
03/26/93	ARL-21-3-C-1	351376	3298	3281	1.59%	0.956			3433	3466	1.0%	
03/26/93	ARL-21-3-C-1	343323	3222									
03/26/93	ARL-21-3-C-1	354099	3323									
03/26/93	ARL-22-3-C-2	65492	32	32	0.82%				33			
03/26/93	ARL-22-3-C-2	66002	32									
03/26/93	ARL-22-3-C-2	66603	32									
03/26/93	ARL-23-3-D-	319713	3002	2928	2.42%	0.935			3132	3166	1.1%	
03/26/93	ARL-23-3-D-	310818	2919									
03/26/93	ARL-23-3-D-	304609	2861									
03/26/93	ARL-24-3-D-	65115	31	31	0.99%				34			
03/26/93	ARL-24-3-D-	66054	32									
03/26/93	ARL-24-3-D-	64767	31									

Results of Quad Run 3, 2,4-Toluene Diisocyanate

Date Analyze	Sample Name	AREA	TDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 7827.81 ug
04/03/93	ARL-25-4-A-	198810	1875	1832	2.88%	0.866			2114	2132	0.9%	
04/03/93	ARL-25-4-A-	195931	1848									
04/07/93	ARL-25-4-A-	187888	1773									
04/03/93	ARL-26-4-A-	33336	17	16	6.88%				18			
04/03/93	ARL-26-4-A-	32875	16									
04/07/93	ARL-26-4-A-	29079	15									
04/03/93	ARL-27-4-B-1	200805	1893	1864	2.57%	0.883			2112	2139	1.2%	
04/03/93	ARL-27-4-B-1	200538	1891									
04/07/93	ARL-27-4-B-1	191767	1809									
04/03/93	ARL-28-4-B-2	49506	24	23	2.79%				27			
04/03/93	ARL-28-4-B-2	48281	24									
04/07/93	ARL-28-4-B-2	46705	23									
04/03/93	ARL-29-4-C-1	100115	9358	9329	0.99%	0.859	1816	7513	2113	9694	3.1%	97%
04/03/93	ARL-29-4-C-1	987039	9226									
04/07/93	ARL-29-4-C-1	100603	9404									
04/03/93	ARL-30-4-C-2	124507	59	58	2.18%				67			
04/03/93	ARL-30-4-C-2	122754	58									
04/07/93	ARL-30-4-C-2	119182	57									
04/03/93	ARL-31-4-D-	100493	9393	9429	0.83%	0.836	1767	7661	2113	9805	1.4%	98%
04/03/93	ARL-31-4-D-	101835	9519									
04/07/93	ARL-31-4-D-	100287	9374									
04/03/93	ARL-32-4-D-	53598	26	26	2.70%				30			
04/03/93	ARL-32-4-D-	53113	26									
04/07/93	ARL-32-4-D-	50832	25									

Results of Quad Run 4, 2,4-Toluene Diisocyanate

Date Analyze	Sample Name	AREA	TDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 7827.81 ug
04/03/93	ARL-33-5-A-	130976	12237	12014	4.18%	0.967	5030	6985	5203	12233	0.9%	89%
04/03/93	ARL-33-5-A-	132380	12367									
04/07/93	ARL-33-5-A-	122422	11439									
04/07/93	ARL-34-5-A-	72585	35	45	18.79%				46			
04/03/93	ARL-34-5-B-1	103486	49									
04/03/93	ARL-34-5-B-1	103836	49									
04/03/93	ARL-35-5-B-1	136999	12798	12588	3.75%	0.983	5112	7476	5203	12717	0.7%	96%
04/03/93	ARL-35-5-B-1	138290	12919									
04/07/93	ARL-35-5-B-1	128946	12047									
04/03/93	ARL-36-5-B-2	84360	40	37	14.63%				38			
04/03/93	ARL-36-5-B-2	85164	41									
04/07/93	ARL-36-5-B-2	64462	31									
04/07/93	ARL-37-5-C-1	511915	4795	4810	1.26%	0.976			4929	4947	0.4%	
04/07/93	ARL-37-5-C-1	520667	4877									
04/07/93	ARL-37-5-C-1	507945	4758									
04/07/93	ARL-38-5-C-2	36452	18	17	6.41%				18			
04/07/93	ARL-38-5-C-2	36462	18									
04/07/93	ARL-38-5-C-2	32321	16									
04/07/93	ARL-39-5-D-	542066	5076	5054	1.11%	0.923			5477	5522	0.8%	
04/07/93	ARL-39-5-D-	532851	4990									
04/07/93	ARL-39-5-D-	544154	5096									
04/07/93	ARL-40-5-D-	90692	43	42	4.57%				45			
04/07/93	ARL-40-5-D-	82975	40									
04/07/93	ARL-40-5-D-	89246	43									

Results of Quad Run 5, 2,4-Toluene Diisocyanate

Date Analyze	Sample Name	AREA	TDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 7827.81 ug
04/05/93	ARL-41-6-A-	861252	8053	7888	3.53%	0.994			7936	8042	1.3%	
04/05/93	ARL-41-6-A-	860232	8044									
04/07/93	ARL-41-6-A-	809094	7567									
04/05/93	ARL-42-6-A-	227095	107	105	3.91%				105			
04/05/93	ARL-42-6-A-	228142	107									
04/07/93	ARL-42-6-A-	212430	100									
04/05/93	ARL-43-6-B-1	815730	7629	7488	4.37%	0.996			7519	7608	1.2%	
04/05/93	ARL-43-6-B-1	825689	7722									
04/07/93	ARL-43-6-B-1	760533	7114									
04/05/93	ARL-44-6-B-2	197908	93	88	7.73%				89			
04/05/93	ARL-44-6-B-2	193894	91									
04/07/93	ARL-44-6-B-2	170746	81									
04/05/93	ARL-45-6-C-1	165682	15474	15201	2.86%	0.977	7547	7654	7727	15471	1.1%	98%
04/05/93	ARL-45-6-C-1	165212	15430									
04/07/93	ARL-45-6-C-1	157388	14700									
04/05/93	ARL-46-6-C-2	187832	89	88	6.02%				90			
04/05/93	ARL-46-6-C-2	195647	92									
04/07/93	ARL-46-6-C-2	173379	82									
04/05/93	ARL-47-6-D-	164987	15409	15173	1.92%	0.957	7392	7782	7727	15610	1.3%	99%
04/05/93	ARL-47-6-D-	163432	15264									
04/07/93	ARL-47-6-D-	158967	14847									
04/05/93	ARL-48-6-D-	220417	104	96	8.38%				101			
04/05/93	ARL-48-6-D-	206802	97									
04/07/93	ARL-48-6-D-	186023	88									

Results of Quad Run 6, 2,4-Toluene Diisocyanate

A	Date Analyze	Sample Name	AREA	TDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 7827.81 ug
04	04/05/93	ARL-49-7-A-	108131	10106	10094	0.43%	0.881	2248	7846	2552	10450	2.0%	100%
04	04/05/93	ARL-49-7-A-	107495	10046									
04	04/07/93	ARL-49-7-A-	108402	10131									
04	04/05/93	ARL-50-7-A-	98427	47	46	3.26%				52			
04	04/05/93	ARL-50-7-A-	96270	46									
04	04/07/93	ARL-50-7-A-	92145	44									
04	04/05/93	ARL-51-7-B-1	963252	9005	9003	0.78%	0.904	2308	6694	2552	9290	1.7%	86%
04	04/05/93	ARL-51-7-B-1	970463	9072									
04	04/07/93	ARL-51-7-B-1	955412	8931									
04	04/05/93	ARL-52-7-B-2	83965	40	39	3.09%				44			
04	04/05/93	ARL-52-7-B-2	83998	40									
04	04/07/93	ARL-52-7-B-2	79455	38									
04	04/05/93	ARL-53-7-C-1	230346	2169	2160	1.76%	0.853			2531	2558	1.1%	
04	04/05/93	ARL-53-7-C-1	232911	2193									
04	04/07/93	ARL-53-7-C-1	224911	2118									
04	04/05/93	ARL-54-7-C-2	49290	24	23	5.81%				27			
04	04/05/93	ARL-54-7-C-2	49749	24									
04	04/07/93	ARL-54-7-C-2	44499	22									
04	04/05/93	ARL-55-7-D-	237247	2233	2180	2.10%	0.847			2574	2616	1.6%	
04	04/05/93	ARL-55-7-D-	228829	2155									
04	04/07/93	ARL-55-7-D-	228660	2153									
04	04/05/93	ARL-56-7-D-	75486	36	36	1.52%				42			
04	04/05/93	ARL-56-7-D-	75034	36									
04	04/07/93	ARL-56-7-D-	73273	35									

R Results of Quad Run 7, 2,4-Toluene Diisocyanate

Date Analyze	Sample Name	AREA	TDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 7827.81 ug
04/06/93	ARL-57-8-A-	374801	3516	3521	0.51%	0.875			4025	4086	1.5%	
04/06/93	ARL-57-8-A-	377410	3540									
04/06/93	ARL-57-8-A-	373681	3506									
04/06/93	ARL-58-8-A-	111353	53	53	0.76%				61			
04/06/93	ARL-58-8-A-	112493	53									
04/06/93	ARL-58-8-A-	113066	54									
04/06/93	ARL-59-8-B-1	406883	3815	3805	0.86%	0.842			4520	4579	1.3%	
04/06/93	ARL-59-8-B-1	401924	3769									
04/06/93	ARL-59-8-B-1	408657	3832									
04/06/93	ARL-60-8-B-2	105005	50	50	1.09%				59			
04/06/93	ARL-60-8-B-2	104950	50									
04/06/93	ARL-60-8-B-2	102971	49									
04/06/93	ARL-61-8-C-1	113701	10625	10561	0.76%	0.863	3689	6872	4273	11197	1.2%	88%
04/06/93	ARL-61-8-C-1	112056	10472									
04/06/93	ARL-61-8-C-1	113285	10586									
04/06/93	ARL-62-8-C-2	94647	45	45	0.91%				52			
04/06/93	ARL-62-8-C-2	95991	46									
04/06/93	ARL-62-8-C-2	94335	45									
04/06/93	ARL-63-8-D-	110875	10362	10315	0.59%	0.905	3866	6449	4273	10770	1.1%	82%
04/06/93	ARL-63-8-D-	109627	10245									
04/06/93	ARL-63-8-D-	110607	10337									
04/06/93	ARL-64-8-D-	92259	44	44	0.48%				49			
04/06/93	ARL-64-8-D-	92558	44									
04/06/93	ARL-64-8-D-	91667	44									

Results of Quad Run 8, 2,4-Toluene Diisocyanate

APPENDIX B

FIELD TEST #2 DATA

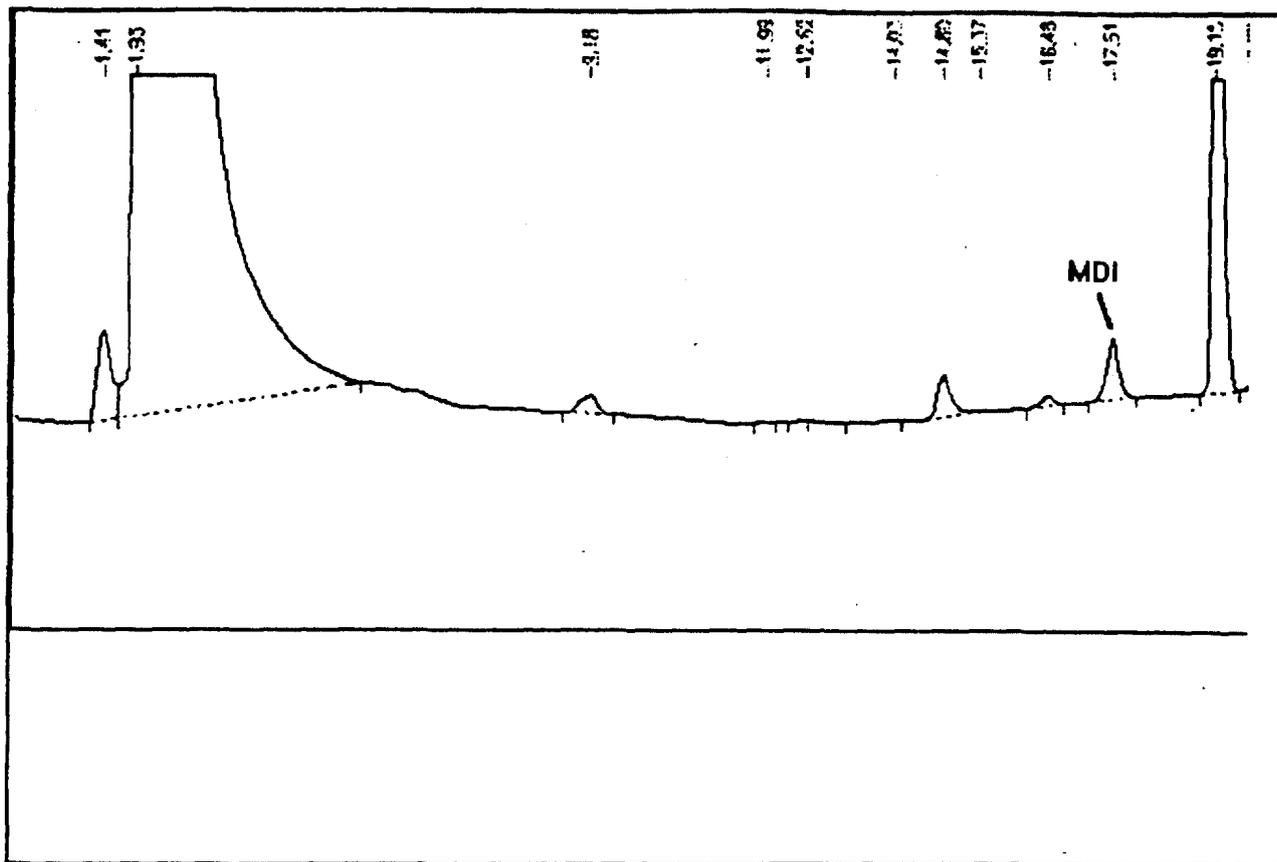


Figure 1 First Impinger, Unspiked Train

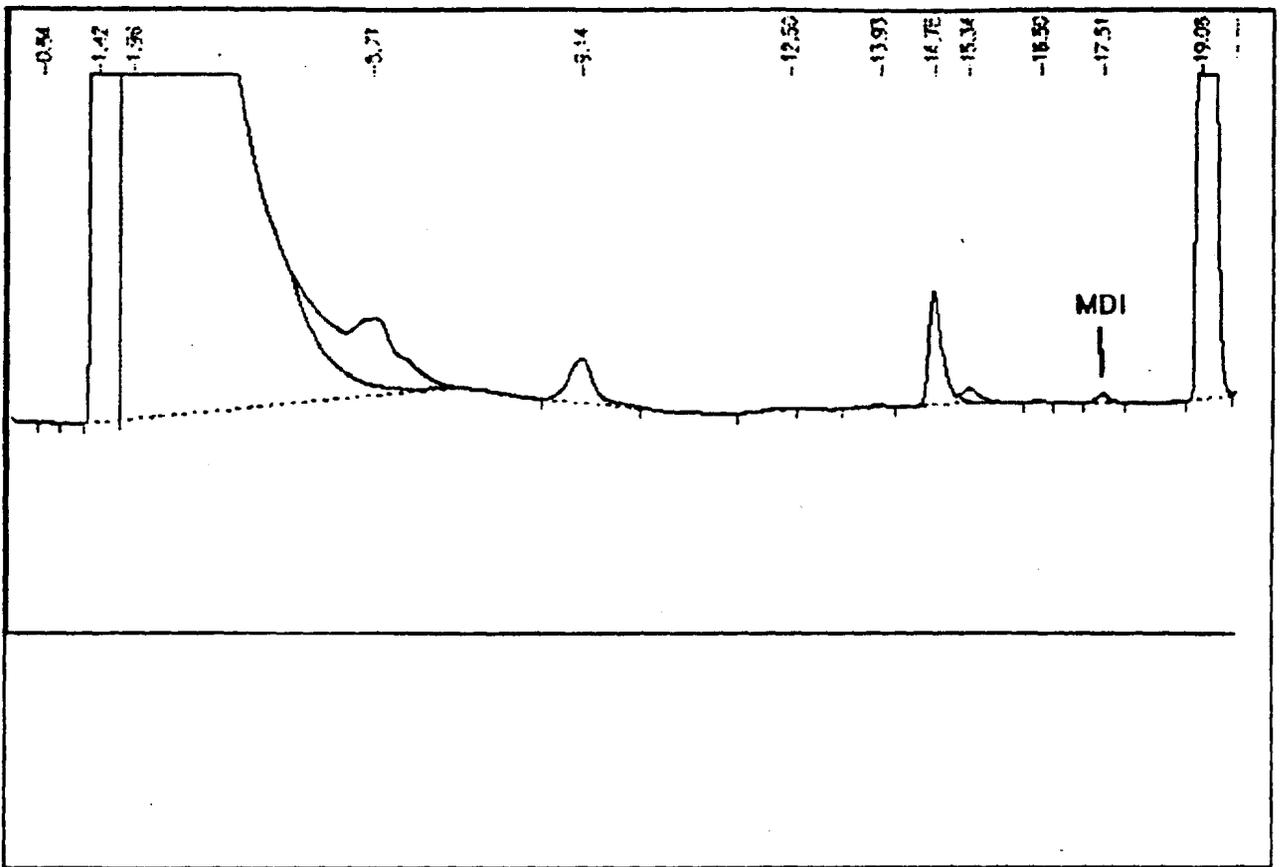


Figure 2 Second Impinger, Unspiked Train

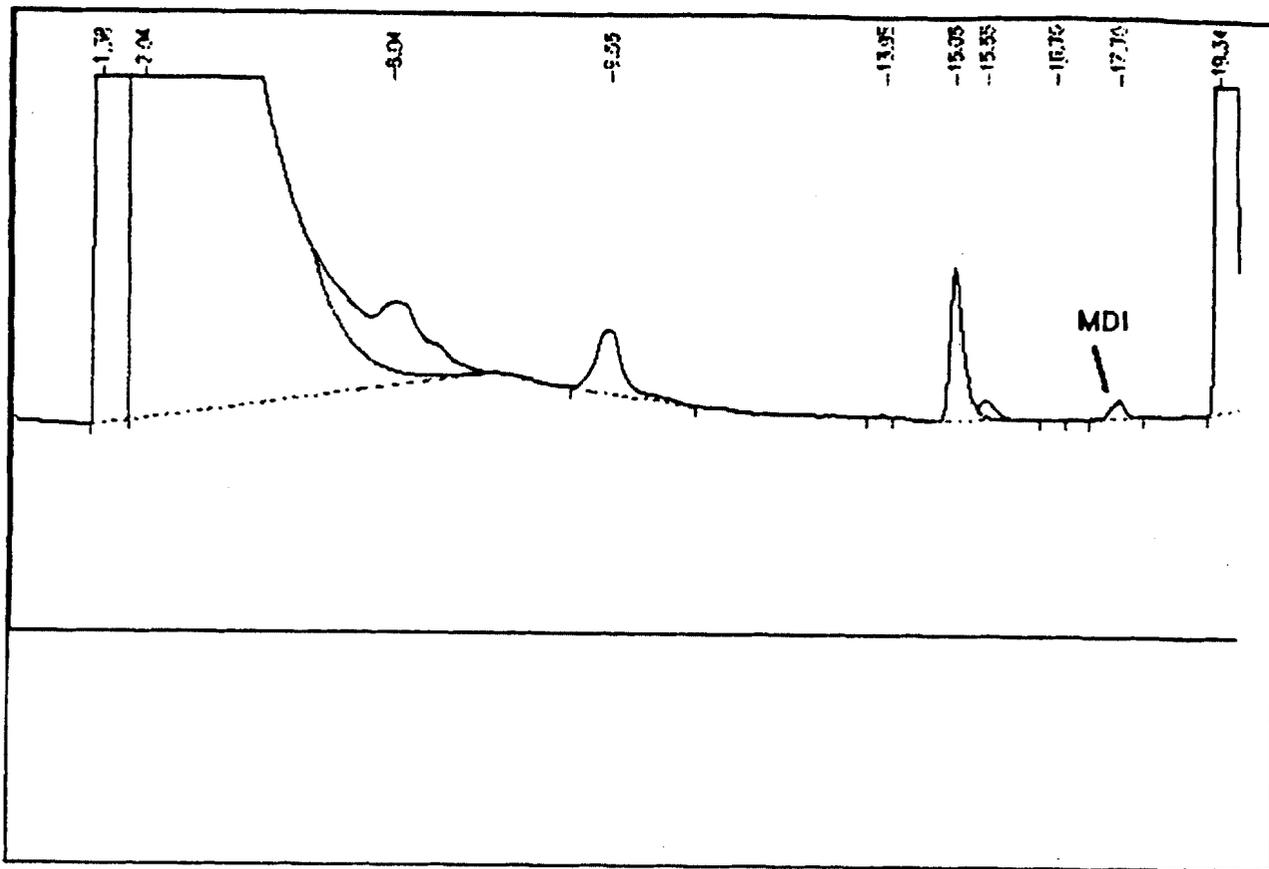


Figure 4 Second Impinger, Spiked Train

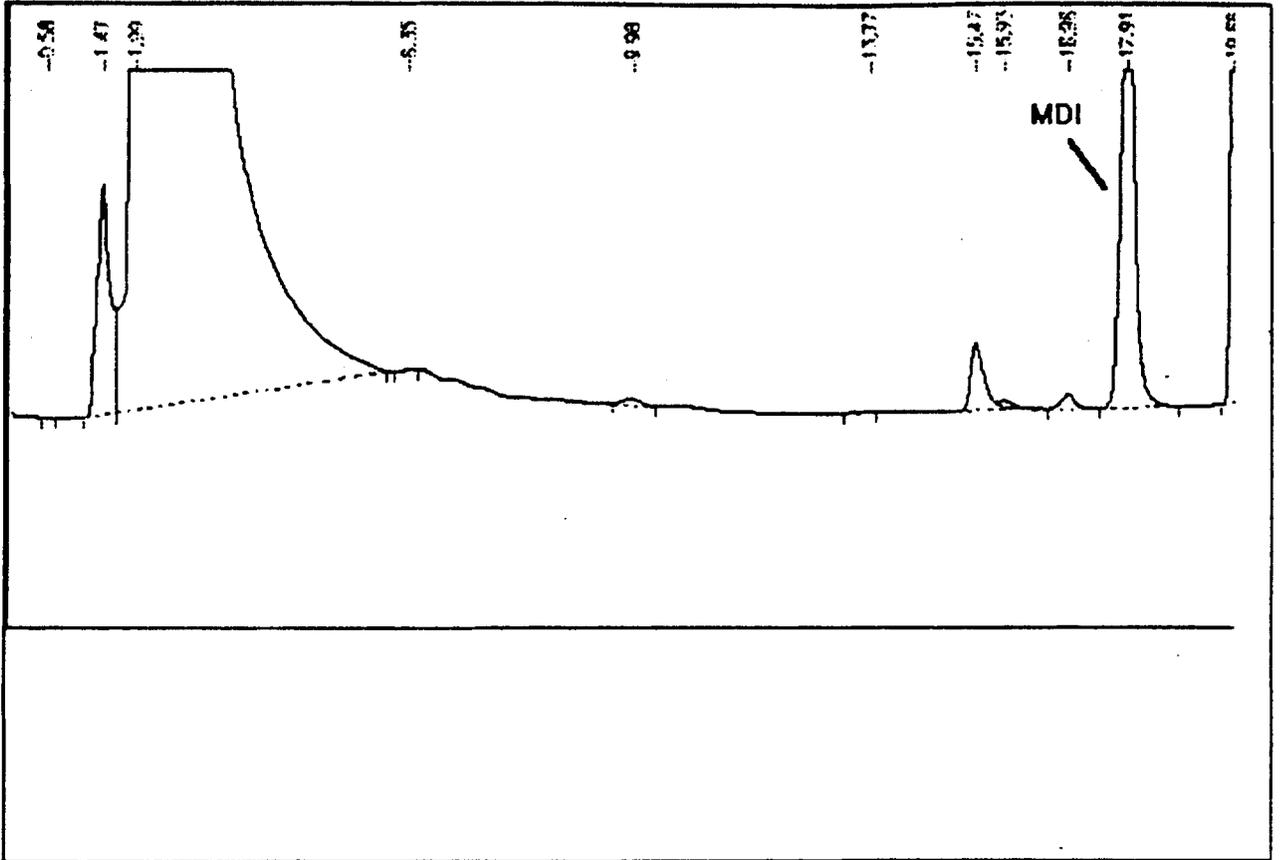
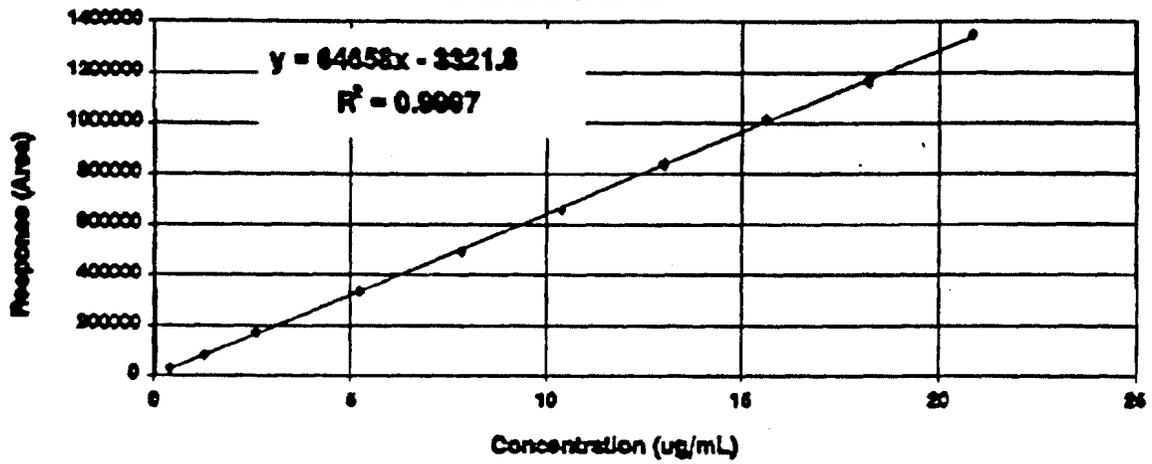


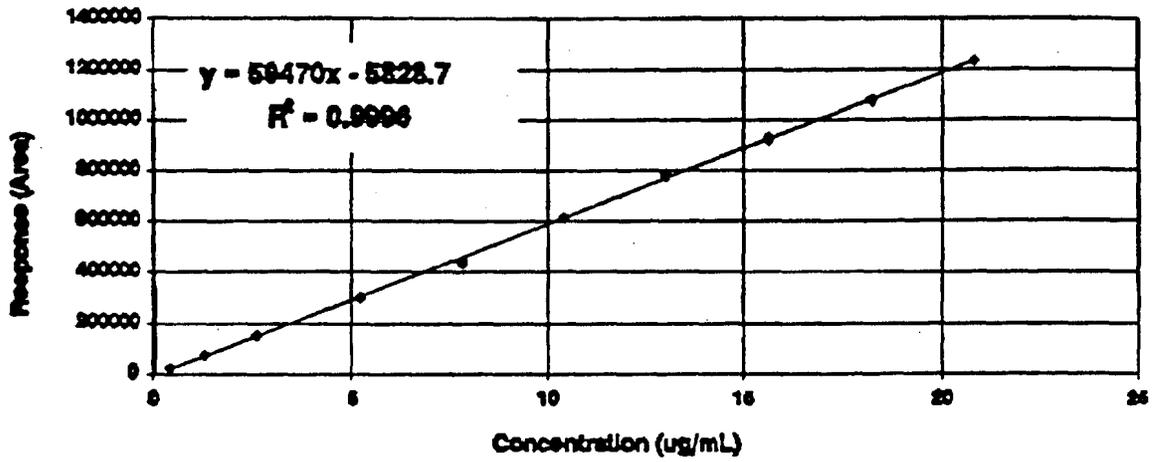
Figure 3 First Impinger, Spiked Train

Methylene Diphenyl Diisocyanate Calibration
10-05-83 to 10-25-83



Calibration Level	Concentration	Response
Level 1	0.42	26437
Level 1	0.42	27152
Level 2	1.3	82346
Level 2	1.3	82454
Level 3	2.6	171316
Level 3	2.6	171784
Level 4	5.21	336045
Level 4	5.21	331465
Level 5	7.81	489610
Level 5	7.81	491409
Level 6	10.41	659429
Level 6	10.41	659504
Level 7	13.02	847342
Level 7	13.02	832295
Level 8	15.62	1012427
Level 8	15.62	1018235
Level 9	18.23	1162730
Level 9	18.23	1170752
Level 10	20.83	1349358
Level 10	20.83	1354650

Methylene Diphenyl Diisocyanate Calibration
10-26-83 to 11-12-83



Calibration Level	Concentration	Response
Level 1	0.42	24161
Level 1	0.42	22958
Level 2	1.3	74601
Level 2	1.3	72852
Level 3	2.6	150042
Level 3	2.6	151968
Level 4	5.21	300672
Level 4	5.21	297226
Level 5	7.81	446611
Level 5	7.81	437046
Level 6	10.41	619398
Level 6	10.41	608767
Level 7	13.02	786446
Level 7	13.02	778228
Level 8	15.62	933050
Level 8	15.62	918745
Level 9	18.23	1078163
Level 9	18.23	1072337
Level 10	20.83	1236063
Level 10	20.83	1226891

Date Analyze	Sample Name	Area Count	MDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 651 ug
10/06/93	ISO-01-1-A-1	493597	768.5	766.74	0.229%	0.968	106.35	660.39	109.87	775.01	4.2%	101%
10/06/93	ISO-01-1-A-1	490836	764.2									
10/06/93	ISO-01-1-A-1	492840	767.3									
10/06/93	ISO-02-1-A-2	7353	4.15	4.61	14.96%				4.76			
10/06/93	ISO-02-1-A-2	10598	5.40									
10/06/93	ISO-02-1-A-2	7695	4.28									
10/06/93	ISO-03-1-B-1	472243	735.5	736.73	0.25%	0.964	105.91	630.82	109.87	743.76	2.7%	97%
10/06/93	ISO-03-1-B-1	472438	735.8									
10/06/93	ISO-03-1-B-1	474375	738.8									
10/06/93	ISO-04-1-B-2	16302	3.04	2.97	6.90%				3.08			
10/06/93	ISO-04-1-B-2	16839	3.13									
10/06/93	ISO-04-1-B-2	14323	2.74									
10/06/93	ISO-05-1-C-1	60729	99.13	98.60	0.66%	0.951			103.68	112.96	8.2%	
10/06/93	ISO-05-1-C-1	60519	98.80									
10/06/93	ISO-05-1-C-1	59915	97.87									
10/06/93	ISO-06-1-C-2	19403	8.80	8.83	5.10%				9.28			
10/06/93	ISO-06-1-C-2	20652	9.29									
10/06/93	ISO-06-1-C-2	18327	8.39									
10/06/93	ISO-07-1-D-1	68950	111.8	111.18	0.62%	0.958			116.05	119.19	2.6%	
10/06/93	ISO-07-1-D-1	68552	111.2									
10/06/93	ISO-07-1-D-1	68060	110.4									
10/06/93	ISO-08-1-D-2	20498	3.69	3.01	49.18%				3.14			
10/06/93	ISO-08-1-D-2	22600	4.02									
10/06/93	ISO-08-1-D-2	5094	1.31									

Results for Quad Run 1, Methylene Diphenyl Diisocyanate

Date Analyze	Sample Name	Area Count	MDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 651 ug
10/06/93	ISO-09-2-A-1	34679	58.84	58.19	1.39%	0.95			61.25	63.10	2.9%	
10/06/93	ISO-09-2-A-1	33669	57.28									
10/06/93	ISO-09-2-A-1	34418	58.44						1.85			
10/06/93	ISO-10-2-A-2	8473	1.83	1.76	3.96%							
10/06/93	ISO-10-2-A-2	7917	1.75									
10/06/93	ISO-10-2-A-2	7582	1.69									
10/06/93	ISO-11-2-B-1	39680	66.58	65.68	1.86%	0.957			68.64	76.56	10.4%	
10/06/93	ISO-11-2-B-1	39430	66.19									
10/06/93	ISO-11-2-B-1	38201	64.29						7.93			
10/09/93	ISO-12-2-B-2	16159	7.55	7.58	2.43%							
10/09/93	ISO-12-2-B-2	16763	7.78									
10/09/93	ISO-12-2-B-2	15823	7.42									
10/07/93	ISO-13-2-C-1	475039	739.8	739.44	0.10%	0.957	62.15	677.29	64.94	751.06	12.0%	104%
10/07/93	ISO-13-2-C-1	474217	738.5									
10/07/93	ISO-13-2-C-1	475057	739.8						8.84			
10/09/93	ISO-14-2-C-2	18276	8.37	8.46	0.95%							
10/09/93	ISO-14-2-C-2	18682	8.53									
10/09/93	ISO-14-2-C-2	18557	8.48									
10/07/93	ISO-15-2-D-1	406626	634.0	635.28	0.37%	0.958	62.21	573.07	64.94	664.15	28.7%	88%
10/07/93	ISO-15-2-D-1	406444	633.7									
10/07/93	ISO-15-2-D-1	409194	638.0									
10/09/93	ISO-16-2-D-2	61035	24.90	25.05	0.73%				26.15			
10/09/93	ISO-16-2-D-2	61272	24.99									
10/09/93	ISO-16-2-D-2	61944	25.25									

Results for Quad Run 2, Methylene Diphenyl Diisocyanate

Date Analyze	Sample Name	Area Count	MDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 651 ug
10/27/93	ISO-17-3-A-1	363243	620.6	621.14	0.32%	1.005	77.35	543.79	76.97	626.97	7.5%	84%
10/27/93	ISO-17-3-A-1	362545	619.4									
10/27/93	ISO-17-3-A-1	364861	623.3									
10/27/93	ISO-18-3-A-2	7817	5.75	6.24	8.02%				6.21			
10/27/93	ISO-18-3-A-2	8924	6.22									
10/27/93	ISO-18-3-A-2	10196	6.75									
10/27/93	ISO-19-3-B-1	401880	685.5	689.57	0.51%	0.973	74.89	614.69	76.97	697.51	7.1%	94%
10/27/93	ISO-19-3-B-1	405144	691.0									
10/27/93	ISO-19-3-B-1	405722	692.0									
10/27/93	ISO-20-3-B-2	7741	5.72	5.70	1.11%				5.86			
10/27/93	ISO-20-3-B-2	7526	5.63									
10/27/93	ISO-20-3-B-2	7826	5.75									
10/27/93	ISO-21-3-C-1	38742	75.01	72.49	5.33%	0.959			75.59	80.67	6.3%	
10/27/93	ISO-21-3-C-1	38385	74.41									
10/27/93	ISO-21-3-C-1	34594	68.04									
10/27/93	ISO-22-3-C-2	5600	4.82	4.87	2.06%				5.08			
10/27/93	ISO-22-3-C-2	5569	4.81									
10/27/93	ISO-22-3-C-2	5997	4.99									
10/29/93	ISO-23-3-D-1	37788	73.41	74.98	3.89%	0.957			78.34	87.48	10.4%	
10/29/93	ISO-23-3-D-1	37647	73.17									
10/29/93	ISO-23-3-D-1	40723	78.34									
10/29/93	ISO-24-3-D-2	15627	9.04	8.74	3.26%				9.14			
10/29/93	ISO-24-3-D-2	14897	8.73									
10/29/93	ISO-24-3-D-2	14272	8.47									

Results for Quad Run 3, Methylene Diphenyl Diisocyanate

Date Analyze	Sample Name	Area Count	MDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 651 ug
10/29/93	ISO-25-4-A-1	48901	92.10	93.21	1.05%	0.996			93.58	99.37	5.8%	
10/29/93	ISO-25-4-A-1	50002	93.95									
10/29/93	ISO-25-4-A-1	49783	93.58									
10/29/93	ISO-26-4-A-2	7674	5.69	5.77	2.02%				5.79			
10/29/93	ISO-26-4-A-2	8165	5.90									
10/29/93	ISO-26-4-A-2	7699	5.70									
10/29/93	ISO-27-4-B-1	53821	100.3	101.29	0.81%	0.972			104.21	127.39	18.2%	
10/29/93	ISO-27-4-B-1	54760	101.9									
10/29/93	ISO-27-4-B-1	54527	101.5									
10/29/93	ISO-28-4-B-2	48072	22.68	22.54	0.60%				23.18			
10/29/93	ISO-28-4-B-2	47431	22.41									
10/29/93	ISO-28-4-B-2	47715	22.53									
10/29/93	ISO-29-4-C-1	413058	704.3	704.11	0.25%	0.984	97.31	606.80	98.89	717.22	10.4%	93%
10/29/93	ISO-29-4-C-1	411771	702.2									
10/29/93	ISO-29-4-C-1	413847	705.7									
10/29/93	ISO-30-4-C-2	21704	11.59	11.35	2.04%				11.53			
10/29/93	ISO-30-4-C-2	20613	11.13									
10/29/93	ISO-30-4-C-2	21041	11.31									
10/29/93	ISO-31-4-D-1	432161	736.5	741.82	0.74%	0.975	96.42	645.40	98.89	753.66	8.6%	99%
10/29/93	ISO-31-4-D-1	435119	741.4									
10/29/93	ISO-31-4-D-1	438688	747.4									
10/29/93	ISO-32-4-D-2	15875	9.14	9.13	0.24%				9.36			
10/29/93	ISO-32-4-D-2	15860	9.14									
10/29/93	ISO-32-4-D-2	15780	9.10									

Results for Quad Run 4, Methylene Diphenyl Diisocyanate

Date Analyze	Sample Name	Area Count	MDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 651 ug
10/29/93	ISO-33-5-A-1	272479	468.0	474.89	1.25%	0.996	115.69	359.20	116.15	482.60	5.9%	55%
10/29/93	ISO-33-5-A-1	278571	478.2									
10/29/93	ISO-33-5-A-1	278649	478.3									
10/29/93	ISO-34-5-A-2	11154	7.16	7.21	0.99%				7.24			
10/29/93	ISO-34-5-A-2	11229	7.19									
10/29/93	ISO-34-5-A-2	11479	7.29									
10/29/93	ISO-35-5-B-1	423922	722.6	725.28	0.58%	0.974	113.13	612.15	116.15	734.51	5.1%	94%
10/29/93	ISO-35-5-B-1	424158	723.0									
10/29/93	ISO-35-5-B-1	428378	730.1									
10/29/93	ISO-36-5-B-2	8381	5.99	6.05	2.04%				6.21			
10/29/93	ISO-36-5-B-2	8845	6.19									
10/29/93	ISO-36-5-B-2	8304	5.96									
10/29/93	ISO-37-5-C-1	67004	122.5	122.90	0.37%	0.955			128.70	145.50	11.6%	
10/29/93	ISO-37-5-C-1	67146	122.7									
10/29/93	ISO-37-5-C-1	67524	123.4									
10/29/93	ISO-38-5-C-2	31151	15.56	16.05	2.65%				16.81			
10/29/93	ISO-38-5-C-2	32995	16.34									
10/29/93	ISO-38-5-C-2	32787	16.25									
10/29/93	ISO-39-5-D-1	52926	98.87	99.15	1.39%	0.957			103.61	111.40	7.0%	
10/29/93	ISO-39-5-D-1	52381	97.95									
10/29/93	ISO-39-5-D-1	53991	100.6									
10/29/93	ISO-40-5-D-2	12307	7.64	7.45	2.87%				7.79			
10/29/93	ISO-40-5-D-2	11304	7.22									
10/29/93	ISO-40-5-D-2	11957	7.49									

Results for Quad Run 5, Methylene Diphenyl Diisocyanate

Date Analyze	Sample Name	Area Count	MDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 651 ug
10/07/93	ISO-41-6-A-1	65851	107.0	106.58	0.44%	0.979			108.86	117.00	7.0%	
10/07/93	ISO-41-6-A-1	65546	106.5									
10/07/93	ISO-41-6-A-1	65240	106.1									
10/09/93	ISO-42-6-A-2	17215	7.96	7.97	0.40%				8.14			
10/09/93	ISO-42-6-A-2	17339	8.01									
10/09/93	ISO-42-6-A-2	17181	7.95									
10/07/93	ISO-43-6-B-1	66381	107.8	107.83	0.38%	0.975			110.60	121.73	9.1%	
10/07/93	ISO-43-6-B-1	66611	108.2									
10/07/93	ISO-43-6-B-1	66079	107.4									
10/09/93	ISO-44-6-B-2	26754	11.65	10.86	6.32%				11.13			
10/09/93	ISO-44-6-B-2	23788	10.50									
10/09/93	ISO-44-6-B-2	23586	10.42									
10/07/93	ISO-45-6-C-1	404345	630.5	630.81	0.44%	0.963	105.67	525.14	109.73	650.12	12.2%	81%
10/07/93	ISO-45-6-C-1	406402	633.7									
10/07/93	ISO-45-6-C-1	402837	628.1									
10/09/93	ISO-46-6-C-2	34313	14.57	14.69	0.73%				15.26			
10/09/93	ISO-46-6-C-2	34749	14.74									
10/09/93	ISO-46-6-C-2	34832	14.77									
10/07/93	ISO-47-6-D-1	411067	640.9	641.30	0.09%	0.955	104.79	536.51	109.73	656.13	8.3%	82%
10/07/93	ISO-47-6-D-1	411769	642.0									
10/07/93	ISO-47-6-D-1	411109	640.9									
10/09/93	ISO-48-6-D-2	20575	9.26	9.44	2.81%				9.89			
10/09/93	ISO-48-6-D-2	20748	9.32									
10/09/93	ISO-48-6-D-2	21842	9.75									

Results for Quad Run 6, Methylene Diphenyl Diisocyanate



Analyze Date	Sample Name	Area Count	MDI ug	Average ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalized to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalized (ug)	% Total in 2nd	% Recovery from target 651 ug
11/03/93	ISO-57-8-A-1	130082	228.5	230.00	0.58%	0.934			246.25	253.83	3.0%	
11/03/93	ISO-57-8-A-1	131028	230.1									
11/03/93	ISO-57-8-A-1	131649	231.2									
11/03/93	ISO-58-8-A-2	11159	7.16	7.08	1.20%				7.58			
11/03/93	ISO-58-8-A-2	10757	6.99									
11/03/93	ISO-58-8-A-2	11000	7.09									
11/03/93	ISO-59-8-B-1	55781	103.6	104.40	0.88%	0.906			115.23	122.01	5.6%	
11/03/93	ISO-59-8-B-1	56046	104.1									
11/03/93	ISO-59-8-B-1	56835	105.4									
11/03/93	ISO-60-8-B-2	8397	6.00	6.14	2.06%				6.78			
11/03/93	ISO-60-8-B-2	8975	6.24									
11/03/93	ISO-60-8-B-2	8830	6.18									
11/03/93	ISO-61-8-C-1	418712	713.8	718.42	0.55%	0.923	166.83	551.59	180.74	738.52	3.3%	85%
11/03/93	ISO-61-8-C-1	422777	720.7									
11/03/93	ISO-61-8-C-1	422718	720.6									
11/03/93	ISO-62-8-C-2	7787	5.74	5.71	2.22%				6.18			
11/03/93	ISO-62-8-C-2	7962	5.82									
11/03/93	ISO-62-8-C-2	7375	5.57									
11/03/93	ISO-63-8-D-1	409013	697.5	703.77	0.85%	0.909	164.30	539.47	180.74	727.51	3.9%	83%
11/03/93	ISO-63-8-D-1	412913	704.1									
11/03/93	ISO-63-8-D-1	416140	709.5									
11/03/93	ISO-64-8-D-2	9567	6.49	6.64	2.00%				7.30			
11/03/93	ISO-64-8-D-2	10003	6.67									
11/03/93	ISO-64-8-D-2	10181	6.75									

Results for Quad Run 8, Methylene Diphenyl Diisocyanate

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Date Analyze	Sample Name	Area Count	MDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 651 ug
11/03/93	ISO-65-9-A-1	405596	691.8	691.05	0.35%	1.412	88.96	602.09	63.00	669.40	6.4%	92%
11/03/93	ISO-65-9-A-1	406277	692.9									
11/03/93	ISO-65-9-A-1	403504	688.3									
11/03/93	ISO-66-9-A-2	8602	6.08	6.08	0.27%				4.31			
11/03/93	ISO-66-9-A-2	8551	6.06									
11/03/93	ISO-66-9-A-2	8627	6.09									
11/03/93	ISO-67-9-B-1	374573	639.6	641.33	0.27%	1.374	86.56	554.76	63.00	621.85	6.1%	85%
11/03/93	ISO-67-9-B-1	375457	641.1									
11/03/93	ISO-67-9-B-1	376633	643.1									
11/03/93	ISO-68-9-B-2	7662	5.69	5.62	1.14%				4.09			
11/03/93	ISO-68-9-B-2	7389	5.57									
11/03/93	ISO-68-9-B-2	7412	5.58									
11/03/93	ISO-69-9-C-1	43004	82.18	81.69	0.56%	1.375			59.41	63.50	6.4%	
11/03/93	ISO-69-9-C-1	42670	81.62									
11/03/93	ISO-69-9-C-1	42466	81.28									
11/03/93	ISO-70-9-C-2	7309	5.54	5.62	1.49%				4.09			
11/03/93	ISO-70-9-C-2	7707	5.71									
11/03/93	ISO-70-9-C-2	7500	5.62									
11/03/93	ISO-71-9-D-1	47835	90.30	91.90	1.53%	1.38			66.59	71.53	6.9%	
11/03/93	ISO-71-9-D-1	49090	92.41									
11/03/93	ISO-71-9-D-1	49423	92.97									
11/05/93	ISO-72-9-D-2	10357	6.82	6.82	2.26%				4.94			
11/05/93	ISO-72-9-D-2	10715	6.97									
11/05/93	ISO-72-9-D-2	9980	6.66									

Results for Quad Run 9, Methylene Diphenyl Diisocyanate

A	Date Analyze	Sample Name	Area Count	MDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 651 ug
11	11/05/93	ISO-73-10-A-1	70604	128.5	129.44	0.64%	0.944			137.12	145.18	5.6%	
11	11/05/93	ISO-73-10-A-1	71147	129.5									
11	11/05/93	ISO-73-10-A-1	71592	130.2									
11	11/05/93	ISO-74-10-A-2	12077	7.54	7.61	3.25%				8.06			
11	11/05/93	ISO-74-10-A-2	12881	7.88									
11	11/05/93	ISO-74-10-A-2	11736	7.40									
11	11/05/93	ISO-75-10-B-1	69677	127.0	127.46	0.34%	0.918			138.85	144.96	4.2%	
11	11/05/93	ISO-75-10-B-1	70193	127.8									
11	11/05/93	ISO-75-10-B-1	69940	127.4									
11	11/05/93	ISO-76-10-B-2	7736	5.72	5.60	1.79%				6.11			
11	11/05/93	ISO-76-10-B-2	7345	5.56									
11	11/05/93	ISO-76-10-B-2	7303	5.54									
11	11/05/93	ISO-77-10-C-1	441870	752.8	757.79	0.57%	0.934	128.88	628.91	137.99	775.46	5.8%	97%
11	11/05/93	ISO-77-10-C-1	446414	760.4									
11	11/05/93	ISO-77-10-C-1	446182	760.0									
11	11/05/93	ISO-78-10-C-2	13011	7.94	7.99	2.27%				8.56			
11	11/05/93	ISO-78-10-C-2	12797	7.85									
11	11/05/93	ISO-78-10-C-2	13628	8.20									
11	11/05/93	ISO-79-10-D-1	458042	780.0	784.75	0.63%	0.914	126.12	658.63	137.99	804.54	5.4%	101%
11	11/05/93	ISO-79-10-D-1	460606	784.3									
11	11/05/93	ISO-79-10-D-1	463910	789.8									
11	11/05/93	ISO-80-10-D-2	11541	7.32	7.24	1.02%				7.92			
11	11/05/93	ISO-80-10-D-2	11319	7.23									
11	11/05/93	ISO-80-10-D-2	11195	7.17									

R Results for Quad Run 10, Methylene Diphenyl Diisocyanate

Date Analyze	Sample Name	Area Count	MDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 651 ug
11/05/93	ISO-106-11A1	420364	716.6	719.98	0.46%	0.831	100.55	619.43	121.00	745.61	4.1%	95%
11/05/93	ISO-106-11A1	422297	719.9									
11/05/93	ISO-106-11A1	424343	723.3									
11/05/93	ISO-107-11A2	4261	4.26	4.30	1.35%				5.18			
11/05/93	ISO-107-11A2	4321	4.28									
11/05/93	ISO-107-11A2	4524	4.37									
11/05/93	ISO-108-11B1	415214	708.0	706.98	0.56%	0.954	115.44	591.54	121.00	721.95	7.2%	91%
11/05/93	ISO-108-11B1	416604	710.3									
11/05/93	ISO-108-11B1	411978	702.5									
11/05/93	ISO-109-11B2	15657	9.05	8.97	0.76%				9.41			
11/05/93	ISO-109-11B2	15441	8.96									
11/05/93	ISO-109-11B2	15339	8.92									
11/05/93	ISO-110-11C1	58685	108.5	107.78	0.75%	0.93			115.90	121.95	5.0%	
11/05/93	ISO-110-11C1	57725	106.9									
11/05/93	ISO-110-11C1	58287	107.8									
11/05/93	ISO-111-11C2	7279	5.53	5.63	2.16%				6.05			
11/05/93	ISO-111-11C2	7430	5.59									
11/05/93	ISO-111-11C2	7838	5.76									
11/05/93	ISO-112-11D1	62280	114.5	115.26	0.51%	0.914			126.11	132.75	5.0%	
11/05/93	ISO-112-11D1	62946	115.7									
11/05/93	ISO-112-11D1	62815	115.4									
11/05/93	ISO-113-11D2	8705	6.13	6.07	1.00%				6.64			
11/05/93	ISO-113-11D2	8416	6.01									
11/05/93	ISO-113-11D2	8584	6.08									

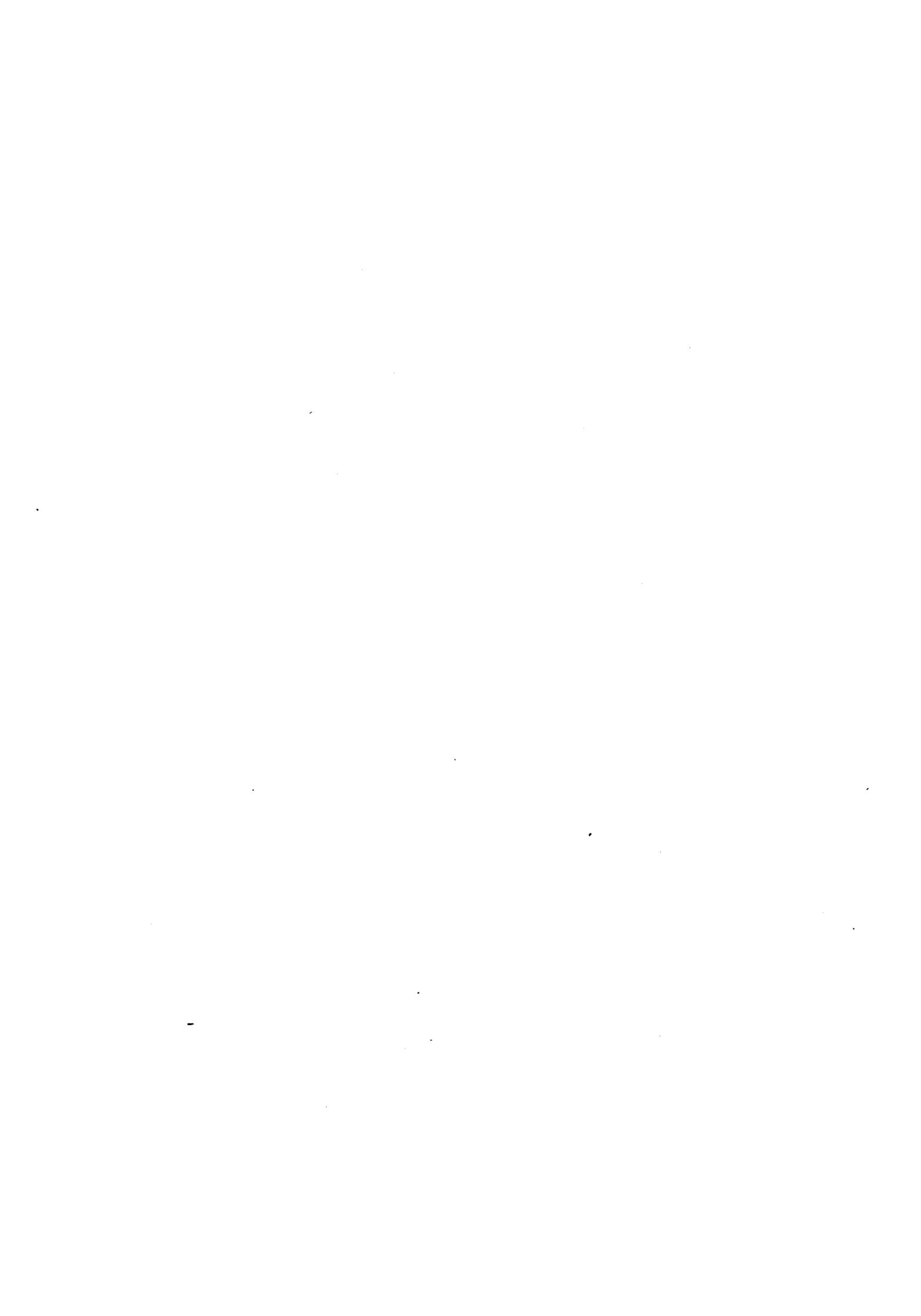
Results for Quad Run 11, Methylene Diphenyl Diisocyanate

Date Analyze	Sample Name	Area Count	MDI ug	Average ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 651 ug
11/08/93	ISO-114-12A1	27917	56.81	56.05	1.17%	0.939			59.70	63.78	6.4%	
11/08/93	ISO-114-12A1	27251	55.69									
11/08/93	ISO-114-12A1	27229	55.66						4.08			
11/08/93	ISO-115-12A2	3197	3.81	3.83	0.63%							
11/08/93	ISO-115-12A2	3311	3.86									
11/08/93	ISO-115-12A2	3241	3.83						62.78	67.40	6.9%	
11/08/93	ISO-116-12B1	28075	57.08	58.07	1.50%	0.925						
11/08/93	ISO-116-12B1	28872	58.42									
11/08/93	ISO-116-12B1	29048	58.71						4.62			
11/08/93	ISO-117-12B2	4551	4.38	4.27	2.28%							
11/08/93	ISO-117-12B2	4117	4.20									
11/08/93	ISO-117-12B2	4195	4.23									
11/08/93	ISO-118-12C1	395850	675.4	680.70	0.77%	0.94	57.56	623.14	61.24	689.39	7.6%	96%
11/08/93	ISO-118-12C1	402079	685.9									
11/08/93	ISO-118-12C1	398989	680.7									
11/08/93	ISO-119-12C2	5322	4.71	4.72	0.55%				5.02			
11/08/93	ISO-119-12C2	5301	4.70									
11/08/93	ISO-119-12C2	5416	4.74									
11/08/93	ISO-120-12D1	386000	658.8	663.11	1.01%	0.915	56.03	607.08	61.24	673.58	7.9%	93%
11/08/93	ISO-120-12D1	386441	659.6									
11/08/93	ISO-120-12D1	393096	670.8									
11/08/93	ISO-121-12D2	5561	4.81	4.81	0.23%				5.26			
11/08/93	ISO-121-12D2	5608	4.83									
11/08/93	ISO-121-12D2	5563	4.81									

Results for Quad Run 12, Methylene Diphenyl Diisocyanate

APPENDIX C

FIELD TEST #3 DATA



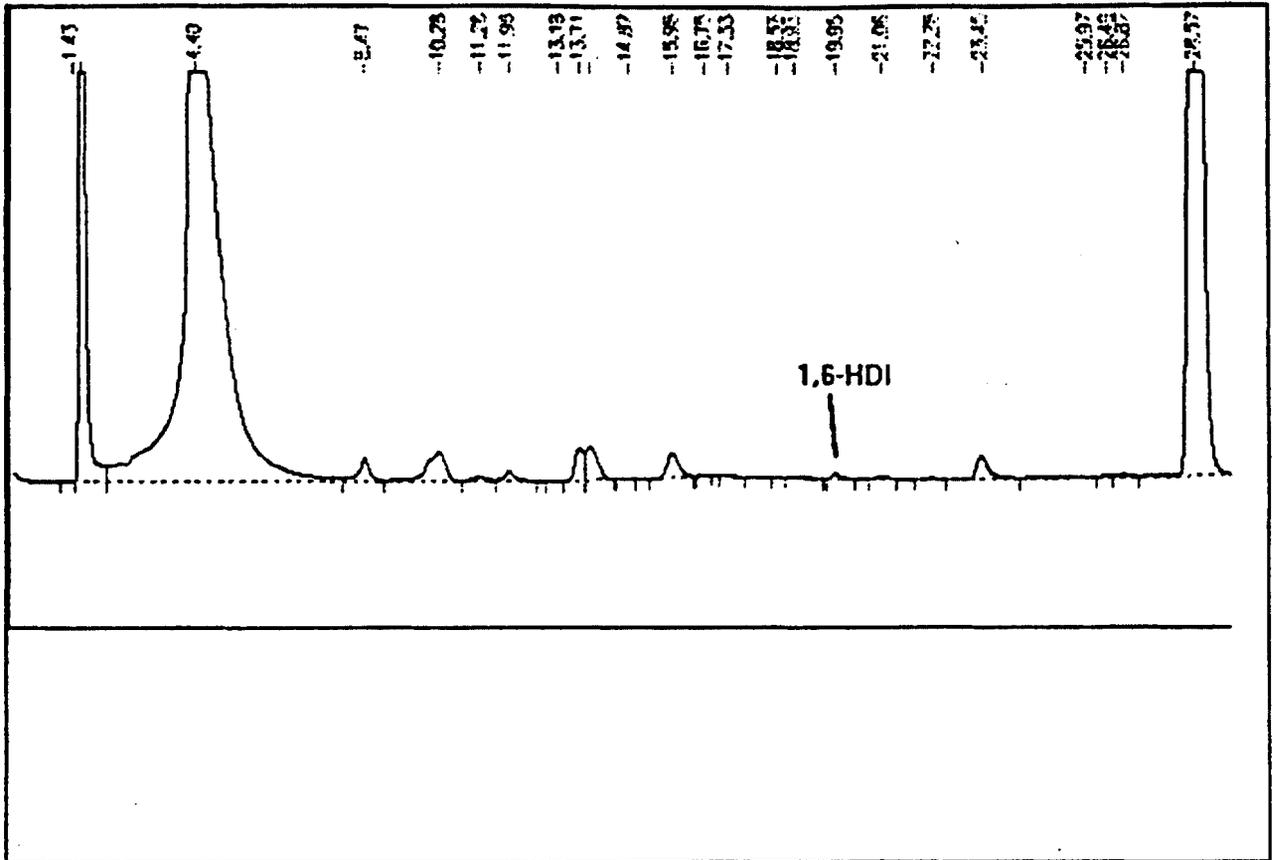


Figure 1 First Impinger, Unspiked Train

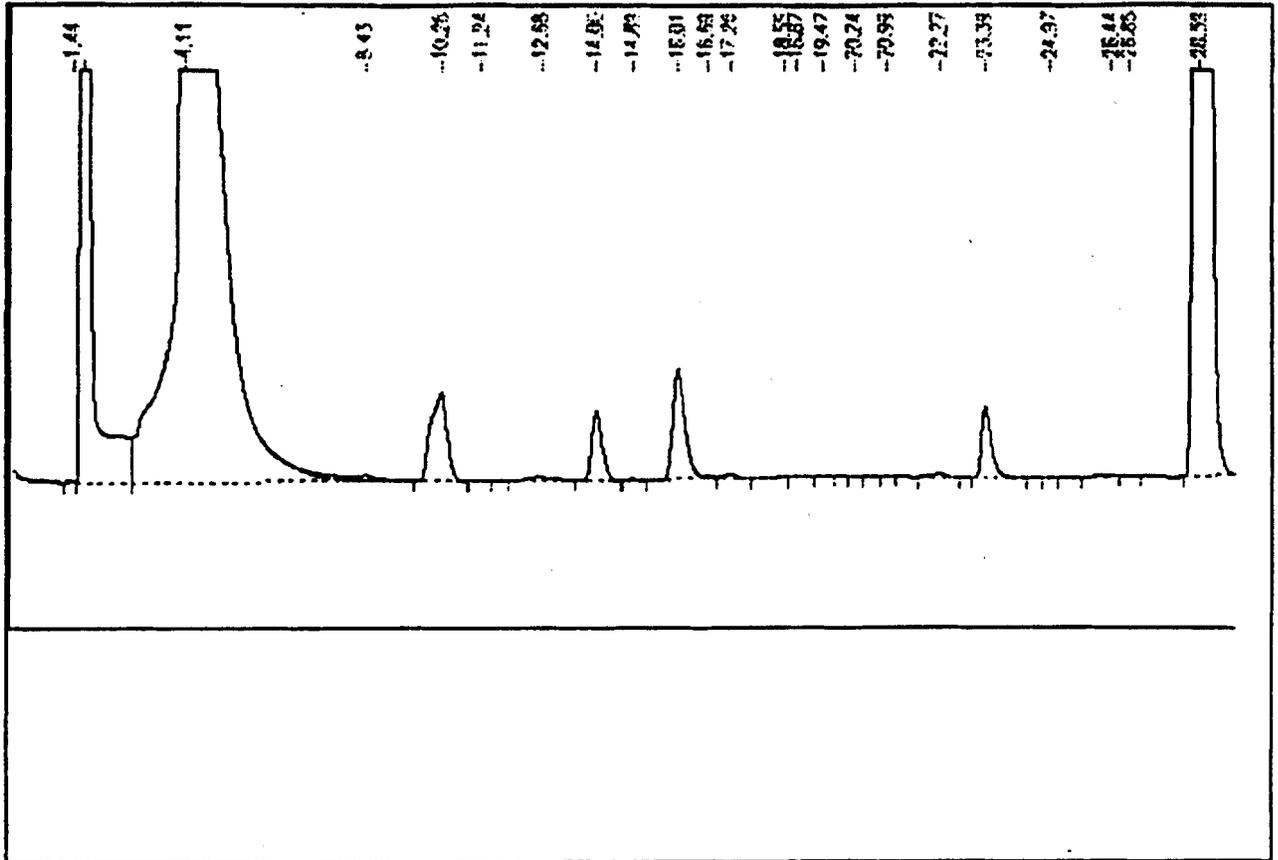


Figure 2 Second Impinger, Unspiked Train

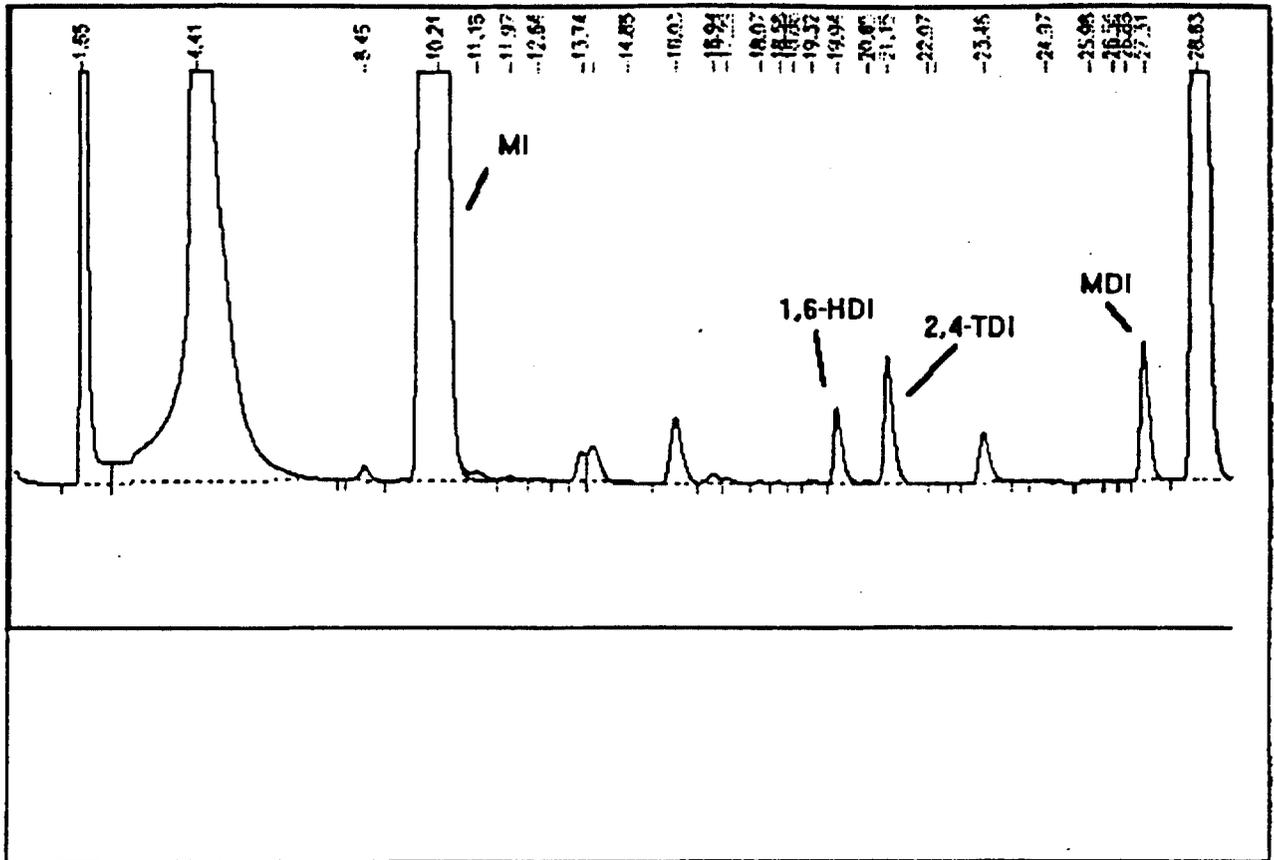


Figure 3 First Impinger, Spiked Train

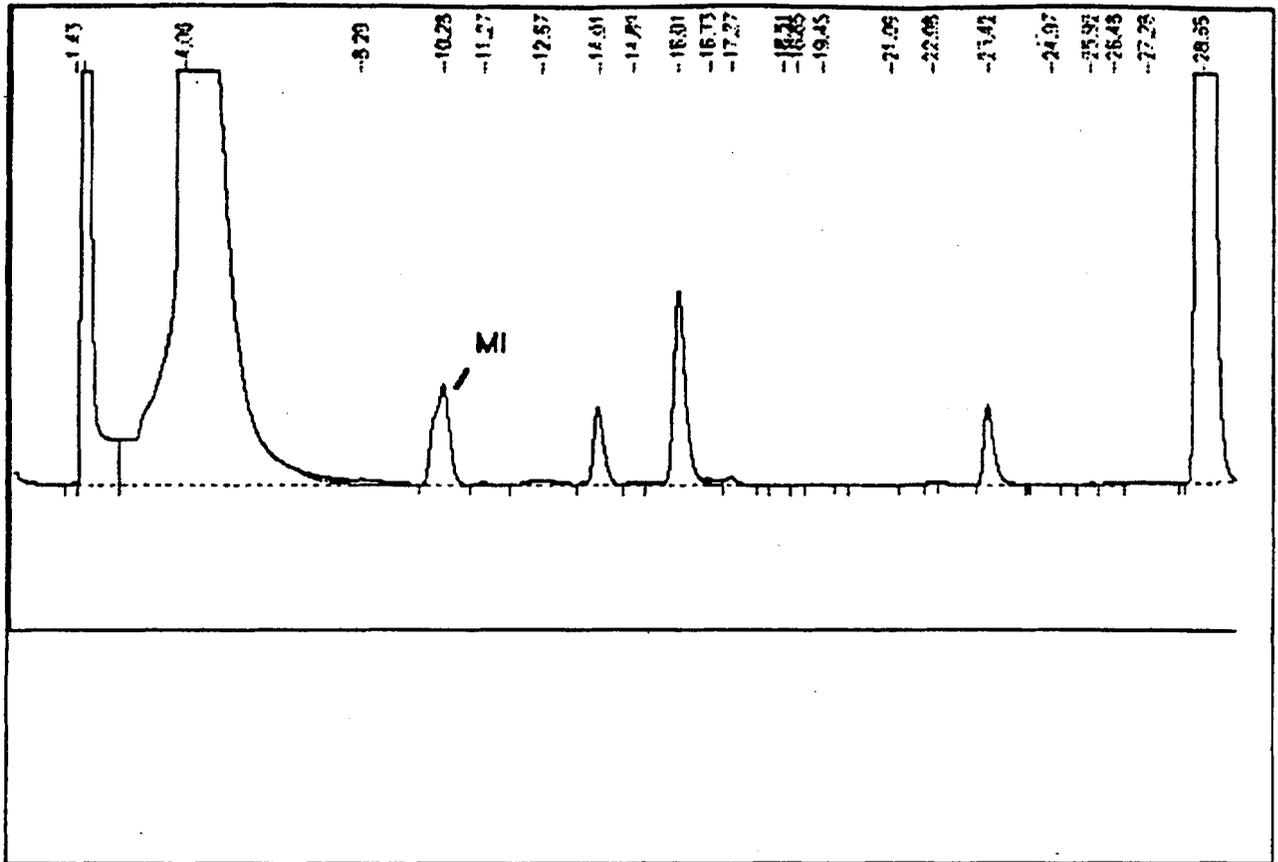
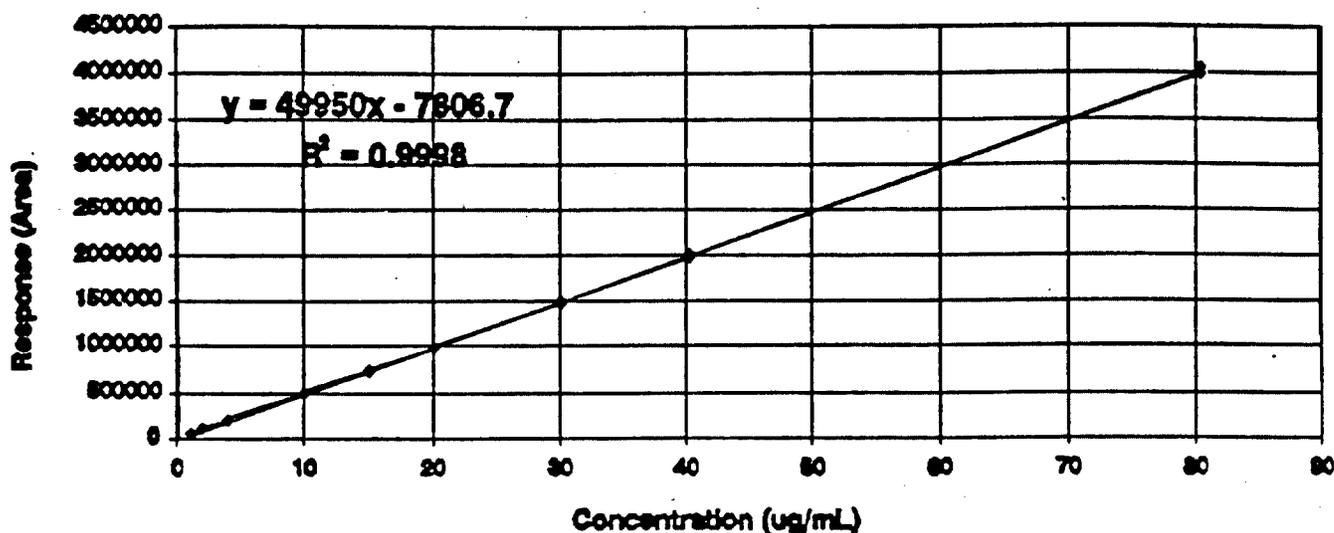


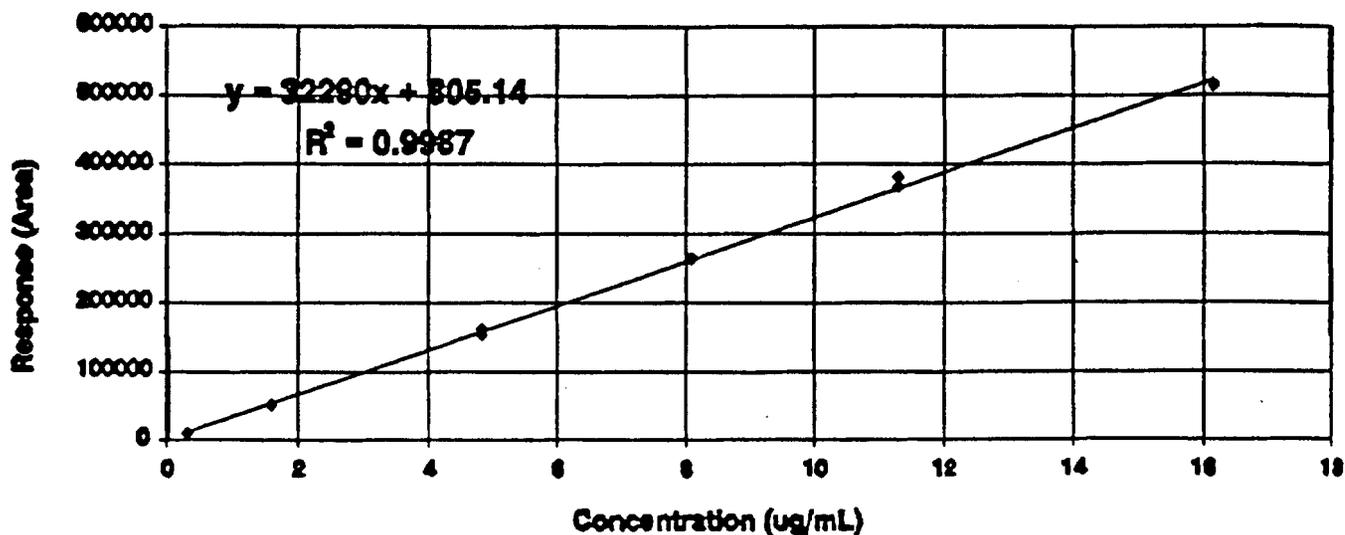
Figure 4 Second Impinger, Spiked Train

Methyl Isocyanate Calibration



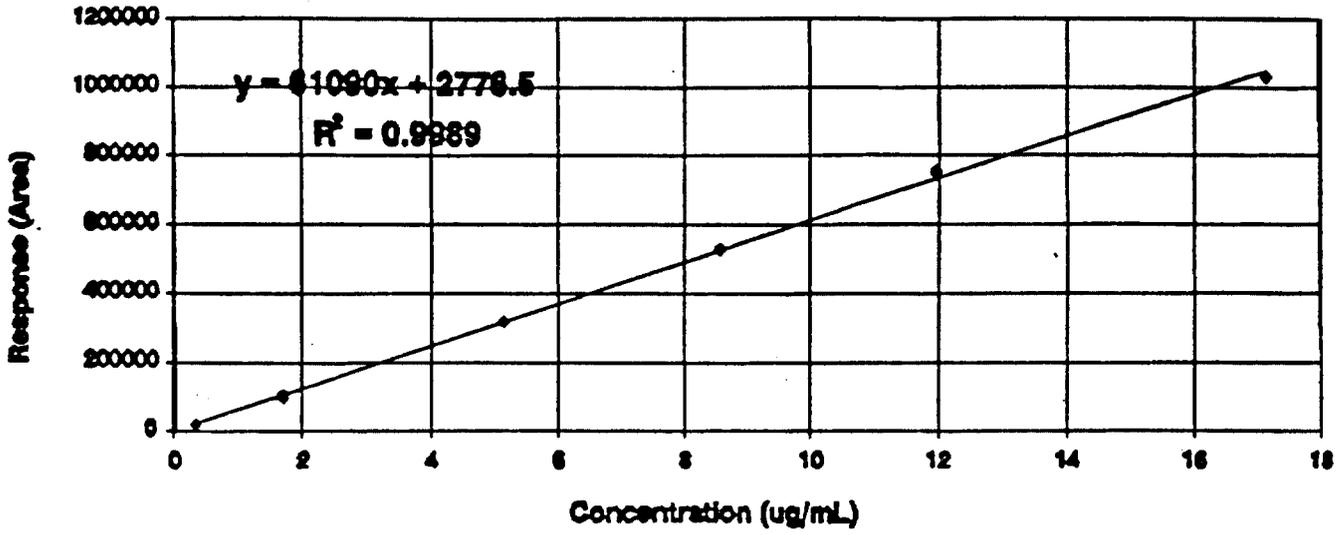
Calibration Level	Concentration	Response
Level 1	1.006	50628
Level 1	1.006	50518
Level 2	2.011	101209
Level 2	2.011	101826
Level 3	4.013	201489
Level 3	4.013	203770
Level 4	10.06	495882
Level 4	10.06	492688
Level 5	15.08	741034
Level 5	15.08	736319
Level 6	20.11	985869
Level 6	20.11	989369
Level 7	30.17	1467813
Level 7	30.17	1498656
Level 8	40.21	1973514
Level 8	40.21	2012386
Level 9	80.45	3994006
Level 9	80.45	4052225

Hexamethylene Diisocyanate Calibration



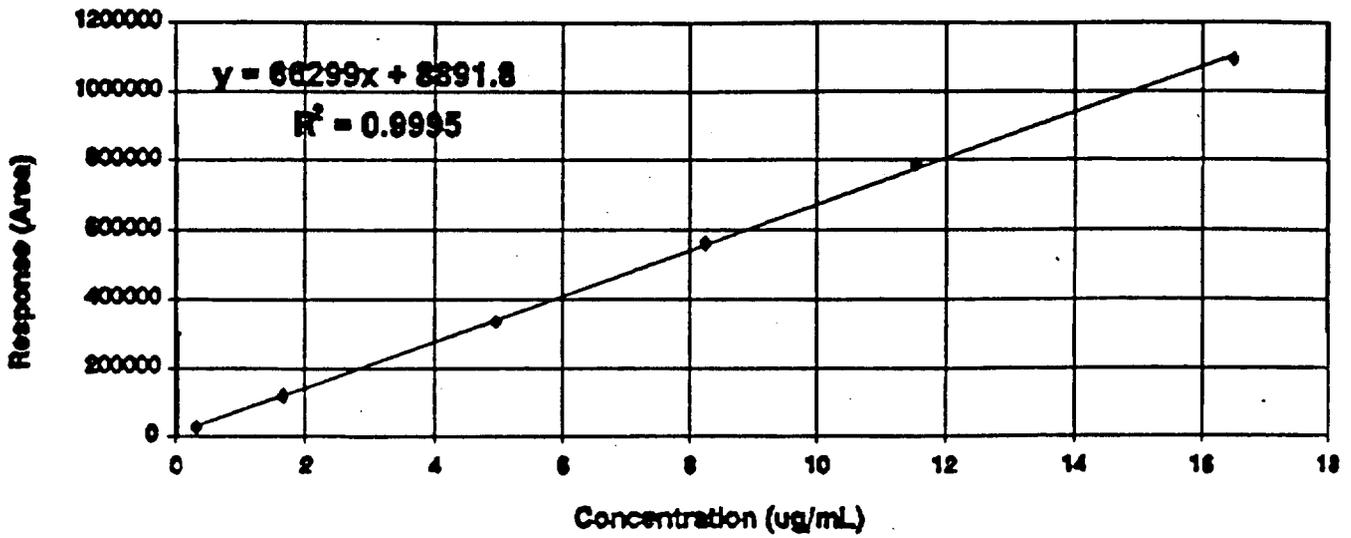
Calibration Level	Concentration	Response
Level 1	0.3228	9123
Level 1	0.3228	9333
Level 2	1.614	50424
Level 2	1.614	50210
Level 3	4.842	160130
Level 3	4.842	153578
Level 4	8.070	265301
Level 4	8.070	263942
Level 5	11.30	368932
Level 5	11.30	381747
Level 6	16.14	516971
Level 6	16.14	510984

2,4-Toluene Diisocyanate Calibration



Calibration Level	Concentration	Response
Level 1	0.3424	19414
Level 1	0.3424	20201
Level 2	1.712	99554
Level 2	1.712	105812
Level 3	5.136	315892
Level 3	5.136	315757
Level 4	8.560	526182
Level 4	8.560	534137
Level 5	11.98	752968
Level 5	11.98	758243
Level 6	17.12	1028560
Level 6	17.12	1036454

Methylene Diphenyl Diisocyanate Calibration



Calibration Level	Concentration	Response
Level 1	0.3298	24244
Level 1	0.3298	28766
Level 2	1.649	122868
Level 2	1.649	114177
Level 3	4.947	330084
Level 3	4.947	336970
Level 4	8.245	555274
Level 4	8.245	564116
Level 5	11.54	787511
Level 5	11.54	788112
Level 6	16.49	1095694
Level 6	16.49	1087220

Date Analyze	Sample Name	Area Count	MI ug	Average ug	%CV Injection	Dry Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 10060 ug
06/08/9	ARL-01-1A1-	832512	10514	10554.43	0.62%	1.062929486	186.47	10367.96	175.43	10666.21	41.2%	103%
06/08/9	ARL-01-1A1-	841770	10630									
06/08/9	ARL-01-1A1-	832856	10519									
06/07/9	ARL-02-1A2	643810	130	130.55	0.29%				122.82			
06/07/9	ARL-02-1A2	642720	130									
06/07/9	ARL-02-1A2	646351	131									
06/08/9	ARL-03-1B1-	844758	10668	10627.82	0.71%	1.103535844	193.59	10434.23	175.43	10721.36	38.9%	104%
06/08/9	ARL-03-1B1-	845352	10675									
06/08/9	ARL-03-1B1-	834617	10541									
06/07/9	ARL-04-1B2	603779	122	123.27	0.60%				111.71			
06/07/9	ARL-04-1B2	609128	124									
06/07/9	ARL-04-1B2	610913	124									
06/09/9	ARL-05-1C1-	7972	198	198.71	0.53%	1.098806931			180.84	296.98	39.1%	0%
06/09/9	ARL-05-1C1-	8113	199									
06/09/9	ARL-05-1C1-	8125	199									
06/08/9	ARL-06-1C2	626383	127	127.61	0.77%				116.14			
06/08/9	ARL-06-1C2	635247	129									
06/08/9	ARL-06-1C2	627209	127									
06/09/9	ARL-07-1D1-	7765	195	193.97	0.44%	1.140942399			170.01	269.33	36.9%	0%
06/09/9	ARL-07-1D1-	7681	194									
06/09/9	ARL-07-1D1-	7631	193									
06/08/9	ARL-08-1D2	557245	113	113.31	0.16%				99.32			
06/08/9	ARL-08-1D2	559034	113									
06/08/9	ARL-08-1D2	558319	113									

Results for Quad Run 1, Methyl Isocyanate

Date Analyze	Sample Name	Area Count	MI ug	Average ug	%CV Injection	Dry Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 10060 ug
06/12/9	ARL-09-2A1-	7382	190	190.35	4.69%	1.022521345			186.16	303.68	38.7%	
06/12/9	ARL-09-2A1-	8132	199									
06/12/9	ARL-09-2A1-	6708	182									
06/11/9	ARL-10-2A2	592339	120	120.17	0.05%				117.52			
06/11/9	ARL-10-2A2	592781	120									
06/11/9	ARL-10-2A2	592176	120									
06/12/9	ARL-11-2B1-	8104	199	198.95	0.92%	1.025154812			194.07	311.76	37.7%	
06/12/9	ARL-11-2B1-	8226	201									
06/12/9	ARL-11-2B1-	7934	197									
06/11/9	ARL-12-2B2	597523	121	120.65	2.01%				117.69			
06/11/9	ARL-12-2B2	581576	118									
06/11/9	ARL-12-2B2	605387	123									
06/12/9	ARL-13-2C1-	850183	10736	10675.41	0.52%	1.055340571	200.64	10474.77	190.12	10783.20	38.4%	104%
06/12/9	ARL-13-2C1-	841406	10626									
06/12/9	ARL-13-2C1-	844538	10665									
06/12/9	ARL-14-2C2	616072	125	124.86	0.15%				118.32			
06/12/9	ARL-14-2C2	616744	125									
06/12/9	ARL-14-2C2	614884	125									
06/12/9	ARL-15-2D1-	842822	10643	10527.26	1.13%	1.101298814	209.37	10317.88	190.12	10616.89	36.4%	103%
06/12/9	ARL-15-2D1-	834016	10533									
06/12/9	ARL-15-2D1-	823789	10405									
06/12/9	ARL-16-2D2	591932	120	119.92	0.11%				108.89			
06/12/9	ARL-16-2D2	590977	120									
06/12/9	ARL-16-2D2	590673	120									

Results for Quad Run 2, Methyl Isocyanate

Date Anal_ yze	Sample Name	Area Count	MI ug	Average ug	%CV Injection	Dry Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 10060 ug
06/22/94	ARL-17-3A1-	863108	10897	10773.32	1.02%	0.981093798	185.22	10588.09	188.79	10891.70	37.8%	105%
06/22/94	ARL-17-3A1-	850210	10736									
06/22/94	ARL-17-3A1-	846293	10687									
06/21/94	ARL-18-3A2	552361	112	112.64	0.38%				114.81			
06/21/94	ARL-18-3A2	556117	113									
06/21/94	ARL-18-3A2	556036	113									
06/22/94	ARL-19-3B1-	850031	10734	10837.06	0.84%	0.992052418	187.29	10649.77	188.79	10962.76	39.7%	106%
06/22/94	ARL-19-3B1-	861289	10874									
06/22/94	ARL-19-3B1-	863574	10903									
06/21/94	ARL-20-3B2	599890	122	123.21	1.27%				124.19			
06/21/94	ARL-20-3B2	607441	123									
06/21/94	ARL-20-3B2	615515	125									
06/22/94	ARL-21-3C1-	7633	193	193.17	0.12%	0.980753996			196.96	316.13	37.7%	
06/22/94	ARL-21-3C1-	7646	193									
06/22/94	ARL-21-3C1-	7612	193									
06/21/94	ARL-22-3C2	578617	117	116.88	0.62%				119.17			
06/21/94	ARL-22-3C2	571887	116									
06/22/94	ARL-22-3C2	577491	117									
06/22/94	ARL-23-3D1-	7058	186	185.69	1.11%	1.028014813			180.63	288.66	37.4%	
06/22/94	ARL-23-3D1-	7180	188									
06/22/94	ARL-23-3D1-	6856	184									
06/22/94	ARL-24-3D2	549225	112	111.05	1.09%				108.03			
06/22/94	ARL-24-3D2	540073	110									
06/22/94	ARL-24-3D2	551425	112									

Results for Quad Run 3, Methyl Isocyanate

Date Analyze	Sample Name	Area Count	MI ug	Average ug	%CV Injection	Dry Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 10060 ug
06/26/9	ARL-25-4A1-	7882	196	227.65	13.99%	0.996186677			228.52	341.25	33.0%	
06/26/9	ARL-25-4A1-	10314	227									
06/26/9	ARL-25-4A1-	12976	260									
06/25/9	ARL-26-4A2	553414	112	112.30	0.73%				112.72			
06/25/9	ARL-26-4A2	548888	111									
06/25/9	ARL-26-4A2	557045	113									
06/26/9	ARL-27-4B1-	7835	196	216.00	9.61%	1.009523912			213.96	295.11	27.5%	
06/26/9	ARL-27-4B1-	9365	215									
06/26/9	ARL-27-4B1-	11154	237									
06/25/9	ARL-28-4B2	400670	82	81.92	0.17%				81.15			
06/25/9	ARL-28-4B2	401541	82									
06/25/9	ARL-28-4B2	402028	82									
06/26/9	ARL-29-4C1-	874987	11046	10971.79	0.59%	0.99607341	220.37	10751.42	221.24	11093.66	35.4%	107%
06/26/9	ARL-29-4C1-	866603	10941									
06/26/9	ARL-29-4C1-	865602	10928									
06/26/9	ARL-30-4C2	601207	122	120.53	1.17%				121.00			
06/26/9	ARL-30-4C2	587175	119									
06/26/9	ARL-30-4C2	594266	121									
06/26/9	ARL-31-4D1-	771878	9756	9858.93	1.30%	1.070178599	236.77	9622.17	221.24	9959.34	34.4%	96%
06/26/9	ARL-31-4D1-	776894	9818									
06/26/9	ARL-31-4D1-	791614	10003									
06/26/9	ARL-32-4D2	614968	125	124.07	0.44%				115.94			
06/26/9	ARL-32-4D2	609731	124									
06/26/9	ARL-32-4D2	611099	124									

Results for Quad Run 4, Methyl Isocyanate

Date Analyze	Sample Name	Area Count	MI ug	Average ug	%CV Injection	Dry Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 10060 ug
06/29/9	ARL-33-5A1-	824733	10417	10407.32	0.11%	1.021332038	154.19	10253.13	150.97	10524.07	44.3%	102%
06/29/9	ARL-33-5A1-	822927	10395									
06/29/9	ARL-33-5A1-	824210	10410									
06/28/9	ARL-24-5A2	599831	122	122.53	2.95%				119.97			
06/28/9	ARL-34-5A2	588773	119									
06/28/9	ARL-34-5A2	624063	127									
06/29/9	ARL-35-5B1-	859474	10852	10821.63	0.24%	1.03011026	155.52	10666.11	150.97	10935.88	44.0%	106%
06/29/9	ARL-35-5B1-	855736	10805									
06/29/9	ARL-35-5B1-	855979	10808									
06/28/9	ARL-36-5B2	612106	124	122.37	1.38%				118.79			
06/28/9	ARL-36-5B2	595255	121									
06/28/9	ARL-36-5B2	602965	122									
06/29/9	ARL-37-5C1-	1469	116	183.44	31.91%	1.036453234			176.99	296.93	40.4%	
06/29/9	ARL-37-5C1-	9238	213									
06/29/9	ARL-37-5C1-	9864	221									
06/29/9	ARL-38-5C2	611668	124	124.31	0.55%				119.94			
06/29/9	ARL-38-5C2	610714	124									
06/29/9	ARL-38-5C2	617050	125									
06/29/9	ARL-39-5D1-	901	109	136.01	31.23%	1.088499599			124.95	217.34	42.5%	
06/29/9	ARL-39-5D1-	1305	114									
06/29/9	ARL-39-5D1-	6971	185									
06/29/9	ARL-40-5D2	591941	120	100.56	48.39%				92.38			
06/29/9	ARL-40-5D2	217815	45									
06/29/9	ARL-40-5D2	673709	136									

Results for Quad Run 5, Methyl Isocyanate

Date Analyze	Sample	Area Count	MI ug	Average ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 10060 ug
07/15/94	ARL-41-6A1-	7185	188	207.39	8.68%	1.031327885			201.09	310.75	35.3%	
07/15/94	ARL-41-6A1-	9122	212									
07/15/94	ARL-41-6A1-	9993	223									
07/14/94	ARL-42-6A2	54947	112	113.09	1.25%				109.65			
07/14/94	ARL-42-6A2	56335	114									
07/14/94	ARL-42-6A2	55837	113									
07/15/94	ARL-43-6B1-MI	5048	161	217.20	24.61%	1.047949874			207.26	322.03	35.6%	
07/15/94	ARL-43-6B1-MI	10054	224									
07/15/94	ARL-43-6B1-MI	13542	267									
07/14/94	ARL-44-6B2	59400	120	120.27	0.83%				114.76			
07/14/94	ARL-44-6B2	58747	119									
07/14/94	ARL-44-6B2	59729	121									
07/15/94	ARL-45-6C1-MI	84360	1065	10790.76	1.11%	1.056020175	215.62	10575.14	204.18	10899.79	37.1%	105%
07/15/94	ARL-45-6C1-MI	85910	1084									
07/15/94	ARL-45-6C1-MI	86107	1087									
07/15/94	ARL-46-6C2	62748	127	127.22	0.21%				120.47			
07/15/94	ARL-46-6C2	62643	127									
07/15/94	ARL-46-6C2	62903	127									
07/15/94	ARL-47-6D1-MI	75970	9604	9831.84	2.02%	1.107386936	226.10	9605.74	204.18	9920.60	35.2%	95%
07/15/94	ARL-47-6D1-MI	78539	9925									
07/15/94	ARL-47-6D1-MI	78875	9967									
07/15/94	ARL-48-6D2	59368	120	122.57	1.60%				110.68			
07/15/94	ARL-48-6D2	60659	123									
07/15/94	ARL-48-6D2	61295	124									

1 Results for Quad Run 6, Methyl Isocyanate

Date Analyze	Sample	Area Count	MI ug	Average ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 100660 ug
07/18/94	ARL-49-7A1-	85418	1078	10624.68	1.32%	1.017027877	218.20	10406.49	214.54	10752.78	38.0%	103%
07/18/94	ARL-49-7A1-	83587	1055									
07/18/94	ARL-49-7A1-	83392	1053									
07/17/94	ARL-50-7A2	65727	133	133.99	0.63%				131.75			
07/17/94	ARL-50-7A2	66143	134									
07/17/94	ARL-50-7A2	66570	135									
07/18/94	ARL-51-7B1-MI	83251	1051	10636.02	1.01%	1.028071447	220.57	10415.45	214.54	10754.89	36.8%	104%
07/18/94	ARL-51-7B1-MI	84552	1067									
07/18/94	ARL-51-7B1-MI	84867	1071									
07/17/94	ARL-52-7B2	63776	129	128.40	1.35%				124.90			
07/17/94	ARL-52-7B2	63934	130									
07/18/94	ARL-52-7B2	62362	126									
07/18/94	ARL-53-7C1-MI	8168	200	210.29	8.34%	1.066497409			197.18	275.15	28.3%	
07/18/94	ARL-53-7C1-MI	8214	200									
07/18/94	ARL-53-7C1-MI	10623	231									
07/18/94	ARL-54-7C2	40827	83	83.16	0.17%				77.97			
07/18/94	ARL-54-7C2	40682	83									
07/18/94	ARL-54-7C2	40765	83									
07/18/94	ARL-55-7D1-MI	6450	178	246.38	28.47%	1.062391466			231.91	343.84	32.6%	
07/18/94	ARL-55-7D1-MI	11552	242									
07/18/94	ARL-55-7D1-MI	17656	319									
07/18/94	ARL-56-7D2	58627	119	118.91	0.40%				111.92			
07/18/94	ARL-56-7D2	58845	119									
07/18/94	ARL-56-7D2	58368	118									

Results for Quad Run 7, Methyl Isocyanate

Date Analyze	Sample	Area Count	MI ug	Average ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 10060 ug
07/20/94	ARL-57-8A1-	8695	206	204.18	1.26%	1.085214844			188.15	291.83	35.5%	
07/20/94	ARL-57-8A1-	8284	201									
07/20/94	ARL-57-8A1-	8565	205									
07/19/94	ARL-58-8A2	52558	107	112.52	4.43%				103.69			
07/19/94	ARL-58-8A2	56680	115									
07/19/94	ARL-58-8A2	57034	116									
07/20/94	ARL-59-8B1-MI	8104	199	320.34	33.28%	1.008985892			317.48	428.84	26.0%	
07/20/94	ARL-59-8B1-MI	21125	362									
07/20/94	ARL-59-8B1-MI	24148	400									
07/19/94	ARL-60-8B2	54548	111	112.36	1.36%				111.36			
07/19/94	ARL-60-8B2	55413	113									
07/19/94	ARL-60-8B2	56068	114									
07/20/94	ARL-61-8C1-MI	83911	1059	10609.25	0.64%	1.018698571	257.54	10351.71	252.81	10716.60	30.7%	103%
07/20/94	ARL-61-8C1-MI	83524	1054									
07/20/94	ARL-61-8C1	84589	1068									
07/20/94	ARL-62-8C2	55273	112	114.17	1.48%				112.07			
07/20/94	ARL-62-8C2	56665	115									
07/20/94	ARL-62-8C2	56801	115									
07/20/94	ARL-63-8D1-MI	83674	1056	10550.97	0.30%	1.045344724	264.28	10286.69	252.81	10642.57	29.0%	102%
07/20/94	ARL-63-8D1-MI	83700	1057									
07/20/94	ARL-63-8D1-MI	83255	1051									
07/20/94	ARL-64-8D2	51490	105	107.73	2.77%				103.06			
07/20/94	ARL-64-8D2	53138	108									
07/20/94	ARL-64-8D2	54468	111									

Results for Quad Run 8, Methyl Isocyanate

Date Analyze	Sample	Area Count	MI ug	Average ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 10060 ug
07/22/94	ARL-65-9A1-	83850	1058	10569.38	0.34%	1.010911438	407.56	10161.82	403.16	10672.83	21.1%	101%
07/22/94	ARL-65-9A1-	83363	1052									
07/22/94	ARL-65-9A1-	83858	1059									
07/21/94	ARL-66-9A2	52615	107	109.03	2.15%				107.85			
07/21/94	ARL-66-9A2	53486	109									
07/21/94	ARL-66-9A2	54938	112									
07/22/94	ARL-67-9B1-MI	85673	1081	10966.96	1.47%	1.023625702	412.68	10554.28	403.16	11057.59	19.9%	105%
07/22/94	ARL-67-9B1-MI	86695	1094									
07/22/94	ARL-67-9B1-MI	88235	1113									
07/21/94	ARL-68-9B2	49908	101	102.52	1.17%				100.15			
07/21/94	ARL-68-9B2	50295	102									
07/22/94	ARL-68-9B2	51082	104									
07/22/94	ARL-69-9C1-MI	27190	438	567.68	19.81%	1.025239762			553.71	673.41	17.8%	
07/22/94	ARL-69-9C1-MI	43164	638									
07/22/94	ARL-69-9C1-MI	42325	627									
07/22/94	ARL-70-9C2	60375	122	122.72	0.89%				119.70			
07/22/94	ARL-70-9C2	60057	122									
07/22/94	ARL-70-9C2	61123	124									
07/22/94	ARL-71-9D1-MI	10569	230	268.41	12.58%	1.06253305			252.61	373.07	32.3%	
07/22/94	ARL-71-9D1-MI	14793	283									
07/22/94	ARL-71-9D1-MI	15574	293									
07/22/94	ARL-72-9D2	59823	121	127.99	5.32%				120.46			
07/22/94	ARL-72-9D2	66615	135									
07/22/94	ARL-72-9D2	63018	128									

Results for Quad Run 9, Methyl Isocyanate

Date Analyze	Sample	Area Count	MI ug	Average ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 10060 ug
07/28/94	ARL-73-10A1-	7560	192	263.10	23.61%	1.019349858			258.11	390.77	33.9%	
07/28/94	ARL-73-10A1-	15299	289									
07/28/94	ARL-73-10A1-	16806	308									
07/27/94	ARL-74-10A2	646697	131	135.23	2.69%				132.66			
07/27/94	ARL-74-10A2	677221	137									
07/27/94	ARL-74-10A2	679041	138									
07/28/94	ARL-75-10B1-	8548	205	212.86	4.95%	1.024871643			207.69	327.61	36.6%	
07/28/94	ARL-75-10B1-	8902	209									
07/28/94	ARL-75-10B1-	10151	225									
07/27/94	ARL-76-10B2	593786	120	122.90	1.75%				119.92			
07/27/94	ARL-76-10B2	613769	124									
07/28/94	ARL-76-10B2	610706	124									
07/28/94	ARL-77-10C1-	748803	9467	9717.13	2.26%	1.055397205	245.80	9471.33	232.90	9908.45	46.7%	94%
07/28/94	ARL-77-10C1-	775818	9805									
07/28/94	ARL-77-10C1	781740	9879									
07/28/94	ARL-78-10C2	104819	211	215.53	1.70%				204.22			
07/28/94	ARL-78-10C2	108313	218									
07/28/94	ARL-78-10C2	107503	217									
07/28/94	ARL-79-10D1-	807276	1019	10500.17	2.67%	1.059673048	246.80	10253.37	232.90	10599.38	32.7%	102%
07/28/94	ARL-79-10D1-	835248	1054									
07/28/94	ARL-79-10D1-	851596	1075									
07/28/94	ARL-80-10D2	579080	117	119.86	2.12%				113.11			
07/28/94	ARL-80-10D2	589223	120									
07/28/94	ARL-80-10D2	604356	123									

Results for Quad Run 10, Methyl Isocyanate

Date Analyze	Sample	Area Count	MI ug	Average ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 10060 ug
07/30/94	ARL-81-11A1-	84137	1062	10652.90	0.49%	1.02014273	357.15	10295.75	350.09	10730.82	19.5%	102%
07/30/94	ARL-81-11A1-	84096	1062									
07/30/94	ARL-81-11A1-	84839	1071									
07/29/94	ARL-82-11A2	41591	85	86.69	1.92%				84.98			
07/29/94	ARL-82-11A2	42770	87									
07/29/94	ARL-82-11A2	43198	88									
07/30/94	ARL-83-11B1-	82001	1035	10454.75	0.91%	1.034131252	362.04	10092.71	350.09	10562.45	25.5%	100%
07/30/94	ARL-83-11B1-	82810	1045									
07/30/94	ARL-83-11B1-	83510	1054									
07/29/94	ARL-84-11B2	60999	124	123.74	1.76%				119.65			
07/29/94	ARL-84-11B2	59954	122									
07/29/94	ARL-84-11B2	62128	126									
07/30/94	ARL-85-11C1-	11187	238	403.21	36.70%	1.066157606			378.19	474.91	20.4%	
07/30/94	ARL-85-11C1-	28148	450									
07/30/94	ARL-85-11C1-	33944	522									
07/30/94	ARL-86-11C2	48340	98	103.11	4.22%				96.71			
07/30/94	ARL-86-11C2	52596	107									
07/30/94	ARL-86-11C2	51236	104									
07/30/94	ARL-87-11D1-	9490	216	352.89	33.78%	1.095946929			322.00	410.60	21.6%	
07/30/94	ARL-87-11D1-	24673	406									
07/30/94	ARL-87-11D1-	27044	436									
07/30/94	ARL-88-11D2	46114	94	97.10	3.19%				88.60			
07/30/94	ARL-88-11D2	47844	97									
07/30/94	ARL-88-11D2	49205	100									

Results for Quad Run 11, Methyl Isocyanate

Date Analyze	Sample	Area Count	MI ug	Average ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 10060 ug
08/12/94	ARL-89-12A1-	27631	443	402.33	9.58%	0.998197174			403.06	526.69	23.5%	
08/12/94	ARL-89-12A1-	21536	367									
08/12/94	ARL-89-12A1-	23872	396									
08/11/94	ARL-90-12A2	58761	119	123.42	3.01%				123.64			
08/11/94	ARL-90-12A2	62284	126									
08/11/94	ARL-90-12A2	61548	125									
08/12/94	ARL-91-12B1-	8104	199	203.46	1.86%	1.029713824			197.58	344.44	42.6%	
08/12/94	ARL-91-12B1-	8565	205									
08/12/94	ARL-91-12B1-	8695	206									
08/11/94	ARL-92-12B2	70311	142	151.22	6.41%				146.86			
08/11/94	ARL-92-12B2	74043	150									
08/11/94	ARL-92-12B2	79911	162									
08/12/94	ARL-93-12C1-	91399	1153	11669.21	1.05%	1.04636413	314.24	11354.97	300.32	11793.18	31.5%	113%
08/12/94	ARL-93-12C1-	93307	1177									
08/12/94	ARL-93-12C1	92734	1170									
08/11/94	ARL-94-12C2	67009	136	144.28	5.28%				137.89			
08/11/94	ARL-94-12C2	72575	147									
08/12/94	ARL-94-12C2	74280	150									
08/12/94	ARL-95-12D1-	84791	1070	10897.35	1.99%	1.043419178	313.36	10583.99	300.32	11017.68	30.8%	105%
08/12/94	ARL-95-12D1-	85947	1085									
08/12/94	ARL-95-12D1-	88196	1113									
08/12/94	ARL-96-12D2	67553	137	139.16	2.28%				133.37			
08/12/94	ARL-96-12D2	68109	138									
08/12/94	ARL-96-12D2	70531	143									

Results for Quad Run 12, Methyl Isocyanate

Date Analyzed	Sample Name	Area Count	HDI ug	Average ug	%CV Injections	Dry Standard Meter Volume (dscm)	Unspiked Normalized to Spike (ug)	Recovered Spike (ug)	Amount Normalize to 1 m3	Total Normalize (ug)	% Total in 2nd	% from 161.4 ug
06/07/94	ARL-01-1A1	231052	178.3	175.58	1.39%	1.062929486	13.87	161.70	13.05	175.00	1.9%	100%
06/07/94	ARL-01-1A1	224892	173.5									
06/07/94	ARL-01-1A1	226792	175.0									
06/07/94	ARL-02-1A2	1884	0.3	0.26	31.50%				0.25			
06/07/94	ARL-02-1A2	1362	0.2									
06/07/94	ARL-02-1A2	1722	0.3									
06/07/94	ARL-03-1B1	222048	171.3	172.29	0.99%	1.103535844	14.40	157.88	13.05	170.94	0.0%	98%
06/07/94	ARL-03-1B1	222075	171.3									
06/07/94	ARL-03-1B1	225870	174.3									
06/07/94	ARL-04-1B2	370	0.0	0.00	NA				0.00			
06/07/94	ARL-04-1B2	412	0.0									
06/07/94	ARL-04-1B2	303	0.0									
06/08/94	ARL-05-1C1	19643	14.6	14.79	1.43%	1.098806931			13.46	13.53	0.5%	
06/08/94	ARL-05-1C1	20188	15.0									
06/08/94	ARL-05-1C1	19902	14.8									
06/08/94	ARL-06-1C2	406	0.0	0.07	173.21%				0.07			
06/08/94	ARL-06-1C2	583	0.0									
06/08/94	ARL-06-1C2	1502	0.2									
06/08/94	ARL-07-1D1	18844	14.0	14.43	2.98%	1.140942399			12.64	12.64	0.0%	
06/08/94	ARL-07-1D1	19527	14.5									
06/08/94	ARL-07-1D1	19939	14.8									
06/08/94	ARL-08-1D2	324	0.0	0.00	NA				0.00			
06/08/94	ARL-08-1D2	0	0.0									
06/08/94	ARL-08-1D2	0	0.0									

Results from Quad Run 1, Hexamethylene Diisocyanate

Date Analyze	Sample Name	Area Count	HDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 161.4 ug
06/11/94	ARL-09-2A1	87789	67.3	67.39	0.09%	1.022521345			65.90	66.71	1.2%	
06/11/94	ARL-09-2A1	87931	67.5									
06/11/94	ARL-09-2A1	87807	67.4									
06/11/94	ARL-10-2A2	3478	0.8	0.83	3.92%				0.81			
06/11/94	ARL-10-2A2	3377	0.8									
06/11/94	ARL-10-2A2	3587	0.9									
06/11/94	ARL-11-2B1	89836	68.9	68.36	1.48%	1.025154812			66.68	66.68	0.0%	
06/11/94	ARL-11-2B1	89860	69.0									
06/11/94	ARL-11-2B1	87592	67.2									
06/11/94	ARL-12-2B2	947	0.0	0.00	NA				0.00			
06/11/94	ARL-12-2B2	747	0.0									
06/11/94	ARL-12-2B2	899	0.0									
06/12/94	ARL-13-2C1	313161	241.8	239.96	0.82%	1.055340571	69.96	170.00	66.29	236.52	0.3%	105%
06/12/94	ARL-13-2C1	310959	240.1									
06/12/94	ARL-13-2C1	308095	237.9									
06/12/94	ARL-14-2C2	1522	0.2	0.24	9.45%				0.22			
06/12/94	ARL-14-2C2	1646	0.3									
06/12/94	ARL-14-2C2	1524	0.2									
06/12/94	ARL-15-2D1	304294	235.0	236.29	0.54%	1.101298814	73.01	163.28	66.29	230.31	1.1%	101%
06/12/94	ARL-15-2D1	307565	237.5									
06/12/94	ARL-15-2D1	306133	236.4									
06/12/94	ARL-16-2D2	3200	0.7	0.81	14.02%				0.74			
06/12/94	ARL-16-2D2	3854	0.9									
06/12/94	ARL-16-2D2	3238	0.8									

Results from Quad Run 2, Hexamethylene Diisocyanate

Date Analyze	Sample Name	Area Count	HDI ug	Average ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 161.4 ug
06/21/94	ARL-17-3A1	319102	246.4	246.84	0.19%	0.981093798	85.18	161.66	86.82	248.75	0.3%	100%
06/21/94	ARL-17-3A1	319478	246.7									
06/21/94	ARL-17-3A1	320305	247.4									
06/21/94	ARL-18-3A2	1659	0.3	0.26	7.21%				0.27			
06/21/94	ARL-18-3A2	1581	0.2									
06/21/94	ARL-18-3A2	1699	0.3									
06/21/94	ARL-19-3B1	329155	254.2	256.14	0.66%	0.992052418	86.13	170.01	86.82	257.56	0.8%	105%
06/21/94	ARL-19-3B1	333227	257.4									
06/21/94	ARL-19-3B1	332529	256.8									
06/21/94	ARL-20-3B2	3180	0.7	0.72	7.70%				0.73			
06/21/94	ARL-20-3B2	3306	0.8									
06/21/94	ARL-20-3B2	2949	0.7									
06/21/94	ARL-21-3C1	112091	86.2	86.34	0.72%	0.980753996			88.03	88.66	0.7%	
06/21/94	ARL-21-3C1	113214	87.0									
06/21/94	ARL-21-3C1	111656	85.8									
06/21/94	ARL-22-3C2	2925	0.7	0.61	6.46%				0.62			
06/21/94	ARL-22-3C2	2717	0.6									
06/22/94	ARL-22-3C2	2692	0.6									
06/22/94	ARL-23-3D1	114651	88.1	88.01	0.34%	1.028014813			85.61	86.53	1.1%	
06/22/94	ARL-23-3D1	114747	88.2									
06/22/94	ARL-23-3D1	114027	87.7									
06/22/94	ARL-24-3D2	4437	1.1	0.95	16.25%				0.92			
06/22/94	ARL-24-3D2	3544	0.8									
06/22/94	ARL-24-3D2	3616	0.9									

Results from Quad Run 3, Hexamethylene Diisocyanate

Date Analyze	Sample Name	Area Count	HDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 161.4 ug
06/25/94	ARL-25-4A1	13670	10.0	10.18	3.92%	0.996186677			10.22	10.22	0.0%	
06/25/94	ARL-25-4A1	14547	10.6									
06/25/94	ARL-25-4A1	13642	9.9									
06/25/94	ARL-26-4A2	364	0.0	0.00	NA				0.00			
06/25/94	ARL-26-4A2	548	0.0									
06/25/94	ARL-26-4A2	604	0.0									
06/25/94	ARL-27-4B1	15429	11.3	11.63	4.58%	1.009523912			11.52	11.52	0.0%	
06/25/94	ARL-27-4B1	15437	11.3									
06/25/94	ARL-27-4B1	16623	12.2									
06/25/94	ARL-28-4B2	346	0.0	0.00	NA				0.00			
06/25/94	ARL-28-4B2	792	0.0									
06/25/94	ARL-28-4B2	0	0.0									
06/26/94	ARL-29-4C1	230258	177.7	166.94	11.65%	0.99607341	10.83	156.12	10.87	166.99	0.0%	97%
06/26/94	ARL-29-4C1	187425	144.5									
06/26/94	ARL-29-4C1	231605	178.7									
06/26/94	ARL-30-4C2	0	0.0	0.00	NA				0.00			
06/26/94	ARL-30-4C2	749	0.0									
06/26/94	ARL-30-4C2	716	0.0									
06/26/94	ARL-31-4D1	229232	176.9	174.23	1.42%	1.070178599	11.63	162.60	10.87	173.57	1.0%	101%
06/26/94	ARL-31-4D1	225386	173.9									
06/26/94	ARL-31-4D1	222899	172.0									
06/26/94	ARL-32-4D2	893	0.0	0.11	173.21%				0.11			
06/26/94	ARL-32-4D2	1911	0.3									
06/26/94	ARL-32-4D2	600	0.0									

Results from Quad Run 4, Hexamethylene Diisocyanate

Date Analyze	Sample Name	Area Count	HDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 161.4 ug
06/28/94	ARL-33-5A1	240959	185.9	187.09	0.59%	1.021332038	23.32	163.77	22.83	186.60	0.0%	101%
06/28/94	ARL-33-5A1	243810	188.1									
06/28/94	ARL-33-5A1	242581	187.2									
06/28/94	ARL-24-5A2	586	0.0	0.00	NA				0.00			
06/28/94	ARL-34-5A2	669	0.0									
06/28/94	ARL-34-5A2	729	0.0									
06/28/94	ARL-35-5B1	240317	185.4	184.46	0.47%	1.03011026	23.52	160.94	22.83	183.77	0.0%	100%
06/28/94	ARL-35-5B1	238248	183.8									
06/28/94	ARL-35-5B1	238594	184.1									
06/28/94	ARL-36-5B2	464	0.0	0.00	NA				0.00			
06/28/94	ARL-36-5B2	839	0.0									
06/28/94	ARL-36-5B2	446	0.0									
06/29/94	ARL-37-5C1	32427	24.5	24.59	0.65%	1.036453234			23.72	23.72	0.0%	
06/29/94	ARL-37-5C1	32798	24.8									
06/29/94	ARL-37-5C1	32464	24.5									
06/29/94	ARL-38-5C2	428	0.0	0.00	NA				0.00			
06/29/94	ARL-38-5C2	445	0.0									
06/29/94	ARL-38-5C2	476	0.0									
06/29/94	ARL-39-5D1	30468	23.0	23.89	3.41%	1.088499599			21.94	21.94	0.0%	
06/29/94	ARL-39-5D1	32039	24.2									
06/29/94	ARL-39-5D1	32461	24.5									
06/29/94	ARL-40-5D2	610	0.0	0.00	NA				0.00			
06/29/94	ARL-40-5D2	0	0.0									
06/29/94	ARL-40-5D2	780	0.0									

Results from Quad Run 5, Hexamethylene Diisocyanate

Date Analyze	Sample	Area Count	HDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 161.4 ug
07/14/94	ARL-41-6A1	64674	49.5	49.32	0.26%	1.031327885			47.82	48.10	0.6%	
07/14/94	ARL-41-6A1	64340	49.2									
07/14/94	ARL-41-6A1	64508	49.3									
07/14/94	ARL-42-6A2	1696	0.3	0.29	4.26%				0.28			
07/14/94	ARL-42-6A2	1774	0.3									
07/14/94	ARL-42-6A2	1752	0.3									
07/14/94	ARL-43-6B1	69121	52.9	51.91	1.64%	1.047949874			49.54	49.54	0.0%	
07/14/94	ARL-43-6B1	67228	51.4									
07/14/94	ARL-43-6B1	67209	51.4									
07/14/94	ARL-44-6B2	764	0.0	0.00	NA				0.00			
07/14/94	ARL-44-6B2	918	0.0									
07/14/94	ARL-44-6B2	1115	0.0									
07/14/94	ARL-45-6C1	277217	214.0	217.42	1.43%	1.056020175	51.41	166.01	48.68	214.69	0.0%	103%
07/15/94	ARL-45-6C1	285085	220.1									
07/15/94	ARL-45-6C1	282559	218.1									
07/15/94	ARL-46-6C2	674	0.0	0.00	NA				0.00			
07/15/94	ARL-46-6C2	752	0.0									
07/15/94	ARL-46-6C2	536	0.0									
07/15/94	ARL-47-6D1	268770	207.5	207.17	0.33%	1.107386936	53.91	153.26	48.68	203.17	2.4%	95%
07/15/94	ARL-47-6D1	267376	206.4									
07/15/94	ARL-47-6D1	269017	207.7									
07/15/94	ARL-48-6D2	4728	1.2	1.35	9.05%				1.22			
07/15/94	ARL-48-6D2	5318	1.4									
07/15/94	ARL-48-6D2	5482	1.4									

Results from Quad Run 6, Hexamethylene Diisocyanate

Date Analyze	Sample	Area Count	HDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 161.4 ug
07/17/94	ARL-49-7A1	264516	204.2	205.47	0.55%	1.017027877	40.58	164.89	39.90	205.07	0.7%	102%
07/17/94	ARL-49-7A1	267101	206.2									
07/17/94	ARL-49-7A1	266943	206.1									
07/17/94	ARL-50-7A2	1224	0.1	0.29	55.94%				0.28			
07/17/94	ARL-50-7A2	2272	0.5									
07/17/94	ARL-50-7A2	1725	0.3									
07/17/94	ARL-51-7B1	270471	208.8	200.77	3.87%	1.028071447	41.02	159.75	39.90	199.93	0.7%	99%
07/17/94	ARL-51-7B1	250414	193.3									
07/17/94	ARL-51-7B1	259479	200.3									
07/17/94	ARL-52-7B2	904	0.0	0.29	173.21%				0.28			
07/17/94	ARL-52-7B2	3614	0.9									
07/18/94	ARL-52-7B2	829	0.0									
07/18/94	ARL-53-7C1	55404	42.3	43.97	3.65%	1.066497409			41.23	42.29	2.5%	
07/18/94	ARL-53-7C1	57856	44.2									
07/18/94	ARL-53-7C1	59524	45.5									
07/18/94	ARL-54-7C2	6287	1.7	1.13	86.60%				1.06			
07/18/94	ARL-54-7C2	6257	1.7									
07/18/94	ARL-54-7C2	771	0.0									
07/18/94	ARL-55-7D1	51441	39.2	40.98	6.37%	1.062391466			38.57	38.73	0.4%	
07/18/94	ARL-55-7D1	57607	44.0									
07/18/94	ARL-55-7D1	52153	39.8									
07/18/94	ARL-56-7D2	962	0.0	0.17	92.08%				0.16			
07/18/94	ARL-56-7D2	1806	0.3									
07/18/94	ARL-56-7D2	1460	0.2									

Results from Quad Run 7, Hexamethylene Diisocyanate

Date Analyze	Sample	Area Count	HDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 161.4 ug
07/19/94	ARL-57-8A1	19344	14.4	16.43	11.18%	1.085214844			15.14	15.22	0.5%	
07/19/94	ARL-57-8A1	23847	17.8									
07/19/94	ARL-57-8A1	22890	17.1									
07/19/94	ARL-58-8A2	614	0.0	0.08	173.21%				0.08			
07/19/94	ARL-58-8A2	0	0.0									
07/19/94	ARL-58-8A2	1607	0.2									
07/19/94	ARL-59-8B1	19954	14.8	15.98	6.46%	1.008985892			15.83	15.83	0.0%	
07/19/94	ARL-59-8B1	21842	16.3									
07/19/94	ARL-59-8B1	22527	16.8									
07/19/94	ARL-60-8B2	438	0.0	0.00	NA				0.00			
07/19/94	ARL-60-8B2	410	0.0									
07/19/94	ARL-60-8B2	343	0.0									
07/20/94	ARL-61-8C1	233350	180.0	182.52	1.28%	1.018698571	15.78	166.74	15.49	182.29	0.4%	103%
07/20/94	ARL-61-8C1	236912	182.8									
07/20/94	ARL-61-8C1	239366	184.7									
07/20/94	ARL-62-8C2	470	0.0	0.06	173.21%				0.06			
07/20/94	ARL-62-8C2	572	0.0									
07/20/94	ARL-62-8C2	1400	0.2									
07/20/94	ARL-63-8D1	216097	166.7	170.36	1.93%	1.045344724	16.19	154.17	15.49	169.65	0.0%	96%
07/20/94	ARL-63-8D1	222097	171.3									
07/20/94	ARL-63-8D1	224320	173.1									
07/20/94	ARL-64-8D2	496	0.0	0.00	NA				0.00			
07/20/94	ARL-64-8D2	328	0.0									
07/20/94	ARL-64-8D2	320	0.0									

Results from Quad Run 8, Hexamethylene Diisocyanate

Date Analyze	Sample	Area Count	HDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 161.4 ug
07/21/94	ARL-65-9A1	222086	171.3	178.15	4.82%	1.010911438	10.81	167.34	10.69	178.03	0.0%	104%
07/21/94	ARL-65-9A1	227279	175.3									
07/21/94	ARL-65-9A1	243353	187.8									
07/21/94	ARL-66-9A2	0	0.0	0.00	NA				0.00			
07/21/94	ARL-66-9A2	489	0.0									
07/21/94	ARL-66-9A2	0	0.0									
07/21/94	ARL-67-9B1	212215	163.7	164.57	1.14%	1.023625702	10.95	153.63	10.69	164.32	0.0%	95%
07/21/94	ARL-67-9B1	211732	163.3									
07/21/94	ARL-67-9B1	216147	166.7									
07/21/94	ARL-68-9B2	426	0.0	0.00	NA				0.00			
07/21/94	ARL-68-9B2	0	0.0									
07/22/94	ARL-68-9B2	444	0.0									
07/22/94	ARL-69-9C1	15053	11.0	12.75	12.60%	1.025239762			12.43	12.43	0.0%	
07/22/94	ARL-69-9C1	19168	14.2									
07/22/94	ARL-69-9C1	17576	13.0									
07/22/94	ARL-70-9C2	0	0.0	0.00	NA				0.00			
07/22/94	ARL-70-9C2	0	0.0									
07/22/94	ARL-70-9C2	0	0.0									
07/22/94	ARL-71-9D1	12168	8.8	9.51	8.25%	1.06253305			8.95	8.95	0.0%	
07/22/94	ARL-71-9D1	14176	10.4									
07/22/94	ARL-71-9D1	12937	9.4									
07/22/94	ARL-72-9D2	392	0.0	0.00	NA				0.00			
07/22/94	ARL-72-9D2	785	0.0									
07/22/94	ARL-72-9D2	452	0.0									

Results from Quad Run 9, Hexamethylene Diisocyanate

Date Analyze	Sample	Area Count	HDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 161.4 ug
07/27/94	ARL-73-10A1	160556	123.7	122.76	0.72%	1.019349858			120.43	121.23	0.7%	
07/27/94	ARL-73-10A1	159244	122.7									
07/27/94	ARL-73-10A1	158284	121.9									
07/27/94	ARL-74-10A2	4639	1.2	0.82	40.64%				0.80			
07/27/94	ARL-74-10A2	3165	0.7									
07/27/94	ARL-74-10A2	2546	0.5									
07/27/94	ARL-75-10B1	153114	117.9	119.57	1.26%	1.024871643			116.67	118.13	1.2%	
07/27/94	ARL-75-10B1	156919	120.9									
07/27/94	ARL-75-10B1	155694	119.9									
07/27/94	ARL-76-10B2	3515	0.8	1.50	40.72%				1.46			
07/27/94	ARL-76-10B2	6010	1.6									
07/28/94	ARL-76-10B2	7403	2.0									
07/28/94	ARL-77-10C1	338257	261.3	270.43	2.94%	1.055397205	125.12	145.31	118.55	264.69	0.7%	90%
07/28/94	ARL-77-10C1	355502	274.6									
07/28/94	ARL-77-10C1	356515	275.4									
07/28/94	ARL-78-10C2	1382	0.2	0.87	75.37%				0.82			
07/28/94	ARL-78-10C2	5594	1.5									
07/28/94	ARL-78-10C2	3877	1.0									
07/28/94	ARL-79-10D1	363628	280.9	288.81	2.37%	1.059673048	125.62	163.18	118.55	282.41	0.6%	101%
07/28/94	ARL-79-10D1	378574	292.5									
07/28/94	ARL-79-10D1	379278	293.0									
07/28/94	ARL-80-10D2	4058	1.0	0.72	53.45%				0.68			
07/28/94	ARL-80-10D2	3646	0.9									
07/28/94	ARL-80-10D2	1720	0.3									

Results from Quad Run 10, Hexamethylene Diisocyanate

Date Analyze	Sample	Area Count	HDI ug	Average ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 161.4 ug
07/29/94	ARL-81-11A1	238152	183.8	184.82	0.87%	1.02014273	26.90	157.91	26.37	184.28	0.0%	98%
07/29/94	ARL-81-11A1	238469	184.0									
07/29/94	ARL-81-11A1	241914	186.7									
07/29/94	ARL-82-11A2	1074	0.0	0.00	NA				0.00			
07/29/94	ARL-82-11A2	336	0.0									
07/29/94	ARL-82-11A2	427	0.0									
07/29/94	ARL-83-11B1	227318	175.4	178.95	2.85%	1.034131252	27.27	151.68	26.37	178.05	0.0%	94%
07/29/94	ARL-83-11B1	229014	176.7									
07/29/94	ARL-83-11B1	239477	184.8									
07/29/94	ARL-84-11B2	494	0.0	0.00	NA				0.00			
07/29/94	ARL-84-11B2	436	0.0									
07/29/94	ARL-84-11B2	507	0.0									
07/30/94	ARL-85-11C1	35931	27.2	28.51	4.87%	1.066157606			26.74	26.74	0.0%	
07/30/94	ARL-85-11C1	37460	28.4									
07/30/94	ARL-85-11C1	39501	30.0									
07/30/94	ARL-86-11C2	709	0.0	0.00	NA				0.00			
07/30/94	ARL-86-11C2	638	0.0									
07/30/94	ARL-86-11C2	474	0.0									
07/30/94	ARL-87-11D1	37220	28.2	28.49	1.35%	1.095946929			26.00	26.00	0.0%	
07/30/94	ARL-87-11D1	37431	28.4									
07/30/94	ARL-87-11D1	38164	28.9									
07/30/94	ARL-88-11D2	322	0.0	0.00	NA				0.00			
07/30/94	ARL-88-11D2	556	0.0									
07/30/94	ARL-88-11D2	410	0.0									

Results from Quad Run 11, Hexamethylene Diisocyanate

Date Analyze	Sample	Area Count	HDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 161.4 ug
08/11/94	ARL-89-12A1	8083	5.6	4.33	77.79%	0.998197174			4.34	8.50	49.0%	
08/11/94	ARL-89-12A1	1459	0.5									
08/11/94	ARL-89-11A1	9660	6.9									
08/11/94	ARL-90-12A2	10996	3.2	4.16	65.46%				4.17			
08/11/94	ARL-90-12A2	24177	7.2									
08/11/94	ARL-90-12A2	7519	2.1									
08/11/94	ARL-91-12B1	32175	24.3	16.83	74.11%	1.029713824			16.35	20.73	21.2%	
08/11/94	ARL-91-12B1	31513	23.8									
08/11/94	ARL-91-12B1	3945	2.4									
08/11/94	ARL-92-12B2	15105	4.4	4.52	20.29%				4.39			
08/11/94	ARL-92-12B2	18494	5.5									
08/11/94	ARL-92-12B2	12596	3.7									
08/11/94	ARL-93-12C1	249435	192.5	189.38	1.65%	1.04636413	10.82	178.56	10.34	190.74	15.1%	111%
08/11/94	ARL-93-12C1	241373	186.3									
08/11/94	ARL-93-12C1	245414	189.4									
08/11/94	ARL-94-12C2	7085	1.9	1.93	5.04%				1.84			
08/11/94	ARL-94-12C2	6684	1.8									
08/12/94	ARL-94-12C2	7299	2.0									
08/12/94	ARL-95-12D1	244209	188.5	195.06	2.94%	1.043419178	10.79	184.27	10.34	195.20	5.4%	114%
08/12/94	ARL-95-12D1	257186	198.5									
08/12/94	ARL-95-12D1	256841	198.2									
08/12/94	ARL-96-12D2	983	0.0	0.62	87.11%				0.59			
08/12/94	ARL-96-12D2	3602	0.9									
08/12/94	ARL-96-12D2	3977	1.0									

Results from Quad Run 12, Hexamethylene Diisocyanate

Date Analyze	Sample Name	Area Count	TDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 171.2 ug
06/07/94	ARL-01-1A1	424607	172.6	172.48	0.77%	1.062929486	2.10	170.38	1.98	172.35	0.0%	100%
06/07/94	ARL-01-1A1	427280	173.7									
06/07/94	ARL-01-1A1	420848	171.1									
06/07/94	ARL-02-1A2	1250	0.0	0.00	NA				0.00			
06/07/94	ARL-02-1A2	1810	0.0									
06/07/94	ARL-02-1A2	2041	0.0									
06/07/94	ARL-03-1B1	417128	169.6	171.44	1.05%	1.103535844	2.18	169.26	1.98	171.24	0.0%	99%
06/07/94	ARL-03-1B1	422140	171.6									
06/07/94	ARL-03-1B1	425883	173.1									
06/07/94	ARL-04-1B2	0	0.0	0.00	NA				0.00			
06/07/94	ARL-04-1B2	784	0.0									
06/07/94	ARL-04-1B2	448	0.0									
06/08/94	ARL-05-1C1	7402	1.9	1.87	2.81%	1.098806931			1.70	1.70	0.0%	
06/08/94	ARL-05-1C1	7198	1.8									
06/08/94	ARL-05-1C1	7434	1.9									
06/08/94	ARL-06-1C2	652	0.0	0.00	NA				0.00			
06/08/94	ARL-06-1C2	612	0.0									
06/08/94	ARL-06-1C2	0	0.0									
06/08/94	ARL-07-1D1	12076	3.8	2.57	41.80%	1.140942399			2.25	2.25	0.0%	
06/08/94	ARL-07-1D1	7453	1.9									
06/08/94	ARL-07-1D1	7612	2.0									
06/08/94	ARL-08-1D2	0	0.0	0.00	NA				0.00			
06/08/94	ARL-08-1D2	0	0.0									
06/08/94	ARL-08-1D2	0	0.0									

Results of Quad 1, 2,4-Toluene Diisocyanate

Date Analyze	Sample Name	Area Count	TDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 171.2 ug
06/11/94	ARL-09-2A1	7781	2.0	2.05	3.90%	1.022521345			2.01	2.01	0.0%	
06/11/94	ARL-09-2A1	7998	2.1									
06/11/94	ARL-09-2A1	7610	2.0									
06/11/94	ARL-10-2A2	640	0.0	0.00	NA				0.00			
06/11/94	ARL-10-2A2	892	0.0									
06/11/94	ARL-10-2A2	1609	0.0									
06/11/94	ARL-11-2B1	8227	2.2	2.22	3.61%	1.025154812			2.17	2.17	0.0%	
06/11/94	ARL-11-2B1	8396	2.3									
06/11/94	ARL-11-2B1	8007	2.1									
06/11/94	ARL-12-2B2	0	0.0	0.00	NA				0.00			
06/11/94	ARL-12-2B2	0	0.0									
06/11/94	ARL-12-2B2	1129	0.0									
06/12/94	ARL-13-2C1	447695	182.1	178.92	1.60%	1.055340571	2.20	176.72	2.09	178.81	0.0%	103%
06/12/94	ARL-13-2C1	438178	178.2									
06/12/94	ARL-13-2C1	434096	176.5									
06/12/94	ARL-14-2C2	842	0.0	0.00	NA				0.00			
06/12/94	ARL-14-2C2	591	0.0									
06/12/94	ARL-14-2C2	816	0.0									
06/12/94	ARL-15-2D1	431976	175.6	176.54	0.72%	1.101298814	2.30	174.24	2.09	176.33	0.0%	102%
06/12/94	ARL-15-2D1	437712	178.0									
06/12/94	ARL-15-2D1	432850	176.0									
06/12/94	ARL-16-2D2	669	0.0	0.00	NA				0.00			
06/12/94	ARL-16-2D2	939	0.0									
06/12/94	ARL-16-2D2	752	0.0									

Results of Quad 2, 2,4-Toluene Diisocyanate

Date Analyze	Sample Name	Area Count	TDI ug	Average ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 171.2 ug
06/21/94	ARL-17-3A1	442006	179.7	180.98	0.61%	0.981093798	1.99	178.99	2.03	181.01	0.0%	105%
06/21/94	ARL-17-3A1	445894	181.3									
06/21/94	ARL-17-3A1	447136	181.8									
06/21/94	ARL-18-3A2	0	0.0	0.00	NA				0.00			
06/21/94	ARL-18-3A2	0	0.0									
06/21/94	ARL-18-3A2	0	0.0									
06/21/94	ARL-19-3B1	449447	182.8	182.68	0.12%	0.992052418	2.01	180.66	2.03	182.69	0.0%	106%
06/21/94	ARL-19-3B1	449520	182.8									
06/21/94	ARL-19-3B1	448538	182.4									
06/21/94	ARL-20-3B2	0	0.0	0.00	NA				0.00			
06/21/94	ARL-20-3B2	0	0.0									
06/21/94	ARL-20-3B2	0	0.0									
06/21/94	ARL-21-3C1	8446	2.3	2.07	11.21%	0.980753996			2.11	2.11	0.0%	
06/21/94	ARL-21-3C1	7751	2.0									
06/21/94	ARL-21-3C1	7322	1.9									
06/21/94	ARL-22-3C2	0	0.0	0.00	NA				0.00			
06/21/94	ARL-22-3C2	0	0.0									
06/21/94	ARL-22-3C2	0	0.0									
06/22/94	ARL-23-3D1	7558	2.0	2.00	5.67%	1.028014813			1.94	1.94	0.0%	
06/22/94	ARL-23-3D1	7973	2.1									
06/22/94	ARL-23-3D1	7449	1.9									
06/22/94	ARL-24-3D2	0	0.0	0.00	NA				0.00			
06/22/94	ARL-24-3D2	0	0.0									
06/22/94	ARL-24-3D2	1117	0.0									

Results of Quad 3, 2,4-Toluene Diisocyanate

Date Analyze	Sample Name	Area Count	TDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 171.2 ug
06/25/94	ARL-25-4A1	4701	0.8	0.54	60.85%	0.996186677			0.54	0.54	0.0%	
06/25/94	ARL-25-4A1	4370	0.7									
06/25/94	ARL-25-4A1	3186	0.2									
06/25/94	ARL-26-4A2	0	0.0	0.00	NA				0.00			
06/25/94	ARL-26-4A2	2009	0.0									
06/25/94	ARL-26-4A2	0	0.0									
06/25/94	ARL-27-4B1	5338	1.0	0.93	35.36%	1.009523912			0.92	0.97	5.0%	
06/25/94	ARL-27-4B1	4133	0.6									
06/25/94	ARL-27-4B1	5646	1.2									
06/25/94	ARL-28-4B2	2841	0.0	0.05	173.21%				0.05			
06/25/94	ARL-28-4B2	3676	0.1									
06/25/94	ARL-28-4B2	757	0.0									
06/26/94	ARL-29-4C1	441825	179.7	169.61	12.25%	0.99607341	0.72	168.88	0.73	169.61	0.0%	99%
06/26/94	ARL-29-4C1	358850	145.7									
06/26/94	ARL-29-4C1	451028	183.4									
06/26/94	ARL-30-4C2	0	0.0	0.00	NA				0.00			
06/26/94	ARL-30-4C2	0	0.0									
06/26/94	ARL-30-4C2	1407	0.0									
06/26/94	ARL-31-4D1	443918	180.5	178.03	1.24%	1.070178599	0.78	177.25	0.73	177.98	0.0%	104%
06/26/94	ARL-31-4D1	435802	177.2									
06/26/94	ARL-31-4D1	433702	176.3									
06/26/94	ARL-32-4D2	0	0.0	0.00	NA				0.00			
06/26/94	ARL-32-4D2	0	0.0									
06/26/94	ARL-32-4D2	0	0.0									

Results of Quad 4, 2,4-Toluene Diisocyanate

Date Analyzed	Sample Name	Area Count	TDI ug	Average ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 171.2 ug
06/28/94	ARL-33-5A1	442742	180.0	180.43	0.66%	1.021332038	2.33	178.10	2.28	180.38	0.0%	104%
06/28/94	ARL-33-5A1	446948	181.8									
06/28/94	ARL-33-5A1	441327	179.5									
06/28/94	ARL-24-5A2	1005	0.0	0.00	NA				0.00			
06/28/94	ARL-34-5A2	1942	0.0									
06/28/94	ARL-34-5A2	1785	0.0									
06/28/94	ARL-35-5B1	438642	178.4	177.68	0.35%	1.03011026	2.35	175.33	2.28	177.61	0.0%	102%
06/28/94	ARL-35-5B1	435654	177.1									
06/28/94	ARL-35-5B1	436586	177.5									
06/28/94	ARL-36-5B2	1121	0.0	0.00	NA				0.00			
06/28/94	ARL-36-5B2	2712	0.0									
06/28/94	ARL-36-5B2	1440	0.0									
06/29/94	ARL-37-5C1	9393	2.7	2.58	4.28%	1.036453234			2.49	2.49	0.0%	
06/29/94	ARL-37-5C1	8931	2.5									
06/29/94	ARL-37-5C1	8923	2.5									
06/29/94	ARL-38-5C2	0	0.0	0.00	NA				0.00			
06/29/94	ARL-38-5C2	604	0.0									
06/29/94	ARL-38-5C2	478	0.0									
06/29/94	ARL-39-5D1	8122	2.2	2.25	3.86%	1.088499599			2.07	2.15	3.8%	
06/29/94	ARL-39-5D1	8191	2.2									
06/29/94	ARL-39-5D1	8517	2.4									
06/29/94	ARL-40-5D2	712	0.0	0.09	173.21%				0.08			
06/29/94	ARL-40-5D2	0	0.0									
06/29/94	ARL-40-5D2	4392	0.3									

Results of Quad 5, 2,4-Toluene Diisocyanate

Date Analyzed	Sample	Area Count	TDI ug	Average ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 171.2 ug
07/14/94	ARL-41-6A1	6117	1.4	1.36	7.74%	1.031327885			1.32	1.32	0.0%	
07/14/94	ARL-41-6A1	6347	1.5									
07/14/94	ARL-41-6A1	5833	1.3									
07/14/94	ARL-42-6A2	988	0.0	0.00	NA				0.00			
07/14/94	ARL-42-6A2	902	0.0									
07/14/94	ARL-42-6A2	0	0.0									
07/14/94	ARL-43-6B1	7066	1.8	1.83	15.12%	1.047949874			1.75	1.75	0.0%	
07/14/94	ARL-43-6B1	6700	1.6									
07/14/94	ARL-43-6B1	8013	2.1									
07/14/94	ARL-44-6B2	682	0.0	0.00	NA				0.00			
07/14/94	ARL-44-6B2	0	0.0									
07/14/94	ARL-44-6B2	1638	0.0									
07/14/94	ARL-45-6C1	39204	159.3	172.76	6.75%	1.056020175	1.62	171.14	1.53	172.67	0.0%	100%
07/15/94	ARL-45-6C1	44026	179.0									
07/15/94	ARL-45-6C1	44247	179.9									
07/15/94	ARL-46-6C2	0	0.0	0.00	NA				0.00			
07/15/94	ARL-46-6C2	0	0.0									
07/15/94	ARL-46-6C2	0	0.0									
07/15/94	ARL-47-6D1	42306	172.0	171.21	0.40%	1.107386936	1.70	169.51	1.53	171.04	0.0%	99%
07/15/94	ARL-47-6D1	42002	170.8									
07/15/94	ARL-47-6D1	42032	170.9									
07/15/94	ARL-48-6D2	0	0.0	0.00	NA				0.00			
07/15/94	ARL-48-6D2	0	0.0									
07/15/94	ARL-48-6D2	732	0.0									

Results of Quad 6, 2,4-Toluene Diisocyanate

Date Analyzed	Sample	Area Count	TDI ug	Average ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 171.2 ug
07/17/94	ARL-49-7A1	42612	173.2	174.24	1.13%	1.017027877	2.07	172.17	2.03	174.20	0.0%	101%
07/17/94	ARL-49-7A1	42542	173.0									
07/17/94	ARL-49-7A1	43407	176.5									
07/17/94	ARL-50-7A2	2451	0.0	0.00	NA				0.00			
07/17/94	ARL-50-7A2	2836	0.0									
07/17/94	ARL-50-7A2	2386	0.0									
07/17/94	ARL-51-7B1	42071	171.0	168.12	2.53%	1.028071447	2.09	166.02	2.03	168.11	2.3%	97%
07/17/94	ARL-51-7B1	40164	163.2									
07/17/94	ARL-51-7B1	41840	170.1									
07/17/94	ARL-52-7B2	3674	0.1	0.05	173.21%				0.05			
07/17/94	ARL-52-7B2	749	0.0									
07/18/94	ARL-52-7B2	548	0.0									
07/18/94	ARL-53-7C1	7312	1.9	2.71	27.91%	1.066497409			2.54	2.54	0.0%	
07/18/94	ARL-53-7C1	10024	3.0									
07/18/94	ARL-53-7C1	10844	3.3									
07/18/94	ARL-54-7C2	390	0.0	0.00	NA				0.00			
07/18/94	ARL-54-7C2	0	0.0									
07/18/94	ARL-54-7C2	0	0.0									
07/18/94	ARL-55-7D1	6840	1.7	1.62	5.76%	1.062391466			1.53	1.53	0.0%	
07/18/94	ARL-55-7D1	6910	1.7									
07/18/94	ARL-55-7D1	6486	1.5									
07/18/94	ARL-56-7D2	764	0.0	0.00	NA				0.00			
07/18/94	ARL-56-7D2	0	0.0									
07/18/94	ARL-56-7D2	3291	0.0									

Results of Quad 7, 2,4-Toluene Diisocyanate

Date Analyzed	Sample	Area Count	TDI ug	Average ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 171.2 ug
07/19/94	ARL-57-8A1	4213	0.6	2.09	62.72%	1.085214844			1.92	2.09	8.0%	
07/19/94	ARL-57-8A1	10104	3.0									
07/19/94	ARL-57-8A1	9322	2.7									
07/19/94	ARL-58-8A2	0	0.0	0.18	173.21%				0.17			
07/19/94	ARL-58-8A2	6107	0.5									
07/19/94	ARL-58-8A2	0	0.0									
07/19/94	ARL-59-8B1	6782	1.6	1.92	27.87%	1.008985892			1.90	1.90	0.0%	
07/19/94	ARL-59-8B1	6634	1.6									
07/19/94	ARL-59-8B1	8968	2.5									
07/19/94	ARL-60-8B2	0	0.0	0.00	NA				0.00			
07/19/94	ARL-60-8B2	0	0.0									
07/19/94	ARL-60-8B2	0	0.0									
07/20/94	ARL-61-8C1	43324	176.2	176.07	0.94%	1.018698571	1.95	174.13	1.91	176.04	0.0%	102%
07/20/94	ARL-61-8C1	42888	174.4									
07/20/94	ARL-61-8C1	43697	177.7									
07/20/94	ARL-62-8C2	0	0.0	0.00	NA				0.00			
07/20/94	ARL-62-8C2	0	0.0									
07/20/94	ARL-62-8C2	0	0.0									
07/20/94	ARL-63-8D1	39699	161.3	165.48	2.18%	1.045344724	2.00	163.48	1.91	165.39	0.0%	95%
07/20/94	ARL-63-8D1	41173	167.4									
07/20/94	ARL-63-8D1	41269	167.8									
07/20/94	ARL-64-8D2	0	0.0	0.00	NA				0.00			
07/20/94	ARL-64-8D2	0	0.0									
07/20/94	ARL-64-8D2	0	0.0									

Results of Quad 8, 2,4-Toluene Diisocyanate

Date Analyzed	Sample	Area Count	TDI ug	Average ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 171.2 ug
07/21/94	ARL-65-9A1	42433	172.5	178.37	3.89%	1.010911438	1.71	176.67	1.69	178.36	0.0%	103%
07/21/94	ARL-65-9A1	43424	176.6									
07/21/94	ARL-65-9A1	45738	186.0									
07/21/94	ARL-66-9A2	0	0.0	0.00	NA				0.00			
07/21/94	ARL-66-9A2	1562	0.0									
07/21/94	ARL-66-9A2	0	0.0									
07/21/94	ARL-67-9B1	40981	166.6	166.57	0.37%	1.023625702	1.73	164.84	1.69	166.53	0.0%	96%
07/21/94	ARL-67-9B1	41129	167.2									
07/21/94	ARL-67-9B1	40827	165.9									
07/21/94	ARL-68-9B2	0	0.0	0.00	NA				0.00			
07/21/94	ARL-68-9B2	0	0.0									
07/22/94	ARL-68-9B2	0	0.0									
07/22/94	ARL-69-9C1	5338	1.0	2.80	56.31%	1.025239762			2.73	2.73	0.0%	
07/22/94	ARL-69-9C1	12801	4.1									
07/22/94	ARL-69-9C1	10704	3.2									
07/22/94	ARL-70-9C2	1523	0.0	0.00	NA				0.00			
07/22/94	ARL-70-9C2	609	0.0									
07/22/94	ARL-70-9C2	1044	0.0									
07/22/94	ARL-71-9D1	3875	0.5	0.69	49.95%	1.06253305			0.65	0.65	0.0%	
07/22/94	ARL-71-9D1	4076	0.5									
07/22/94	ARL-71-9D1	5421	1.1									
07/22/94	ARL-72-9D2	0	0.0	0.00	NA				0.00			
07/22/94	ARL-72-9D2	638	0.0									
07/22/94	ARL-72-9D2	933	0.0									

Results of Quad 9, 2,4-Toluene Diisocyanate

Date Analyze	Sample	Area Count	TDI ug	Average ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 171.2 ug
07/27/94	ARL-73-10A1	8116	2.2	2.14	4.23%	1,019349858			2.10	2.15	2.2%	
07/27/94	ARL-73-10A1	8161	2.2									
07/27/94	ARL-73-10A1	7757	2.0									
07/27/94	ARL-74-10A2	3666	0.1	0.05	173.21%				0.05			
07/27/94	ARL-74-10A2	3228	0.0									
07/27/94	ARL-74-10A2	3170	0.0									
07/27/94	ARL-75-10B1	9852	2.9	3.05	7.83%	1,024871643			2.98	2.98	0.0%	
07/27/94	ARL-75-10B1	9934	2.9									
07/27/94	ARL-75-10B1	10902	3.3									
07/27/94	ARL-76-10B2	1281	0.0	0.00	NA				0.00			
07/27/94	ARL-76-10B2	532	0.0									
07/28/94	ARL-76-10B2	344	0.0									
07/28/94	ARL-77-10C1	400993	163.0	167.68	2.44%	1,055397205	2.68	165.00	2.54	167.54	0.0%	96%
07/28/94	ARL-77-10C1	417672	169.8									
07/28/94	ARL-77-10C1	418892	170.3									
07/28/94	ARL-78-10C2	3109	0.0	0.00	NA				0.00			
07/28/94	ARL-78-10C2	2133	0.0									
07/28/94	ARL-78-10C2	2224	0.0									
07/28/94	ARL-79-10D1	431314	175.4	179.81	2.23%	1,059673048	2.69	177.12	2.54	179.66	0.0%	103%
07/28/94	ARL-79-10D1	444905	180.9									
07/28/94	ARL-79-10D1	450289	183.1									
07/28/94	ARL-80-10D2	399	0.0	0.00	NA				0.00			
07/28/94	ARL-80-10D2	542	0.0									
07/28/94	ARL-80-10D2	537	0.0									

Results of Quad 10, 2,4-Toluene Diisocyanate

Date Analyzed	Sample	Area Count	TDI ug	Average ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 171.2 ug
07/29/94	ARL-81-11A1	42635	173.3	173.92	1.13%	1.02014273	2.76	171.16	2.70	173.98	4.0%	100%
07/29/94	ARL-81-11A1	42381	172.3									
07/29/94	ARL-81-11A1	43312	176.1									
07/29/94	ARL-82-11A2	2713	0.0	0.12	173.21%				0.11			
07/29/94	ARL-82-11A2	4896	0.3									
07/29/94	ARL-82-11A2	1717	0.0									
07/29/94	ARL-83-11B1	40764	165.7	169.24	2.46%	1.034131252	2.80	166.44	2.70	169.15	0.0%	97%
07/29/94	ARL-83-11B1	41381	168.2									
07/29/94	ARL-83-11B1	42754	173.8									
07/29/94	ARL-84-11B2	0	0.0	0.00	NA				0.00			
07/29/94	ARL-84-11B2	0	0.0									
07/29/94	ARL-84-11B2	0	0.0									
07/30/94	ARL-85-11C1	8152	2.2	3.04	29.07%	1.066157606			2.85	2.85	0.0%	
07/30/94	ARL-85-11C1	10012	3.0									
07/30/94	ARL-85-11C1	12456	4.0									
07/30/94	ARL-86-11C2	0	0.0	0.00	NA				0.00			
07/30/94	ARL-86-11C2	449	0.0									
07/30/94	ARL-86-11C2	756	0.0									
07/30/94	ARL-87-11D1	8713	2.4	2.80	24.21%	1.095946929			2.55	2.55	0.0%	
07/30/94	ARL-87-11D1	8612	2.4									
07/30/94	ARL-87-11D1	11532	3.6									
07/30/94	ARL-88-11D2	0	0.0	0.00	NA				0.00			
07/30/94	ARL-88-11D2	0	0.0									
07/30/94	ARL-88-11D2	0	0.0									

Results of Quad 11, 2,4-Toluene Diisocyanate

Date Analyzed	Sample	Area Count	TDI ug	Average ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 171.2 ug
08/11/94	ARL-89-12A1	5026	0.9	1.20	70.52%	0.998197174			1.20	1.46	17.6%	
08/11/94	ARL-89-12A1	8021	2.1									
08/11/94	ARL-89-11A1	4068	0.5									
08/11/94	ARL-90-12A2	5264	0.4	0.26	87.05%				0.26			
08/11/94	ARL-90-12A2	4988	0.4									
08/11/94	ARL-90-12A2	418	0.0									
08/11/94	ARL-91-12B1	7048	1.7	1.75	8.94%	1.029713824			1.70	2.01	15.6%	
08/11/94	ARL-91-12B1	6667	1.6									
08/11/94	ARL-91-12B1	7431	1.9									
08/11/94	ARL-92-12B2	5460	0.4	0.32	87.79%				0.31			
08/11/94	ARL-92-12B2	6027	0.5									
08/11/94	ARL-92-12B2	866	0.0									
08/11/94	ARL-93-12C1	44475	180.9	180.44	0.45%	1.04636413	1.52	178.92	1.45	180.37	0.0%	105%
08/11/94	ARL-93-12C1	44138	179.5									
08/11/94	ARL-93-12C1	44493	180.9									
08/11/94	ARL-94-12C2	1124	0.0	0.00	NA				0.00			
08/11/94	ARL-94-12C2	2214	0.0									
08/12/94	ARL-94-12C2	2148	0.0									
08/12/94	ARL-95-12D1	44802	182.2	187.57	2.48%	1.043419178	1.51	186.06	1.45	187.51	0.0%	109%
08/12/94	ARL-95-12D1	46774	190.3									
08/12/94	ARL-95-12D1	46761	190.2									
08/12/94	ARL-96-12D2	964	0.0	0.00	NA				0.00			
08/12/94	ARL-96-12D2	0	0.0									
08/12/94	ARL-96-12D2	392	0.0									

Results of Quad 12, 2,4-Toluene Diisocyanate

Date Analyze	Sample Name	Area Count	MDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 164.9 ug
06/07/94	ARL-01-1A1	435575	160.9	161.95	0.60%	1.062929486	2.41	159.54	2.27	161.81	0.0%	97%
06/07/94	ARL-01-1A1	438936	162.2									
06/07/94	ARL-01-1A1	440609	162.8									
06/07/94	ARL-02-1A2	3472	0.0	0.00	NA				0.00			
06/07/94	ARL-02-1A2	3303	0.0									
06/07/94	ARL-02-1A2	3355	0.0									
06/07/94	ARL-03-1B1	433003	159.9	161.93	1.08%	1.103535844	2.50	159.42	2.27	161.69	0.0%	97%
06/07/94	ARL-03-1B1	440453	162.7									
06/07/94	ARL-03-1B1	441488	163.1									
06/07/94	ARL-04-1B2	1174	0.0	0.00	NA				0.00			
06/07/94	ARL-04-1B2	542	0.0									
06/07/94	ARL-04-1B2	505	0.0									
06/08/94	ARL-05-1C1	16916	3.0	2.99	3.90%	1.098806931			2.72	2.72	0.0%	
06/08/94	ARL-05-1C1	17090	3.1									
06/08/94	ARL-05-1C1	16490	2.9									
06/08/94	ARL-06-1C2	1345	0.0	0.00	NA				0.00			
06/08/94	ARL-06-1C2	7186	0.0									
06/08/94	ARL-06-1C2	1275	0.0									
06/08/94	ARL-07-1D1	14302	2.0	2.07	1.63%	1.140942399			1.81	4.15	56.3%	
06/08/94	ARL-07-1D1	14473	2.1									
06/08/94	ARL-07-1D1	14350	2.1									
06/08/94	ARL-08-1D2	26583	2.7	2.67	1.99%				2.34			
06/08/94	ARL-08-1D2	26235	2.6									
06/08/94	ARL-08-1D2	26940	2.7									

Results of Quad Run 1, Methylene Diphenyl Diisocyanate

Date Analyze	Sample Name	Area Count	MDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 164.9 ug
06/21/94	ARL-17-3A1	455508	168.4	169.08	0.38%	0.981093798	0.34	168.74	0.35	169.09	0.0%	102%
06/21/94	ARL-17-3A1	457443	169.1									
06/21/94	ARL-17-3A1	458920	169.7									
06/21/94	ARL-18-3A2	0	0.0	0.00	NA				0.00			
06/21/94	ARL-18-3A2	0	0.0									
06/21/94	ARL-18-3A2	0	0.0									
06/21/94	ARL-19-3B1	457578	169.2	170.48	0.68%	0.992052418	0.34	170.14	0.35	170.48	0.0%	103%
06/21/94	ARL-19-3B1	461806	170.8									
06/21/94	ARL-19-3B1	463603	171.5									
06/21/94	ARL-20-3B2	0	0.0	0.00	NA				0.00			
06/21/94	ARL-20-3B2	0	0.0									
06/21/94	ARL-20-3B2	0	0.0									
06/21/94	ARL-21-3C1	4588	0.0	0.00	NA	0.980753996			0.00	0.00	0.0%	
06/21/94	ARL-21-3C1	5158	0.0									
06/21/94	ARL-21-3C1	5330	0.0									
06/21/94	ARL-22-3C2	0	0.0	0.00	NA				0.00			
06/21/94	ARL-22-3C2	0	0.0									
06/22/94	ARL-22-3C2	0	0.0									
06/22/94	ARL-23-3D1	10990	0.8	0.71	14.47%	1.028014813			0.69	0.69	0.0%	
06/22/94	ARL-23-3D1	10882	0.8									
06/22/94	ARL-23-3D1	10470	0.6									
06/22/94	ARL-24-3D2	0	0.0	0.00	NA				0.00			
06/22/94	ARL-24-3D2	0	0.0									
06/22/94	ARL-24-3D2	0	0.0									

Results of Quad Run 3, Methylene Diphenyl Diisocyanate

Date Analyze	Sample Name	Area Count	MDI ug	Average ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 164.9 ug
06/25/94	ARL-25-4A1	8634	0.0	0.00	NA	0.996186677			0.00	0.00	0.0%	
06/25/94	ARL-25-4A1	7494	0.0									
06/25/94	ARL-25-4A1	7727	0.0									
06/25/94	ARL-26-4A2	688	0.0	0.00	NA				0.00			
06/25/94	ARL-26-4A2	920	0.0									
06/25/94	ARL-26-4A2	2008	0.0									
06/25/94	ARL-27-4B1	552	0.0	0.00	NA	1.009523912			0.00	0.00	0.0%	
06/25/94	ARL-27-4B1	1413	0.0									
06/25/94	ARL-27-4B1	2347	0.0									
06/25/94	ARL-28-4B2	0	0.0	0.00	NA				0.00			
06/25/94	ARL-28-4B2	0	0.0									
06/25/94	ARL-28-4B2	1619	0.0									
06/26/94	ARL-29-4C1	457081	169.0	158.84	12.68%	0.99607341	0.00	158.84	0.00	158.84	0.0%	96%
06/26/94	ARL-29-4C1	368589	135.6									
06/26/94	ARL-29-4C1	464695	171.9									
06/26/94	ARL-30-4C2	4799	0.0	0.00	NA				0.00			
06/26/94	ARL-30-4C2	786	0.0									
06/26/94	ARL-30-4C2	0	0.0									
06/26/94	ARL-31-4D1	456978	169.0	166.60	1.58%	1.070178599	0.00	166.60	0.00	166.60	0.0%	101%
06/26/94	ARL-31-4D1	451982	167.1									
06/26/94	ARL-31-4D1	443181	163.8									
06/26/94	ARL-32-4D2	0	0.0	0.00	NA				0.00			
06/26/94	ARL-32-4D2	0	0.0									
06/26/94	ARL-32-4D2	0	0.0									

Results of Quad Run 4, Methylene Diphenyl Diisocyanate

Date Analyze	Sample Name	Area Count	MDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 164.9 ug
06/28/94	ARL-33-5A1	448157	165.6	166.25	0.32%	1.021332038	0.63	165.63	0.61	166.24	0.0%	100%
06/28/94	ARL-33-5A1	450647	166.6									
06/28/94	ARL-33-5A1	450565	166.5									
06/28/94	ARL-24-5A2	1241	0.0	0.00	NA				0.00			
06/28/94	ARL-34-5A2	0	0.0									
06/28/94	ARL-34-5A2	0	0.0									
06/28/94	ARL-35-5B1	446648	165.1	164.29	0.41%	1.03011026	0.63	163.66	0.61	164.28	0.0%	99%
06/28/94	ARL-35-5B1	443417	163.9									
06/28/94	ARL-35-5B1	443713	164.0									
06/28/94	ARL-36-5B2	888	0.0	0.00	NA				0.00			
06/28/94	ARL-36-5B2	931	0.0									
06/28/94	ARL-36-5B2	691	0.0									
06/29/94	ARL-37-5C1	12236	1.3	1.27	7.02%	1.036453234			1.22	1.22	0.0%	
06/29/94	ARL-37-5C1	12504	1.4									
06/29/94	ARL-37-5C1	12033	1.2									
06/29/94	ARL-38-5C2	0	0.0	0.00	NA				0.00			
06/29/94	ARL-38-5C2	0	0.0									
06/29/94	ARL-38-5C2	0	0.0									
06/29/94	ARL-39-5D1	0	0.0	0.00	NA	1.088499599			0.00	0.00	0.0%	
06/29/94	ARL-39-5D1	502	0.0									
06/29/94	ARL-39-5D1	615	0.0									
06/29/94	ARL-40-5D2	707	0.0	0.00	NA				0.00			
06/29/94	ARL-40-5D2	707	0.0									
06/29/94	ARL-40-5D2	704	0.0									

Results of Quad Run 5, Methylene Diphenyl Diisocyanate

Date Analyze	Sample	Area Count	MDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 164.9 ug
07/14/94	ARL-41-6A1	767	0.0	0.27	173.21%	1.031327885			0.26	0.26	0.0%	
07/14/94	ARL-41-6A1	11000	0.8									
07/14/94	ARL-41-6A1	1888	0.0									
07/14/94	ARL-42-6A2	703	0.0	0.00	NA				0.00			
07/14/94	ARL-42-6A2	850	0.0									
07/14/94	ARL-42-6A2	2434	0.0									
07/14/94	ARL-43-6B1	7649	0.0	0.00	NA	1.047949874			0.00	0.00	0.0%	
07/14/94	ARL-43-6B1	7699	0.0									
07/14/94	ARL-43-6B1	664	0.0									
07/14/94	ARL-44-6B2	3474	0.0	0.00	NA				0.00			
07/14/94	ARL-44-6B2	3954	0.0									
07/14/94	ARL-44-6B2	2863	0.0									
07/14/94	ARL-45-6C1	448275	165.7	169.26	1.93%	1.056020175	0.14	169.12	0.13	169.25	0.0%	103%
07/15/94	ARL-45-6C1	459759	170.0									
07/15/94	ARL-45-6C1	465248	172.1									
07/15/94	ARL-46-6C2	1538	0.0	0.00	NA				0.00			
07/15/94	ARL-46-6C2	7046	0.0									
07/15/94	ARL-46-6C2	1783	0.0									
07/15/94	ARL-47-6D1	433436	160.1	160.40	0.26%	1.107386936	0.14	160.26	0.13	160.38	0.0%	97%
07/15/94	ARL-47-6D1	433810	160.2									
07/15/94	ARL-47-6D1	435541	160.9									
07/15/94	ARL-48-6D2	6703	0.0	0.00	NA				0.00			
07/15/94	ARL-48-6D2	6931	0.0									
07/15/94	ARL-48-6D2	2350	0.0									

Results of Quad Run 6, Methylene Diphenyl Diisocyanate

Date Analyze	Sample	Area Count	MDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 164.9 ug
07/17/94	ARL-49-7A1	447074	165.2	166.00	1.26%	1.017027877	0.99	165.01	0.97	165.98	0.0%	100%
07/17/94	ARL-49-7A1	455390	168.4									
07/17/94	ARL-49-7A1	444885	164.4									
07/17/94	ARL-50-7A2	623	0.0	0.00	NA				0.00			
07/17/94	ARL-50-7A2	3211	0.0									
07/17/94	ARL-50-7A2	1558	0.0									
07/17/94	ARL-51-7B1	443641	163.9	160.58	3.16%	1.028071447	1.00	159.57	0.97	160.55	0.0%	97%
07/17/94	ARL-51-7B1	419255	154.7									
07/17/94	ARL-51-7B1	441294	163.1									
07/17/94	ARL-52-7B2	837	0.0	0.00	NA				0.00			
07/17/94	ARL-52-7B2	1444	0.0									
07/18/94	ARL-52-7B2	800	0.0									
07/18/94	ARL-53-7C1	9578	0.3	0.09	173.21%	1.066497409			0.08	0.08	0.0%	
07/18/94	ARL-53-7C1	5807	0.0									
07/18/94	ARL-53-7C1	8854	0.0									
07/18/94	ARL-54-7C2	964	0.0	0.00	NA				0.00			
07/18/94	ARL-54-7C2	678	0.0									
07/18/94	ARL-54-7C2	951	0.0									
07/18/94	ARL-55-7D1	13493	1.7	1.98	10.91%	1.062391466			1.87	1.87	0.0%	
07/18/94	ARL-55-7D1	14403	2.1									
07/18/94	ARL-55-7D1	14556	2.1									
07/18/94	ARL-56-7D2	836	0.0	0.00	NA				0.00			
07/18/94	ARL-56-7D2	835	0.0									
07/18/94	ARL-56-7D2	2936	0.0									

Results of Quad Run 7, Methylene Diphenyl Diisocyanate

Date Analyze	Sample	Area Count	MDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 164.9 ug
07/19/94	ARL-57-8A1	9268	0.1	0.05	173.21%	1.085214844			0.04	0.04	0.0%	
07/19/94	ARL-57-8A1	7985	0.0									
07/19/94	ARL-57-8A1	8814	0.0									
07/19/94	ARL-58-8A2	1091	0.0	0.00	NA				0.00			
07/19/94	ARL-58-8A2	1097	0.0									
07/19/94	ARL-58-8A2	720	0.0									
07/19/94	ARL-59-8B1	4387	0.0	0.00	NA	1.008985892			0.00	0.00	0.0%	
07/19/94	ARL-59-8B1	4057	0.0									
07/19/94	ARL-59-8B1	5457	0.0									
07/19/94	ARL-60-8B2	2824	0.0	0.00	NA				0.00			
07/19/94	ARL-60-8B2	3035	0.0									
07/19/94	ARL-60-8B2	1697	0.0									
07/20/94	ARL-61-8C1	450259	166.4	167.46	0.61%	1.018698571	0.02	167.43	0.02	167.46	0.0%	102%
07/20/94	ARL-61-8C1	455658	168.5									
07/20/94	ARL-61-8C1	453014	167.5									
07/20/94	ARL-62-8C2	2070	0.0	0.00	NA				0.00			
07/20/94	ARL-62-8C2	1153	0.0									
07/20/94	ARL-62-8C2	0	0.0									
07/20/94	ARL-63-8D1	415917	153.5	157.68	2.39%	1.045344724	0.02	157.66	0.02	157.68	0.0%	96%
07/20/94	ARL-63-8D1	430024	158.8									
07/20/94	ARL-63-8D1	435233	160.8									
07/20/94	ARL-64-8D2	1316	0.0	0.00	NA				0.00			
07/20/94	ARL-64-8D2	579	0.0									
07/20/94	ARL-64-8D2	1191	0.0									

Results of Quad Run 8, Methylene Diphenyl Diisocyanate

Date Analyze	Sample	Area Count	MDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 164.9 ug
07/21/94	ARL-65-9A1	440103	162.6	168.35	4.20%	1.010911438	0.88	167.47	0.87	168.34	0.0%	102%
07/21/94	ARL-65-9A1	449679	166.2									
07/21/94	ARL-65-9A1	476295	176.2									
07/21/94	ARL-66-9A2	1578	0.0	0.00	NA				0.00			
07/21/94	ARL-66-9A2	4866	0.0									
07/21/94	ARL-66-9A2	1237	0.0									
07/21/94	ARL-67-9B1	419305	154.8	156.72	1.66%	1.023625702	0.89	155.83	0.87	156.70	0.0%	94%
07/21/94	ARL-67-9B1	421905	155.7									
07/21/94	ARL-67-9B1	432345	159.7									
07/21/94	ARL-68-9B2	2213	0.0	0.00	NA				0.00			
07/21/94	ARL-68-9B2	1912	0.0									
07/22/94	ARL-68-9B2	3514	0.0									
07/22/94	ARL-69-9C1	4694	0.0	1.79	87.85%	1.025239762			1.75	1.75	0.0%	
07/22/94	ARL-69-9C1	15317	2.4									
07/22/94	ARL-69-9C1	16716	3.0									
07/22/94	ARL-70-9C2	3006	0.0	0.00	NA				0.00			
07/22/94	ARL-70-9C2	1744	0.0									
07/22/94	ARL-70-9C2	1185	0.0									
07/22/94	ARL-71-9D1	4375	0.0	0.00	NA	1.06253305			0.00	0.00	0.0%	
07/22/94	ARL-71-9D1	3971	0.0									
07/22/94	ARL-71-9D1	1329	0.0									
07/22/94	ARL-72-9D2	900	0.0	0.00	NA				0.00			
07/22/94	ARL-72-9D2	0	0.0									
07/22/94	ARL-72-9D2	4569	0.0									

Results of Quad Run 9, Methylene Diphenyl Diisocyanate

Date Analyze	Sample	Area Count	MDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 164.9 ug
07/27/94	ARL-73-10A1	16067	2.7	1.97	45.55%	1.019349858			1.93	1.93	0.0%	
07/27/94	ARL-73-10A1	14821	2.2									
07/27/94	ARL-73-10A1	11467	1.0									
07/27/94	ARL-74-10A2	2066	0.0	0.00	NA				0.00			
07/27/94	ARL-74-10A2	812	0.0									
07/27/94	ARL-74-10A2	1831	0.0									
07/27/94	ARL-75-10B1	10622	0.7	1.35	46.88%	1.024871643			1.32	1.32	0.0%	
07/27/94	ARL-75-10B1	12893	1.5									
07/27/94	ARL-75-10B1	13897	1.9									
07/27/94	ARL-76-10B2	7314	0.0	0.00	NA				0.00			
07/27/94	ARL-76-10B2	3759	0.0									
07/28/94	ARL-76-10B2	1899	0.0									
07/28/94	ARL-77-10C1	422744	156.1	161.23	3.01%	1.055397205	1.71	159.51	1.62	161.21	4.3%	97%
07/28/94	ARL-77-10C1	438331	161.9									
07/28/94	ARL-77-10C1	448301	165.7									
07/28/94	ARL-78-10C2	9100	0.0	0.08	173.21%				0.07			
07/28/94	ARL-78-10C2	10412	0.2									
07/28/94	ARL-78-10C2	8542	0.0									
07/28/94	ARL-79-10D1	444595	164.3	168.35	2.14%	1.059673048	1.72	166.62	1.62	168.25	0.0%	101%
07/28/94	ARL-79-10D1	458517	169.5									
07/28/94	ARL-79-10D1	462896	171.2									
07/28/94	ARL-80-10D2	1431	0.0	0.00	NA				0.00			
07/28/94	ARL-80-10D2	2005	0.0									
07/28/94	ARL-80-10D2	9026	0.0									

Results of Quad Run 10, Methylene Diphenyl Diisocyanate

Date Analyze	Sample	Area Count	MDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 164.9 ug
07/29/94	ARL-81-11A1	436933	161.4	162.69	0.69%	1.02014273	4.45	158.24	4.36	162.60	0.0%	96%
07/29/94	ARL-81-11A1	441668	163.2									
07/29/94	ARL-81-11A1	442406	163.5									
07/29/94	ARL-82-11A2	4084	0.0	0.00	NA				0.00			
07/29/94	ARL-82-11A2	4066	0.0									
07/29/94	ARL-82-11A2	6913	0.0									
07/29/94	ARL-83-11B1	433463	160.1	160.90	3.08%	1.034131252	4.51	156.38	4.36	160.75	0.0%	95%
07/29/94	ARL-83-11B1	423637	156.4									
07/29/94	ARL-83-11B1	449643	166.2									
07/29/94	ARL-84-11B2	2835	0.0	0.00	NA				0.00			
07/29/94	ARL-84-11B2	1306	0.0									
07/29/94	ARL-84-11B2	7486	0.0									
07/30/94	ARL-85-11C1	24540	5.9	3.93	86.60%	1.066157606			3.68	3.68	0.0%	
07/30/94	ARL-85-11C1	24500	5.9									
07/30/94	ARL-85-11C1	548	0.0									
07/30/94	ARL-86-11C2	729	0.0	0.00	NA				0.00			
07/30/94	ARL-86-11C2	1946	0.0									
07/30/94	ARL-86-11C2	1784	0.0									
07/30/94	ARL-87-11D1	22624	5.2	5.53	14.14%	1.095946929			5.05	5.05	0.0%	
07/30/94	ARL-87-11D1	25928	6.4									
07/30/94	ARL-87-11D1	22112	5.0									
07/30/94	ARL-88-11D2	1101	0.0	0.00	NA				0.00			
07/30/94	ARL-88-11D2	2213	0.0									
07/30/94	ARL-88-11D2	1310	0.0									

Results of Quad Run 11, Methylene Diphenyl Diisocyanate

Date Analyze	Sample	Area Count	MDI ug	Averag ug	%CV Injection	Dry Standard Meter (dscm)	Unspiked Normalize to Spike (ug)	Recovered Spike (ug)	Amount Normalized to 1 m3	Total Normalize (ug)	% Total in 2nd	% Recovery from target 164.9 ug
08/11/94	ARL-89-12A1	24114	5.7	5.07	17.78%	0.998197174			5.07	5.07	0.0%	
08/11/94	ARL-89-12A1	19610	4.0									
08/11/94	ARL-89-11A1	23248	5.4									
08/11/94	ARL-90-12A2	3236	0.0	0.00	NA				0.00			
08/11/94	ARL-90-12A2	3101	0.0									
08/11/94	ARL-90-12A2	1744	0.0									
08/11/94	ARL-91-12B1	20775	4.5	5.33	16.98%	1.029713824			5.18	5.18	0.0%	
08/11/94	ARL-91-12B1	22773	5.2									
08/11/94	ARL-91-12B1	25551	6.3									
08/11/94	ARL-92-12B2	599	0.0	0.00	NA				0.00			
08/11/94	ARL-92-12B2	6396	0.0									
08/11/94	ARL-92-12B2	922	0.0									
08/11/94	ARL-93-12C1	459168	169.8	169.91	0.31%	1.04636413	5.36	164.54	5.13	169.67	0.0%	100%
08/11/94	ARL-93-12C1	460974	170.5									
08/11/94	ARL-93-12C1	458277	169.5									
08/11/94	ARL-94-12C2	510	0.0	0.00	NA				0.00			
08/11/94	ARL-94-12C2	840	0.0									
08/12/94	ARL-94-12C2	3930	0.0									
08/12/94	ARL-95-12D1	453030	174.8	176.11	0.98%	1.043419178	5.35	170.76	5.13	176.14	4.8%	104%
08/12/94	ARL-95-12D1	481048	178.0									
08/12/94	ARL-95-12D1	474373	175.5									
08/12/94	ARL-96-12D2	2526	0.0	0.27	173.21%				0.26			
08/12/94	ARL-96-12D2	6440	0.0									
08/12/94	ARL-96-12D2	14293	0.8									

Results of Quad Run 12, Methylene Diphenyl Diisocyanate

APPENDIX D

SAMPLING METHOD FOR ISOCYANATES

METHOD XXX1

METHOD XXX1 - SAMPLING METHOD FOR ISOCYANATES

NOTE: This method is not inclusive with respect to specifications (e.g., equipment and supplies) and sampling procedures essential to its performance. Some material is incorporated by reference from other EPA methods. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following additional test methods found in 40 CFR Part 60: Method 1, Method 2, Method 3, and Method 5.

1.0 *Scope and Application.*

1.1 This method is applicable to the collection of isocyanate compounds from the emissions associated with manufacturing processes. The following is a list of the isocyanates and the manufacturing process at which the method has been evaluated:

Compound Name	CAS No.	Detection Limits (ng/m ³) ^a	Manufacturing Process
2,4-Toluene Diisocyanate (TDI)	584-84-9	106	Flexible Foam Production
1,6-Hexamethylene Diisocyanate (HDI)	822-06-0	396	Paint Spray Booth
Methylene Diphenyl Diisocyanate (MDI)	101-68-8	112	Pressed Board Production
Methyl Isocyanate (MI)	624-83-9	228	Not used in production

^a Estimated detection limits are based on a sample volume of 1 m³ and a 10 mL sample extraction volume.

2.0 *Summary of Method.*

2.1 Gaseous and/or aerosolized isocyanates are withdrawn from an emission source at an isokinetic sampling rate and are collected in a multicomponent sampling train. The primary components of the train include a heated probe, three impingers containing the derivatizing reagent in toluene, an empty impinger, an impinger containing charcoal and an impinger containing silica gel.

2.2 The collected samples are analyzed by high performance liquid chromatography (HPLC) as described in Method XXX2.

3.0 *Definitions.* Not Applicable.

4.0 *Interferences.*

4.1 The greatest potential for interference comes from an impurity in the derivatizing reagent, 1-(2-pyridyl)piperazine (1,2-PP). This compound may interfere with the resolution of MI from the peak attributed to unreacted 1,2-PP.

4.2 Other interferences that could result in positive or negative bias are (1) alcohols that could compete with the 1,2-PP for reaction with an isocyanate and (2) other compounds that may coelute with one or more of the derivatized isocyanates.

5.0 *Safety.*

5.1 The toxicity of each reagent has been precisely defined. Each isocyanate can produce dangerous levels of hydrogen cyanide (HCN). The exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational

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METHOD XXXI

Safety and Health Administration (OSHA) regulations regarding safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available.

6.0 *Equipment and Supplies.*

6.1 Sample Collection. The following items are required for sample collection:

6.1.1 A schematic of the sampling train used in this method is shown in Figure XXXI-1. This sampling train configuration is adapted from EPA Method 5 procedures, and, as such, the majority of the required equipment is identical to that used in EPA Method 5 determinations. The only new component required is a condenser coil.

6.1.2 Construction details for the basic train components are given in APTD-0581 (see Martin, 1971, in Section 16.0, References); commercial models of this equipment are also available. Additionally, the following subsections list changes to APTD-0581 and identify allowable train configuration modifications.

6.1.3 Basic operating and maintenance procedures for the sampling train are described in APTD-0576 (see Rom, 1972, in Section 16.0, References). As correct usage is important in obtaining valid results, all users should refer to APTD-0576 and adopt the operating and maintenance procedures outlined therein unless otherwise specified. The sampling train consists of the components detailed below.

6.1.3.1 Probe Nozzle. Glass with sharp, tapered (30° angle) leading edge. The taper shall be on the outside to preserve a constant internal diameter. The nozzle shall be buttonhook or elbow design. A range of nozzle sizes suitable for isokinetic sampling should be available in increments of 0.16 cm (1/16 in.), e.g., 0.32-1.27 cm (1/8-1/2 in.), or larger if higher volume sampling trains are used. Each nozzle shall be calibrated according to the procedures outlined in Paragraph 10.1.

6.1.3.2 Probe liner. Borosilicate or quartz-glass tubing with a heating system capable of maintaining a probe gas temperature of 120 ± 14 °C (248 ± 25 °F) at the exit end during sampling. (The tester may opt to operate the equipment at a temperature lower than that specified.) Because the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD-0581 and utilizing the calibration curves of APTD-0576 (or calibrated according to the procedure outlined in APTD-0576) are considered acceptable. Either borosilicate or quartz glass probe liners may be used for stack temperatures up to about 480°C (900 °F). Quartz glass liners shall be used for temperatures between 480 and 900°C (900 and 1650 °F). (The softening temperature for borosilicate is 820 °C (1508 °F), and for quartz glass 1500 °C (2732 °F).) Water-cooling of the stainless steel sheath will be necessary at temperatures approaching and exceeding 500°C.

6.1.3.3 Pitot tube. Type S, as described in Section 2.1 of promulgated EPA Method 2 (Section 6.1 of Reformatted Draft EPA Method 2), or other appropriate devices (see Vollaro, 1976 in Section 16.0, References). The pitot tube shall be attached to the probe to allow constant monitoring of the stack-gas velocity. The impact (high-pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see EPA Method 2, Figure 2-6b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 4.0 of promulgated EPA Method 2 (Section 10.0 of Reformatted Draft EPA Method 2).

6.1.3.4 Differential Pressure Gauge. Inclined manometer or equivalent device as described in Section 2.2 of promulgated EPA Method 2 (Section 10.0 of Reformatted Draft EPA Method 2). One manometer shall be used for velocity-head (ΔP) readings and the other for orifice differential pressure (ΔH) readings.

6.1.3.5 Impinger Train. Six 500 mL impingers are connected in series with leak-free ground-glass joints following immediately after the heated probe. The first impinger shall be of the Greenburg-Smith design with the standard tip. The remaining five impingers shall be of the modified Greenburg-Smith design, modified by replacing the tip with a 1.3-cm (1/2-in.) I.D. glass tube extending about 1.3 cm (1/2 in.) from the bottom of the outer cylinder. The first, second and third impingers shall contain known quantities of the derivatizing reagent in toluene with the first impinger containing 300 mL and 200 mL in the second and third. The fourth impinger remains empty. The fifth impinger is filled with a known amount (2/3 full) of activated charcoal and the sixth with a known amount of desiccant. A water jacketed condenser is placed between the outlet of the first impinger and the inlet to the second impinger to minimize the evaporation of toluene from the first impinger.

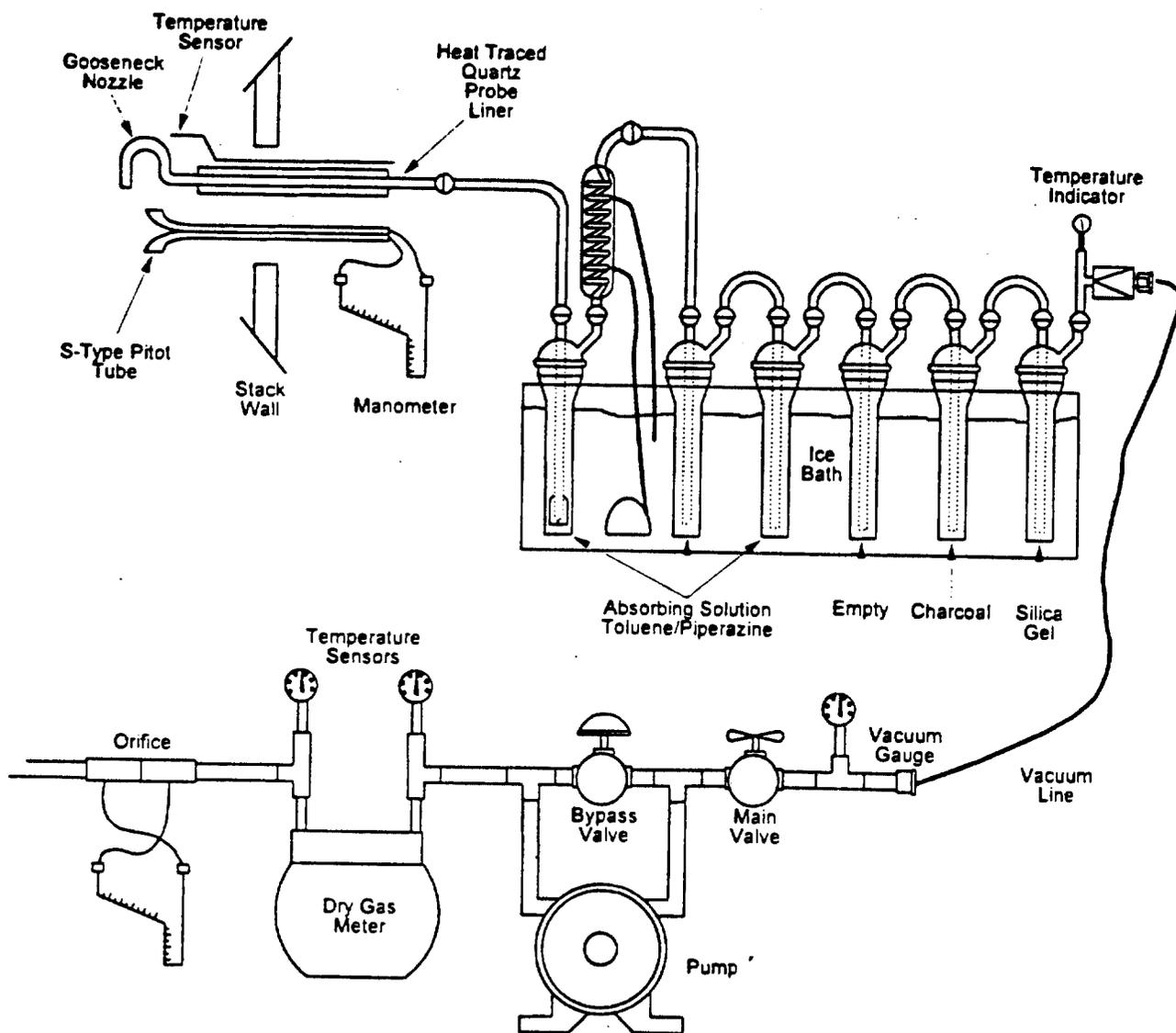


Figure XXX1-1. Isocyanate Sampling Train

METHOD XXX1

6.1.3.6 Metering System. The necessary components are a vacuum gauge, leak-free pump, temperature sensors capable of measuring temperature to within 3 °C (5.4 °F), dry-gas meter capable of measuring volume to within 1%, and related equipment, as shown in Figure XXX1-1. At a minimum, the pump should be capable of 4 cubic feet per minute (cfm) free flow, and the dry-gas meter should have a recording capacity of 0-999.9 cubic feet (cu ft) with a resolution of 0.005 cu ft. Other metering systems capable of maintaining sampling rates within 10% of isokineticity and of determining sample volumes to within 2% may be used. The metering system must be used in conjunction with a pitot tube to enable checks of isokinetic sampling rates. Sampling trains using metering systems designed for flow rates higher than those described in APTD-0581 and APTD-0576 may be used, provided that the specifications of this method are met.

6.1.3.7 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases the barometric reading may be obtained from a nearby National Weather Service station, in which case the station value (which is the absolute barometric pressure) is requested and an adjustment for elevation differences between the weather station and sampling point is applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30-m (100 ft) elevation increase (vice versa for elevation decrease).

6.1.3.8 Gas density determination equipment. Temperature sensor and pressure gauge (as described in Sections 2.3 and 2.4 of promulgated EPA Method 2 (Sections 6.3 and 6.4 of Reformatted Draft EPA Method 2)), and gas analyzer, if necessary (as described in EPA Method 3). The temperature sensor ideally should be permanently attached to the pitot tube or sampling probe in a fixed configuration such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see promulgated EPA Method 2, Figure 2-7 (Reformatted Draft EPA Method 2, Figure 2-4)). As a second alternative, if a difference of no more than 1% in the average velocity measurement is to be introduced, the temperature sensor need not be attached to the probe or pitot tube.

6.1.3.9 Calibration/Field-Preparation Record. A permanently bound laboratory notebook, in which duplicate copies of data may be made as they are being recorded, is required for documenting and recording calibrations and preparation procedures (i.e., silica gel tare weights, quality assurance/quality control check results, dry-gas meter, and thermocouple calibrations, etc.). The duplicate copies should be detachable and should be stored separately in the test program archives.

6.2 Sample Recovery. The following items are required for sample recovery:

6.2.1 Probe Liner. Probe and nozzle brushes; Teflon® bristle brushes with stainless steel wire or Teflon® handles are required. The probe brush shall have extensions constructed of stainless steel, Teflon®, or inert material at least as long as the probe. The brushes shall be properly sized and shaped to brush out the probe liner and the probe nozzle.

6.2.2 Wash Bottles. Three. Teflon® or glass wash bottles are recommended; polyethylene wash bottles should not be used because organic contaminants may be extracted by exposure to organic solvents used for sample recovery.

6.2.3 Glass Sample Storage Containers. Chemically resistant, borosilicate amber glass bottles, 500-mL or 1,000-mL. Bottles should be tinted to prevent action of light on sample. Screw-cap liners shall be either Teflon® or constructed to be leak-free and resistant to chemical attack by organic recovery solvents. Narrow-mouth glass bottles have been found to exhibit less tendency toward leakage.

6.2.4 Graduated Cylinder and/or Balances. To measure impinger contents to the nearest 1 mL or 1 g. Graduated cylinders shall have subdivisions not >2 mL. Laboratory balances capable of weighing to ±0.5 g or better are required.

6.2.5 Plastic Storage Containers. Screw-cap polypropylene or polyethylene containers to store silica gel and charcoal.

6.2.6 Funnel and Rubber Policeman. To aid in transfer of silica gel or charcoal to container (not necessary if silica gel is weighed in field).

6.2.7 Funnels. Glass, to aid in sample recovery.

6.3 Crushed Ice. Quantities ranging from 10-50 lb may be necessary during a sampling run, depending on ambient air temperature.

6.4 Stopcock Grease. The use of silicone grease is not permitted. Silicone grease usage is not necessary if screw-on connectors and Teflon® sleeves or ground-glass joints are used.

METHOD XXXI

7.0 *Reagents and Standards.*

7.1 *Sample Collection Reagents.*

7.1.1 **Charcoal.** Activated, 6-16 mesh. Used to absorb toluene vapors to prevent them from entering the metering device. Use once with each train and discard.

7.1.2 **Silica Gel.** Indicating type, 6-16 mesh. If previously used, dry at 175°C (350 °F) for 2 hours before using. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

7.1.3 **Impinger Solution.** The impinger solution is prepared in the laboratory by mixing a known amount of 1-(2-pyridyl) piperazine (purity 99.5+ %) in toluene (HPLC grade or equivalent). The actual concentration of 1,2-PP should be approximately four times the amount needed to ensure that the capacity of the derivatizing solution is not exceeded. This amount shall be calculated from the stoichiometric relationship between 1,2-PP and the isocyanate of interest and preliminary information about the concentration of the isocyanate in the stack emissions. A concentration of 130 ug/mL of 1,2-PP in toluene can be used as a reference point. This solution should be prepared in the laboratory, stored in a refrigerated area away from light, and used within ten days of preparation.

7.2 *Sample Recovery Reagents.*

7.2.1 **Toluene.** Distilled-in-glass grade is required for sample recovery and cleanup (see NOTE to 7.2.2 below).

7.2.2 **Acetonitrile.** Distilled-in-glass grade is required for sample recovery and cleanup.

NOTE: Organic solvents from metal containers may have a high residue blank and should not be used. Sometimes suppliers transfer solvents from metal to glass bottles; thus blanks shall be run prior to field use and only solvents with a low blank value (<0.001%) shall be used.

8.0 *Sample Collection, Preservation, Storage and Transport.*

8.1 Because of the complexity of this method, field personnel should be trained in and experienced with the test procedures in order to obtain reliable results.

8.2 *Preliminary Field Determinations.*

8.2.1 Select the sampling site and the minimum number of sampling points according to EPA Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and range of velocity heads using EPA Method 2. It is recommended that a leak-check of the pitot lines (see promulgated EPA Method 2, Section 3.1 (Reformatted Draft EPA Method 2, Section 8.1)) be performed. Determine the stack gas moisture content using EPA Approximation Method 4 or its alternatives to establish estimates of isokinetic sampling-rate settings. Determine the stack-gas dry molecular weight, as described in promulgated EPA Method 2, Section 3.6 (Reformatted Draft EPA Method 2, Section 8.6). If integrated EPA Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the sample run.

8.2.2 Select a nozzle size based on the range of velocity heads so that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of promulgated EPA Method 2 (Section 8.2 of Reformatted Draft EPA Method 2)).

8.2.3 Select a suitable probe liner and probe length so that all traverse points can be sampled. For large stacks, to reduce the length of the probe, consider sampling from opposite sides of the stack.

8.2.4 A typical sample volume to be collected is 1 dscm (35.31 dscf). The sample volume can be adjusted as necessitated by analytical detection limit constraints and/or estimated stack concentrations. A maximum limit should be determined to avoid exceeding the capacity of the reagent.

8.2.5 Determine the total length of sampling time needed to obtain the identified minimum volume by comparing the anticipated average sampling rate with the volume requirement. Allocate the same time to all traverse points defined by EPA Method 1. To avoid timekeeping errors, the length of time sampled at each traverse point should be an integer or an integer plus one-half min.

8.2.6 In some circumstances (e.g., batch cycles) it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas-sample volumes. In these cases, the Administrator's approval must first be obtained.

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8.3 Preparation of Sampling Train.

8.3.1 During preparation and assembly of the sampling train, keep all openings where contamination can occur covered with Teflon® film or aluminum foil until just prior to assembly or until sampling is about to begin.

8.3.2 Place 300 mL of the impinger absorbing solution in the first impinger and 200 mL each in the second and third impingers. The fourth impinger shall remain empty. The fifth and sixth impingers shall have 400 g of preweighed charcoal and 200-300 g of silica gel, respectively.

8.3.3 When glass probe liners are used, install the selected nozzle using a Viton®-A O-ring when stack temperatures are <260 °C (500 °F) and a woven glass-fiber gasket when temperatures are higher. See APTD-0576 (Rom, 1972) for details. Other connecting systems utilizing Teflon® ferrules may be used. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

8.3.4 Set up the train as shown in Figure XXX1-1. During assembly, do not use any silicone grease on ground-glass joints. Connect all temperature sensors to an appropriate potentiometer/display unit. Check all temperature sensors at ambient temperature.

8.3.5 Place crushed ice around the impingers.

8.3.6 Turn on the condenser coil coolant recirculating pump and begin monitoring the gas entry temperature. Ensure proper gas entry temperature before proceeding and again before any sampling is initiated. It is important that the gas entry temperature not exceed 50 °C (122 °F), thus minimizing the loss of toluene from the first impinger.

8.3.7 Turn on and set the probe heating systems at the desired operating temperatures. Allow time for the temperature to stabilize.

8.4 Leak-Check Procedures.

8.4.1 Pre-test leak-check.

8.4.1.1 Because the number of additional intercomponent connections in the train (over the EPA Method 5 Train) increases the possibility of leakage, a pre-test leak-check is required.

8.4.1.2 After the sampling train has been assembled, turn on and set the probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton® A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 381-mm Hg (15-in. Hg) vacuum. Leakage rates in excess of 4% of the average sampling rate or >0.00057 m³/min (0.020 cfm), whichever is less, are unacceptable.

NOTE: A lower vacuum may be used, provided that it is not exceeded during the test.

8.4.1.3 The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with the fine-adjust valve fully open and the coarse-adjust valve completely closed. Partially open the coarse-adjust valve and slowly close the fine-adjust valve until the desired vacuum is reached. Do not reverse direction of the fine-adjust valve; this will cause impinger contents to back up in the train. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak-check, as shown below, and start over.

8.4.1.4 When the leak-check is completed, first slowly remove the plug from the inlet to the probe. When the vacuum drops to 127 mm (5 in.) Hg or less, immediately close the coarse-adjust valve. Switch off the pumping system and reopen the fine-adjust valve. Do not reopen the fine-adjust valve until the coarse-adjust valve has been closed. This prevents the reagent in the impingers from being forced backward into the probe and silica gel from being entrained backward into the fifth impinger.

8.4.2 Leak-Checks During Sampling Run.

8.4.2.1 If, during the sampling run, a component change becomes necessary, a leak-check shall be conducted immediately after the interruption of sampling and before the change is made. The leak-check shall be done according to the procedure outlined in Paragraph 8.4.1, except that it shall be done at a vacuum greater than or equal to the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m³/min (0.020 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered. If a higher leakage rate is obtained, the tester shall void the sampling run.

NOTE: Any "correction" of the sample volume by calculation reduces the integrity of the pollutant concentration data generated and must be avoided.

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8.4.2.2 Immediately after a component change, and before sampling is reinitiated, a leak-check similar to a pre-test leak-check must also be conducted.

8.4.3 Post-Test Leak-Check.

8.4.3.1 A leak-check of the sampling train is mandatory at the conclusion of each sampling run. The leak-check shall be performed with the same procedures as those with the pre-test leak-check, except that it shall be conducted at a vacuum greater than or equal to the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m³/min (0.020 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate, correct the sample volume (as shown in Section 12.0 of this method), and consider the data obtained of questionable reliability, or void the sampling run.

8.5 Sampling-Train Operation.

8.5.1 During the sampling run, maintain an isokinetic sampling rate to within 10% of true isokinetic, unless otherwise specified by the Administrator.

8.5.2 For each run, record the data required on a data sheet such as the one shown in Figure XXX1-2. Be sure to record the initial dry-gas meter reading. Record the dry-gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made before and after each leak-check, and when sampling is halted. Take other readings indicated by Figure XXX1-2 at least once at each sample point during each time increment and additional readings when significant changes (20% variation in velocity-head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

8.5.3 Clean the stack access ports prior to the test run to eliminate the chance of collecting deposited material. To begin sampling, verify that the probe heating system is at the specified temperature, remove the nozzle cap, and verify that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point, with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations, are available. These nomographs are designed for use when the Type S pitot-tube coefficient is 0.84 ± 0.02 and the stack-gas equivalent density (dry molecular weight) is equal to 29 ± 4 . APTD-0576 details the procedure for using the nomographs. If the stack-gas molecular weight and the pitot-tube coefficient are outside the above ranges, do not use the nomographs unless appropriate steps (Shigehara, 1974, in Section 16.0, References) are taken to compensate for the deviations.

8.5.4 When the stack is under significant negative pressure (equivalent to the height of the impinger stem), take care to close the coarse-adjust valve before inserting the probe into the stack, to prevent the impinger solutions from backing into the probe. If necessary, the pump may be turned on with the coarse-adjust valve closed.

8.5.5 When the probe is in position, block off the openings around the probe and stack access port to prevent unrepresentative dilution of the gas stream.

8.5.6 Traverse the stack cross section, as required by EPA Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the access port, in order to minimize the chance of extracting deposited material.

8.5.7 During the test run, make periodic adjustments to keep the temperature of the condenser at the proper levels; add more ice and, if necessary, salt to maintain the temperature. Also, periodically check the level and zero of the manometer.

8.5.8 A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

8.5.9 At the end of the sample run, close the coarse-adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry-gas meter reading, and conduct a post-test leak-check. Also,

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leak-check the pitot lines as described in EPA Method 2. The lines must pass this leak-check in order to validate the velocity-head data.

8.5.10 Calculate percent isokineticity (see Section 12.8) to determine whether the run was valid or another test run should be performed.

8.6 Sample Recovery.

8.6.1 Preparation.

8.6.1.1 Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Allow the probe to cool. When the probe can be handled safely, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over the tip to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling down because this will create a vacuum in the train.

8.6.1.2 Before moving the sample train to the cleanup site, remove the probe from the sample train and cap the open outlet, being careful not to lose any condensate that might be present. Cap the impinger inlet. Remove the umbilical cord from the last impinger and cap the impinger.

8.6.1.3 Transfer the probe and the impinger/condenser assembly to the cleanup area. This area should be clean and protected from the weather to minimize sample contamination or loss.

8.6.1.4 Save a portion of all washing solutions (toluene/acetonitrile) used for cleanup as a blank. Transfer 200 mL of each solution directly from the wash bottle being used and place each in a separate, prelabeled glass sample container.

8.6.1.5 Inspect the train prior to and during disassembly and note any abnormal conditions.

8.6.2 Sample Containers.

8.6.2.1 Container No. 1. With the aid of an assistant, rinse the probe/nozzle first with toluene and then with acetonitrile by tilting and rotating the probe while squirting the solvent into the upper end of the probe so that all of the surfaces are wetted with solvent. When using these solvents insure that proper ventilation is available. Let the solvent drain into the container. If particulate is visible, use a Teflon® brush to loosen/remove the particulate and follow with a second rinse of each solvent. After weighing the contents of the first impinger, add it to container No. 1 along with the toluene and acetonitrile rinses of the impinger. (Acetonitrile will always be the final rinse.) If two liquid layers are present add both to the container. After all components have been collected in the container, seal the container, mark the liquid level on the bottle and add the proper label.

8.6.2.2 Container No. 2. After weighing the contents of the second, third and fourth impingers, add them to container No. 2 along with the toluene and acetonitrile rinses of the impingers, the condenser and all connecting glassware. After all components have been collected in the container, seal the container, mark the liquid level on the bottle and add the proper label.

8.6.3 The contents of the fifth and sixth impingers (charcoal and silica gel) can be discarded after they have been weighed.

8.6.4 Sample Preparation for Shipment. Prior to shipment, recheck all sample containers to ensure that the caps are well secured. Seal the lids with Teflon® tape. Ship all samples upright, packed in ice, using the proper shipping materials as prescribed for hazardous materials.

9.0 Quality Control.

9.1 Sampling. See EPA Manual 600/4-77-027b for Method 5 quality control.

9.1.1 Field Blanks. Field blanks must be submitted with the samples collected at each sampling site. The field blanks include the sample bottles containing aliquots of sample recovery solvents, and impinger solutions. At a minimum, one complete sampling train will be assembled in the field staging area, taken to the sampling area, and leak-checked at the beginning and end of the testing (or for the same total number of times as the actual test train). The probe of the blank train shall be heated during the sample test. The train will be recovered as if it were an actual test sample. No gaseous sample will be passed through the sampling train.

9.1.2 Reagent Blanks. An aliquot of toluene, acetonitrile and the impinger solution will be collected in the field as separate samples and returned to the laboratory for analysis to evaluate artifacts that may be observed in the actual samples.

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10.0 Calibration and Standardization.

NOTE: Maintain a laboratory log of all calibrations.

10.1 Probe Nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make measurements at three separate places across the diameter and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

10.2 Pitot Tube Assembly. The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Section 4 of promulgated EPA Method 2 (Section 10.1, Reformatted Draft EPA Method 2), or assigned a nominal coefficient of 0.84 if it is not visibly nicked, dented, or corroded and if it meets design and intercomponent spacing specifications.

10.3 Metering System.

10.3.1 Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576. Instead of physically adjusting the dry-gas meter dial readings to correspond to the wet-test meter readings, calibration factors may be used to correct the gas meter dial readings mathematically to the proper values. Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: Make a 10-min calibration run at 0.00057 m³/min (0.020 cfm); at the end of the run, take the difference of the measured wet-test and dry-gas meter volumes and divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m³/min (0.020 cfm).

10.3.2 After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single intermediate orifice setting (based on the previous field test). The vacuum shall be set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet-test meter and the inlet of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more than 5%, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576.

10.3.3 Leak-check of metering system. That portion of the sampling train from the pump to the orifice meter (see Figure XXX1-1) should be leak-checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13-18 cm (5-7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for 1 min. A loss of pressure on the manometer indicates a leak in the meter box. Leaks, if present, must be corrected.

NOTE: If the dry-gas-meter coefficient values obtained before and after a test series differ by >5%, either the test series shall be voided or calculations for test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

10.4 Probe Heater. The probe-heating system shall be calibrated before its initial use in the field according to the procedure outlined in APTD-0576. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used.

10.5 Temperature Sensors. Each thermocouple must be permanently and uniquely marked on the casing; all mercury-in-glass reference thermometers must conform to ASTM E-1 63 specifications. Thermocouples should be calibrated in the laboratory with and without the use of extension leads. If extension leads are used in the field, the thermocouple readings at ambient air temperatures, with and without the extension lead, must be noted and recorded. Correction is necessary if the use of an extension lead produces a change >1.5%.

10.5.1 Dry-gas meter thermocouples. For the thermocouples used to measure the temperature of the gas leaving the impinger train three-point calibration at ice-water, room-air, and boiling-water temperatures is necessary. Accept the thermocouples only if the readings at all three temperatures agree to $\pm 2^{\circ}\text{C}$ (3.6°F) with those of the absolute value of the reference thermometer.

10.5.2 Probe and stack thermocouples. For the thermocouples used to indicate the probe and stack temperatures, a three-point calibration at ice-water, boiling-water, and hot-oil-bath temperatures must be performed; it is recommended that room-air temperature be added, and that the thermometer and the thermocouple agree to

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within 1.5% at each of the calibration points. A calibration curve (equation) may be constructed (calculated) and the data extrapolated to cover the entire temperature range suggested by the manufacturer.

10.6 Barometer. Adjust the barometer initially and prior to each test series to agree to within ± 2.5 mm Hg (0.1 in. Hg) of the mercury barometer or the corrected barometric pressure value reported by a nearby National Weather Service Station (same altitude above sea level).

10.7 Balance. Calibrate the balance before each test series, using Class-S standard weights; the weights must be within $\pm 0.5\%$ of the standards, or the balance must be adjusted to meet these limits.

11.0 Procedures.

11.1 Sampling Operation. Follow the sampling procedure outlined in Section 8.5.

11.2 Analytical. See Method XXX2 - Analysis for Isocyanates by High Performance Liquid Chromatography (HPLC).

12.0 Data Analysis and Calculations.

12.1 Perform Calculations. Round off figures after the final calculation to the correct number of significant figures.

12.2 Nomenclature.

- A_n = Cross-sectional area of nozzle, m^2 (ft^2).
- B_{ws} = Water vapor in the gas stream, proportion by volume.
- C_d = Type S pitot tube coefficient (nominally 0.84 ± 0.02), dimensionless.
- I = Percent of isokinetic sampling.
- L_1 = Individual leakage rate observed during the leak-check conducted prior to the first component change m^3/min (cfm).
- L_a = Maximum acceptable leakage rate for a leak-check, either pre-test or following a component change; equal to $0.00057 m^3/min$ (0.020 cfm) or 4% of the average sampling rate, whichever is less.
- L_i = Individual leakage rate observed during the leak-check conducted prior to the " i " component change ($i = 1, 2, 3 \dots n$) m^3/min (cfm).
- L_p = Leakage rate observed during the post-test leak-check, m^3/min (cfm).
- M_d = Stack-gas dry molecular weight, g/g-mole (lb/lb-mole).
- M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
- P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).
- P_s = Absolute stack-gas pressure, mm Hg (in. Hg).
- P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
- R = Ideal gas constant, $0.06236 mm\ Hg \cdot m^3/K \cdot g \cdot mole$ ($21.85 in. Hg \cdot ft^3/R \cdot lb \cdot mole$).
- T_m = Absolute average dry-gas meter temperature, K ($^{\circ}R$).
- T_s = Absolute average stack-gas temperature, K ($^{\circ}R$).
- T_{std} = Standard absolute temperature, 293 K ($528^{\circ}R$).
- V_{lc} = Total volume of liquid collected in the impingers, and silica gel, mL.
- V_m = Volume of gas sample as measured by dry-gas meter, dscm (dscf).
- $V_{m(std)}$ = Volume of gas sample measured by the dry-gas meter, corrected to standard conditions, dscm (dscf).
- $V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).
- V_s = Stack-gas velocity, calculated by EPA Method 2, Equation 2-9, using data obtained from EPA Method 5, m/sec (ft/sec).
- γ = Dry-gas-meter calibration factor, dimensionless.
- ΔH = Average pressure differential across the orifice meter, mm H_2O (in. H_2O).
- ρ_w = Density of water, 0.9982 g/mL (0.002201 lb/mL).
- θ = Total sampling time, min.
- θ_1 = Sampling time interval from the beginning of a run until the first component change, min.
- θ_i = Sampling time interval between two successive component changes, beginning with the interval between the first and second changes, min.

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- θ_p = Sampling time interval from the final (n^{th}) component change until the end of the sampling run, min.
 13.6 = Specific gravity of mercury.
 60 = sec/min.
 100 = Conversion to percent.

12.3 Average Dry-Gas-Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure XXX1-2).

12.4 Dry-Gas Volume. Correct the sample measured by the dry-gas meter to standard conditions (20 °C, 760 mm Hg [68 °F, 29.92 in. Hg]) by using Equation XXX1-1:

$$V_{m(\text{std})} = V_m \gamma \frac{T_{\text{std}}}{T_m} \frac{P_{\text{bar}} + \Delta H/13.6}{P_{\text{std}}} = K_1 V_m \gamma \frac{P_{\text{bar}} + \Delta H/13.6}{T_m} \quad \text{Eq. XXX1-1}$$

where:

$$\begin{aligned}
 K_1 &= 0.3853 \text{ K/mm Hg for metric units, or} \\
 K_1 &= 17.64 \text{ °R/in. Hg for English units.}
 \end{aligned}$$

It should be noted that Equation XXX1-1 can be used as written, unless the leakage rate observed during any of the mandatory leak-checks (i.e., the post-test leak-check or leak-checks conducted prior to component changes) exceeds L_s . If L_p or L_i exceeds L_s , Equation XXX1-1 must be modified as follows:

- a. Case I (no component changes made during sampling run): Replace V_m in Equation XXX1-1 with the expression:

$$V_m - (L_p - L_s) \theta$$

- b. Case II (one or more component changes made during the sampling run): Replace V_m in Equation XXX1-1 by the expression:

$$V_m - (L_i - L_s) \theta_i - \sum_{i=2}^N (L_i - L_s) \theta_i - (L_p - L_s) \theta_p$$

and substitute only for those leakage rates (L_i or L_p) that exceed L_s .

12.5 Volume of Water Vapor Condensed.

$$V_{w(\text{std})} = V_{1c} \frac{P_w}{M_w} \frac{RT_{\text{std}}}{P_{\text{std}}} = K_2 V_{1c} \quad \text{Eq. XXX1-2}$$

where:

$$\begin{aligned}
 K_2 &= 0.001333 \text{ m}^3/\text{ml for metric units, or} \\
 K_2 &= 0.04707 \text{ ft}^3/\text{ml for English units.}
 \end{aligned}$$

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12.6 Moisture Content.

$$B_{ws} = \frac{V_{w(sd)}}{V_{m(sd)} + V_{w(sd)}} \quad \text{Eq. XXX1-3}$$

NOTE: In saturated or water-droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation XXX1-3) and a second from the assumption of saturated conditions. The lower of the two values of B_{ws} shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in the NOTE to Section 1.2 of promulgated EPA Method 4 (Section 4.0 of Reformatted Draft EPA Method 4). For the purposes of this method, the average stack-gas temperature may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is ± 1 °C (2 °F).

12.7 Conversion Factors.

<u>From</u>	<u>To</u>	<u>Multiply by</u>
scf	m ³	0.02832
g/ft ³	gr/ft ³	15.43
g/ft ³	lb/ft ³	2.205 x 10 ⁻³
g/ft ³	g/m ³	35.31

12.8 Isokinetic Variation.

12.8.1 Calculation From Raw Data.

$$I = \frac{100 T_s [K_3 V_{ic} + (V_m \gamma / T_m) (P_{bw} + \Delta H / 13.6)]}{60 \theta V_s P_s A_s} \quad \text{Eq. XXX1-4}$$

where:

$$K_3 = 0.003454 \text{ mm Hg} \cdot \text{m}^3 / \text{mL} \cdot \text{K} \text{ for metric units, } \gamma$$

$$K_3 = 0.002669 \text{ in. Hg} \cdot \text{ft}^3 / \text{mL} \cdot \text{°R} \text{ for English units.}$$

12.8.2 Calculation For Intermediate Values.

$$I = \frac{T_s V_{m(sd)} P_{std} 100}{T_{std} V_s \theta A_s P_s 60 (1 - B_{ws})} \quad \text{Eq. XXX1-5}$$

$$= K_4 \frac{T_s V_{m(sd)}}{P_s V_s A_s \theta (1 - B_{ws})}$$

where:

$$K_4 = 4.320 \text{ for metric units, or}$$

$$K_4 = 0.09450 \text{ for English units.}$$

12.8.3 Acceptable Results. If $90\% \leq I \leq 110\%$, the results are acceptable. If the results are low in comparison with the standard and I is beyond the acceptable range, or if I is less than 90%, the Administrator may opt to accept the results.

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12.9 Concentration of Any Given Isocyanate in the Gaseous Emissions.

1. Multiply the concentration of the isocyanate as determined in Method XXX2 by the final concentration volume, typically 10 mL.

$$C_{\text{isocyanate}} \times \text{sample volume (mL)} = \text{amount } (\mu\text{g}) \text{ of isocyanate in sample} \quad \text{Eq. XXX1-6}$$

where:

$$C_{\text{isocyanate}} = \text{concentration of isocyanate as analyzed by Method XXX2 } (\mu\text{g/mL}).$$

2. Sum the amount of isocyanate found in all samples associated with a single train.

$$\text{Total } (\mu\text{g}) = \text{Container No. 1 } (\mu\text{g}) + \text{Container No. 2 } (\mu\text{g}) \quad \text{Eq. XXX1-7}$$

3. Divide the total μg found by the volume of stack gas sampled (m^3).

$$(\text{Total } \mu\text{g}) / (\text{train sample volume}) = \text{concentration of isocyanate } (\mu\text{g}/\text{m}^3) \quad \text{Eq. XXX1-8}$$

13.0 Method Performance.

13.1 Method Performance Evaluation. Evaluation of analytical procedures for a selected series of compounds must include the sample-preparation procedures and each associated analytical determination. The analytical procedures should be challenged by the test compounds spiked at appropriate levels and carried through the procedures.

13.2 Method Detection Limit. The overall method detection limits (lower and upper) must be determined on a compound-by-compound basis because different compounds may exhibit different collection, retention, and extraction efficiencies as well as the instrumental minimum detection limit (MDL). The method detection limit must be quoted relative to a given sample volume. The upper limits for the method must be determined relative to compound retention volumes (breakthrough). Method Detection Limits may vary due to matrix effects and instrument conditions.

13.3 Method Precision and Bias. The overall method precision and bias must be determined on a compound-by-compound basis at a given concentration level. The method precision value would include a combined variability due to sampling, sample preparation, and instrumental analysis. The method bias would be dependent upon the collection, retention, and extraction efficiency of the train components. From evaluation studies to date using a dynamic spiking system, acceptable method biases (per EPA Method 301) have been determined for all four isocyanates. A precision of less than 10% relative standard deviation (RSD) has been calculated from field test data sets which resulted from a series of paired, unspiked and spiked trains.

14.0 *Pollution Prevention.* Not Applicable.

15.0 *Waste Management.* Not Applicable.

16.0 *References.*

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2. Rom, J.J., Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment, Research Triangle Park, NC, U.S. Environmental Protection Agency, March 1972, PB-209 022/BE, APTD-0576, 39 pp.
3. Schlickerieder, L.M., Adams, J.W., and Thrun, K.E., Modified Method 5 Train and Source Assessment Sampling System: Operator's Manual, U.S. Environmental Protection Agency, EPA/600/8-85/003 (1985).
4. Shigehara, R.T., Adjustments in the EPA Nomograph for Different Pitot Tube Coefficients and Dry Molecular Weights, Stack Sampling News, 2:4-11 (October 1974).
5. U.S. Environmental Protection Agency, 40 CFR Part 60, Appendix A, Methods 1-5.

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6. Vollaro, R.F., A Survey of Commercially Available Instrumentation for the Measurement of Low-Range Gas Velocities, Research Triangle Park, NC, U.S. Environmental Protection Agency, Emissions Measurement Branch, November 1976 (unpublished paper).

17.0 *Tables, Diagrams, Flowcharts, and Validation Data.* Not Applicable.

APPENDIX E

ANALYSIS METHOD FOR ISOCYANATES

METHOD XXX2

METHOD XXX2 - ANALYSIS FOR ISOCYANATES BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

1.0 *Scope and Application.*

1.1 Method XXX2 covers the determination of derivatized isocyanates collected by Method XXX1 - Sampling Method for Isocyanates.

Compound Name	CAS No.	Limit of Quantitation ^a
2,4-Toluene Diisocyanate (TDI)	584-84-9	0.036 µg/mL
1,6-Hexamethylene Diisocyanate (HDI)	822-06-0	0.132 µg/mL
Methylene Diphenyl Diisocyanate (MDI)	101-68-8	0.036 µg/mL
Methyl Isocyanate (MI)	624-83-9	NA ^b

^aThe limit of quantitation is for the instrument conditions given in Section 11.5.1 at the 95% confidence level for seven replicate injections.

^bThe limit of quantitation for MI has not been determined.

1.2 This method is restricted to use by, or under the supervision of, analysts experienced in the use of chromatography and in the interpretation of chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 *Summary of Method.*

2.1 The impinger contents from Method XXX1 are concentrated to dryness under vacuum, brought to volume with acetonitrile (ACN) and analyzed by HPLC.

3.0 *Definitions.* Not Applicable.

4.0 *Interferences.*

4.1 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. All of these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by preparing and analyzing laboratory method (or reagent) blanks.

4.1.1 Glassware must be cleaned thoroughly before using. The glassware should be washed with laboratory detergent in hot water followed by rinsing with tap water and distilled water. The glassware may be cleaned by baking in a glassware oven at 400 °C for at least one hour. After the glassware has cooled, the glassware should be rinsed three times with methylene chloride and three times with acetonitrile. Volumetric glassware should not be heated to 400 °C. Rather, after washing and rinsing, volumetric glassware may be rinsed with ACN followed by methylene chloride and allowed to dry in air.

4.1.2 The use of high purity reagents and solvents helps to minimize interference problems in sample analysis.

5.0 *Safety.*

5.1 The toxicity of each reagent has been precisely defined. Each isocyanate can produce dangerous levels of hydrogen cyanide (HCN). The exposure to these chemicals must be reduced to the lowest possible level by

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whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available.

6.0 *Equipment and Supplies.*

- 6.1 Rotary Evaporator. Buchii Model EL-130 or equivalent.
- 6.2 1000 ml round bottom flask for use with rotary evaporator.
- 6.3 Separatory Funnel. 500 mL or larger, with Teflon® Stopcock.
- 6.4 Glass Funnel. Short stemmed or equivalent.
- 6.5 Vials. 15 mL capacity with Teflon® lined caps.
- 6.6 Class A Volumetric Flasks. 10 mL for bringing sample to volume after concentration.
- 6.7 Filter Paper. Scientific Products Grade 370 Qualitative or equivalent.
- 6.8 Buchner Funnel. Porcelain with 100 mm ID or equivalent.
- 6.9 Erlenmeyer Flask. 500 mL with side arm and vacuum source.
- 6.10 HPLC with at least a binary pumping system capable of a programmed gradient.
- 6.11 Column. Alltech Altima C18, 250 mm x 4.6 mm ID, 5µm particle size (or equivalent).
- 6.12 Guard Column. Alltech Hypersil ODS C18, 10 mm x 4.6 mm ID, 5µm particle size (or equivalent).
- 6.13 UV detector at 254 nm.
- 6.14 Data system for measuring peak areas and retention times.

7.0 *Reagents and Standards.*

7.1 Reagent grade chemicals should be used in all tests. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

- 7.2 Toluene, C₆H₅CH₃. HPLC Grade or equivalent.
- 7.3 Acetonitrile, CH₃CN (ACN). HPLC Grade or equivalent.
- 7.4 Methylene Chloride, CH₂CL₂. HPLC Grade or equivalent.
- 7.5 Hexane, C₆H₁₄. Pesticide Grade or equivalent.
- 7.6 Water, H₂O. HPLC Grade or equivalent.
- 7.7 Ammonium Acetate, CH₃CO₂NH₄.
- 7.8 Acetic Acid (glacial), CH₃CO₂H.
- 7.9 1-(2-Pyridyl)piperazine, (1.2-pp). Aldrich, 99.5+% or equivalent.
- 7.10 Absorption Solution. Prepare a solution of 1-(2-pyridyl)piperazine in toluene at a concentration of 40 mg/300 mL. This solution is used for method blanks and method spikes.
- 7.11 Ammonium Acetate Buffer Solution (AAB). Prepare a solution of ammonium acetate in water at a concentration of 0.1 M by transferring 7.705 g of ammonium acetate to a 1000 mL volumetric flask and diluting to volume with HPLC Grade water. Adjust pH to 6.2 with glacial acetic acid.

8.0 *Sample Collection, Preservation, Storage, and Transport.*

8.1 The components from Method XXX1 must be stored at 4°C between the time of sampling and concentration. Each sample should be extracted and concentrated within 30 days after collection and analyzed within 30 days after extraction. The extracted sample must be stored at 4°C.

9.0 *Quality Control.*

- 9.1 The correlation coefficient for the calibration curve must be 0.995 or greater. If the correlation coefficient is less than 0.995, the HPLC system should be examined for problems, and a new calibration curve should be prepared and analyzed.
- 9.2 A solvent blank should be analyzed daily to verify that the system is not contaminated.
- 9.3 A calibration standard should be analyzed prior to any samples being analyzed, after every 10 injections and at the end of the sample set. Samples must be bracketed by calibration standards that have a response that does

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not vary by more than 10% of the target value. If the calibration standards are outside the limit, the samples must be reanalyzed after it is verified that the analytical system is in control.

9.4 A method blank should be prepared and analyzed for every 10 samples concentrated (Section 11.4).

9.5 A method spike should be prepared and analyzed for every 20 samples. The response for each analyte should be within 20% of the expected theoretical value of the method spike (Section 11.3).

10.0 Calibration and Standardization.

10.1 Establish the retention times for each of the isocyanates of interest using the chromatographic conditions provided in Section 11.5.1. The retention times provided in Table 11.5.1-1 are provided as a guide to relative retention times. Prepare derivatized calibration standards (concentrations expressed in terms of the free isocyanate, Section 12.1) according to the procedure in Section 10.1.1. Calibrate the chromatographic system using the external standard technique (Section 10.1.2)

10.1.1 Preparation of calibration standards. Prepare a 100 µg/mL stock solution of the isocyanates of interest from the individual urea as prepared in Sections 11.1.1 and 11.1.2. This is accomplished by dissolving 1 mg of each urea in 10 mL of ACN. Calibration standards are prepared from this stock solution by making appropriate dilutions of aliquots of the stock into ACN. Calibrate the instrument from 1 to 20 µg/mL for HDI, TDI and MDI, and from 1 to 80 µg/mL for MI using at least six calibration points.

10.1.2 External standard calibration procedure. Analyze each derivatized calibration standard using the chromatographic conditions listed in Section 11.5.1 and tabulate peak area against concentration injected.

The working calibration curve must be verified on each working day by the measurement of one or more calibration standards. If the response for any analyte varies from the target response by more than 10%, the test must be repeated using a fresh calibration standard(s) after it is verified that the analytical system is under control. Alternatively, a new calibration curve may be prepared for that compound.

11.0 Procedures.

11.1 Preparation of isocyanate derivatives.

11.1.1 HDI, TDI, MDI.

11.1.1.1 Dissolve 500 mg of each isocyanate in individual 100 mL aliquots of MeCl₂, except for MDI which requires 250 mL of MeCl₂. Transfer a 5 mL aliquot of 1,2-pp (see Section 7.10) to each of the solutions, stir and allow to stand overnight at room temperature. Transfer 150 mL aliquots of hexane to each of the solutions to precipitate the isocyanate-urea. Using a Buchner funnel, vacuum filter the solid-urea and wash with 50 mL of hexane. Dissolve the precipitate in a minimum aliquot of MeCl₂. Repeat the hexane precipitation and filtration twice. After the third filtration, dry the crystals at 50 °C and transfer to bottles for storage. The crystals are stable for at least 21 months when stored at room temperature in a closed container.

Table 11.1.1-1

Molecular Weight of the Free Isocyanates
and the Isocyanate-Urea

Analyte	MW (Free Isocyanate)	MW (Derivative)
1,6-HDI	168	494.44
2,4-TDI	174.16	500.56
MDI	250.25	576.65

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$K = 35.31 \text{ ft}^3/\text{m}^3$ if $V_{m(n\theta)}$ is expressed in English units.

$= 1.00 \text{ m}^3/\text{m}^3$ if $V_{m(n\theta)}$ is expressed in metric units.

$V_{m(n\theta)}$ = Volume of gas sample as measured by a dry gas meter;
corrected to standard conditions, dscm (dscf).

13.0 Method Performance.

13.1 Method detection limit (MDL) concentrations were obtained by determining the standard deviation of the area count for seven replicate injections and then multiplying the standard deviation for seven replicate injections by the student's t-value at the 95% confidence level (3.143).

13.2 This method has been tested for linearity over the range from 2 x MDL to 500 x MDL.

14.0 *Pollution Prevention.* Not Applicable.

15.0 *Waste Management.* Not Applicable.

16.0 *References.* Not Applicable.

17.0 *Tables, Diagrams, Flowcharts, and Validation Data.* Not Applicable.

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