

Field Test and Validation of a Source Test Method for Methylene Diphenyl Diisocyanate

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ABSTRACT

Four isocyanates are listed for regulation in the Clean Air Act Amendments of 1990: hexamethylene-1,6 diisocyanate, methylene diphenyl diisocyanate, and 2,4-toluene diisocyanate, each of which is used in the production of polymers, and methyl isocyanate which is an intermediate in the manufacture of insecticides, such as Sevin® dust.

To support projected regulations, a study is under way to develop a source sampling and analysis method for the four pollutants cited above. In the procedure under development, the isocyanates are collected in a modified Method 5 sampling train and stabilized with a derivatizing reagent, 1-(2-pyridyl)piperazine in toluene. Derivatized samples are then returned to the laboratory and analyzed by High Performance Liquid Chromatography with UV detection (HPLC-UV). An isocyanate generator was developed in the laboratory to provide isocyanate atmospheres for optimization of sampling parameters and chromatographic conditions. The accuracy and precision of the method is determined in the field using train spiking and multiprobe sampling techniques, following the procedures outlined in EPA Method 301.

A field test of the isocyanate method, following EPA Method 301 procedures, was performed at a pressed board manufacturing facility. Results were excellent, with an overall analyte spike recovery of $92.2 \pm 6.5 \%$. The method's limit of quantitation (LOQ) was determined to be 366 ng of MDI/m³.

INTRODUCTION

A class of compounds identified as isocyanates are contained in the list of 189 pollutants to be regulated by the Environmental Protection Agency under Title III of the Clean Air Act Amendments¹ (CAAA) of 1990. There are four isocyanates of interest in the CAAA; methyl isocyanate (MI), hexamethylene 1,6- diisocyanate (HDI), methylene diphenyl diisocyanate (MDI), and 2,4-toluene diisocyanate (TDI).

Isocyanates are used extensively throughout industry. A few examples of their use are in the production of flexible foam products, synthetic rubber products, insecticides, enamel wire coatings,

and in the pressed board industry. Methylene diphenyl diisocyanate is used in industry as an intermediate in the production of polyurethane elastomers, polyurethane lacquer coatings, thermoplastic polyurethane resins, and in the pressed board industry as a constituent in a phenol/formaldehyde binder. Because of their widespread use, isocyanates possess the potential to affect many who are sensitive to this class of chemical compounds. Some of the adverse physiological effects associated with exposure to isocyanates are severe skin and eye irritations, eczema, nausea, and bronchial asthma.² The 1991 OSHA Permissible Exposure Limit (PEL) for MDI is listed at 0.02 ppm and the IDLH Level (Immediately Dangerous to Life and Health) is 10 ppm.³

Several critical problems exist when sampling for isocyanates. They polymerize in the presence of concentrated alkaline compounds, react with water and alcohols, discolor upon exposure to sunlight, and form toxic gases, such as carbon monoxide and hydrogen cyanide, upon decomposition. Consequently, isocyanates must be collected rapidly and stabilized immediately with a derivatizing reagent to insure sample integrity.

The EPA's Source Methods Research Branch, in the Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, North Carolina through a contract with Radian Corporation, Research Triangle Park, NC, has developed a method for the collection, identification, and measurement of two of the isocyanates of interest; 2,4-toluene diisocyanate and methylene diphenyl diisocyanate. TDI collection and analysis was the subject of a previous EPA/AWMA presentation⁴.

In both the TDI and MDI methods, samples are collected at the source using a modification of the EPA Method 5 sampling train (without the in-line filter). Stack gas is withdrawn at a flow rate of 0.5 ft³/min. for approximately sixty minutes through a heated, glass-lined probe and into two impingers containing a solution of the derivatizing reagent, 1-(2-pyridyl)piperazine in toluene [1,2PP]. The first impinger is fitted with a water-cooled condenser on the outlet of the impinger to minimize carryover of the organic solvent into the second impinger. MDI reacts with the derivatizing reagent [1,2PP] to form a stable MDI/urea derivative. When sampling is completed, the probe and connecting glassware are rinsed with toluene and acetonitrile and the rinses are saved for laboratory analysis. Each impinger solution (MDI/urea derivative) is recovered separately and saved for laboratory analysis. All samples are stored in a cooler at 0 to 4° C until returned to the laboratory for analysis by HPLC-UV detection. Quantitation is by a standards/retention time comparison procedure.

EXPERIMENTAL

Laboratory Evaluation

The laboratory study was initially set up to meet seven objectives for the four isocyanates of interest. However, budget constraints required the focus of the study to be limited to two of the isocyanates of interest (TDI and MDI). As mentioned earlier, TDI was the subject of the initial laboratory and field test work. This presentation describes the next phase of the study, the laboratory evaluation and field test of MDI. Seven objectives were planned for the isocyanates of interest and are listed in Table 1. All seven objectives were met for TDI and MDI. Although the focus was limited to TDI and MDI, some of the objectives were met for MI and HDI and are also

listed in Table 1.

Derivative Formation

Efforts to form a stable isocyanate/urea derivative for all four isocyanates, using ethanol as the derivatizing reagent were only marginally successful. Solid derivatives for MDI, HDI, and TDI were obtained, but formation of a derivative for MI was unsuccessful. Chromatograms for derivatized and underivatized isocyanates were compared. Since no chromophore existed for MI or HDI no chromatographic peaks were observed for MI or HDI, either derivatized or underivatized. However, peaks were easily detected for TDI and MDI. Based upon the results and a desire to find a method applicable to all four of the isocyanates of interest, ethanol was eliminated from consideration as a derivatizing agent.

In previous work, Goldberg⁵ and associates used a secondary amine, 1-(2-pyridyl)piperazine as the derivatizing agent while collecting ambient air samples in midget impingers. Since no current source method for isocyanates exists, 1-(2-pyridyl)piperazine was investigated as a possible alternative for ethanol as a derivatizing reagent. Using 1,2PP as the derivatizing reagent resulted in the formation of derivatives for all of the isocyanates of interest. Approximately 0.2 grams of TDI, HDI, MDI was added to separate solutions of 0.3 mL of 1,2PP in 10 mL of acetonitrile (ACN). The solutions were allowed to stand for 24 hours to insure enough time for the reaction to take place. Each solid derivative was then recovered by filtration, rinsed with 150 mL of distilled water and allowed to air dry before being redissolved with acetonitrile and brought to a standardized volume prior to analysis by HPLC. A derivative for the MI was prepared by transferring 100 μ L of MI to 1 mL of ACN and adding 300 μ L of 1,2PP. The solution was shaken for five minutes and then diluted 1:1000 for analysis by HPLC. A 1,2PP solution was prepared as previously mentioned for blank analysis on the HPLC. Also, a solution of the 1,2PP with HDI, MDI, and TDI was prepared to determine the retention time of each derivative. Calibration of the standards was shown to be linear over the operating range of 1 μ g/mL to 48 μ g/mL of the isocyanate derivatives. The results were excellent, demonstrating that a mixture of the three isocyanates could be analyzed with good chromatographic separation and quantitation (see Figure 1).

Isocyanate Generator

An isocyanate atmosphere generator was constructed to provide a source of isocyanates for testing within the laboratory. It was expected that this generator would be applicable to all four of the isocyanates listed in the CAAA, but for the reasons explained earlier the generator was tested only for TDI. The generator test for TDI and the TDI field test confirmed the method's applicability to isocyanate testing and a field test for MDI collection was scheduled.

METHOD VALIDATION

A field test of the method was performed in September, 1993, at a pressed board manufacturing facility, which used MDI as a constituent in the binder for the pressed board process. A modified Method 5 sampling train (with a water-cooled condenser on the outlet of the first impinger) was used to collect source gas from the plant's process stack (see Figure 2). The sample gas stream was passed through a heated glass-lined/stainless steel probe and through two impingers containing

the 1,2PP absorbing solution, one empty impinger (carryover trap), one silica gel impinger, and one impinger containing charcoal (to trap any organic vapors). **Note: any use of stopcock grease while sampling will cause problems during sampling (i.e., foaming of the absorbing solution).** Sampling was performed both isokinetically (0.75 ft³/min) and non-isokinetically (0.5 ft³/min) for 60 minutes. Non-isokinetic sampling was performed in addition to isokinetic sampling to determine the method's collection efficiency in sampling an aerosol source under both conditions. The data in Tables 2 and 3 indicate that for this source, there was no significant difference in the data collected. Two of the sampling trains for each quadruplicate run (as per EPA Method 301 requirements) were spiked with an MDI derivatized standard (MDI/urea derivative in ACN, which was equivalent to 651 µg of underivatized MDI). This was twice the amount of MDI, as indicated by the presurvey, that we could expect to collect in sixty minutes of sampling. Impingers and other glassware used in the sampling train were rinsed first with toluene and then with ACN. Probe rinse and associated glassware rinses were combined with the contents of the first impinger for subsequent analysis by HPLC-UV. Toluene/acetonitrile rinses from the condenser and second and third impingers were also combined for HPLC analysis. Samples were kept on ice at 0 to 4° C until returned to the laboratory.

Operating parameters for the HPLC were as follows:

Instrument:	Rainin HPXL delivery system with Waters 710B WISP autosampler.
Data System:	Nelson 2600 (1 volt)
Column:	Zorbax ODS (4.6 mm ID x 25 cm)
Mobile Phase:	ACN/0.1M ammonium acetate buffer
Gradient:	25:75 ACN/0.1M ammonium acetate buffer, pH 6.2, hold 2 min, then to 60:40 ACN/0.1M ammonium acetate buffer for 19.5 min.
Detector Wavelength:	254 nm
Flow Rate:	2 mL/min.

Results from the field test were excellent (see Tables 2 & 3). The mean recovery of spikes was 91 ± 14 (with an outlier) and $91 \pm 6\%$ for isokinetic and non-isokinetic sampling, respectively. When the outlier for the isokinetic samples was statistically eliminated (using a "rejection quotient"⁶ technique), the recovery for the isokinetic samples improved to $95 \pm 6\%$, as shown in Table 2. The method's overall analyte spike recovery, with the outlier removed, was 92.2 ± 6.5 percent. Breakthrough, as measured by the recoveries in the second impingers, were 10 percent or less, indicating near complete recoveries in the first impinger. Background or emissions concentrations for one hour samples (as determined by analysis of the unspiked trains) ranged from 63 µg/m³ to 254 µg/m³. The method's Limit of Quantitation (LOQ) for MDI, calculated as outlined in EPA Method 301⁷, was determined to be 366 ng/m³. The LOQ of the method is defined as ten times the standard deviation of the mean of the data set whereas the method Limit of Detection (LOD) would be calculated as 3.3 times the standard deviation of the mean of the data set.

CONCLUSIONS

A method has been developed for the collection and analysis of TDI and MDI (as stated earlier, the TDI method was reported on at a previous EPA/AWMA symposium⁴). Method validation procedures are completed for TDI and MDI, and results from the field tests indicate that the TDI/MDI method can now be used to determine stationary source emissions from the manufacturing of flexible foam products and from the pressed board industry. It is anticipated that this method can be successfully applied to the measurement of HDI and MI emissions as well. Current plans are for another field test in the near future, at an industry which emits HDI from its manufacturing process. Conditions not experienced in the sampling of source emissions during the first two field tests (i.e., higher humidity, particulate loadings, and/or warmer stack gas temperatures) are tentatively planned for future field tests.

Finally, based upon the breakthrough data collected during the MDI study, we recommend that when sampling for MDI, a third impinger containing 200 mL of the derivatizing reagent (1,2PP) be used to assure that no sample is lost through the system.

REFERENCES

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DISCLAIMER

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Table 1. Isocyanate project objectives.

No.	Objective Description	MI	MDI	HDI	TDI
1	Find one derivatizing reagent to react rapidly with all four isocyanates	yes ¹	yes	yes	yes
2	Set up analytical HPLC method (for a single chromatographic run)	yes	yes	yes	yes
3	Develop instrument and method detection limits	no	yes	yes	yes
4	Determine spike recovery from derivatizing reagent	no	yes	no	yes
5	construct an isocyanate generator	no	yes ²	no	yes
6	Determine recoveries from spiked Method 5 train	no	yes	no	yes
7	Field test of method and validation	no	yes	no	yes

¹- Yes indicates that objectives have been met. No indicates that an attempt has not been made to meet the objectives.

²- No laboratory testing for MDI using the isocyanate generator was necessary since TDI recoveries using the generator verified established the method's operating parameters. Spike recoveries listed in Tables 2 and 3 confirmed the method's applicability to MDI sampling.

Table 2. MDI spike recoveries while sampling isokinetically.

Run No.	Sampling Rate (ft ³ /min)	Amt. of Spike (μ g MDI)	Spike Recovery (μ g MDI)	Percent Recovery
1A	0.75	651	660	101
1B	"	"	631	97
2C	"	"	677	104
2D	"	"	573	88
3A	"	"	544	84
3B	"	"	615	94
4C	"	"	607	93
4D	"	"	645	99
5A ¹	"	"	359	55
5B	"	"	612	94
Mean/w				91
S/w				14
Mean/wo				95
S/wo				6

¹- Outlier, as determined by the Dixon "rejection quotient" test.

Table 3. Spike recoveries with non-isokinetic sampling.

Run No.	Sampling Rate (ft ³ /min)	Amount of Spike (μg MDI)	Amt. of Spike Recovered (μg MDI)	Percent Recovery
6C	0.5	651	525	81
6D	"	"	537	82
7A	"	"	622	96
7B	"	"	583	90
8C	"	"	552	85
8D	"	"	540	83
9A	"	"	602	92
9B	"	"	555	85
10C	"	"	629	97
10D	"	"	659	101
11A	"	"	619	95
11B	"	"	592	91
12C	"	"	623	96
12D	"	"	607	93
Mean				91
S				6

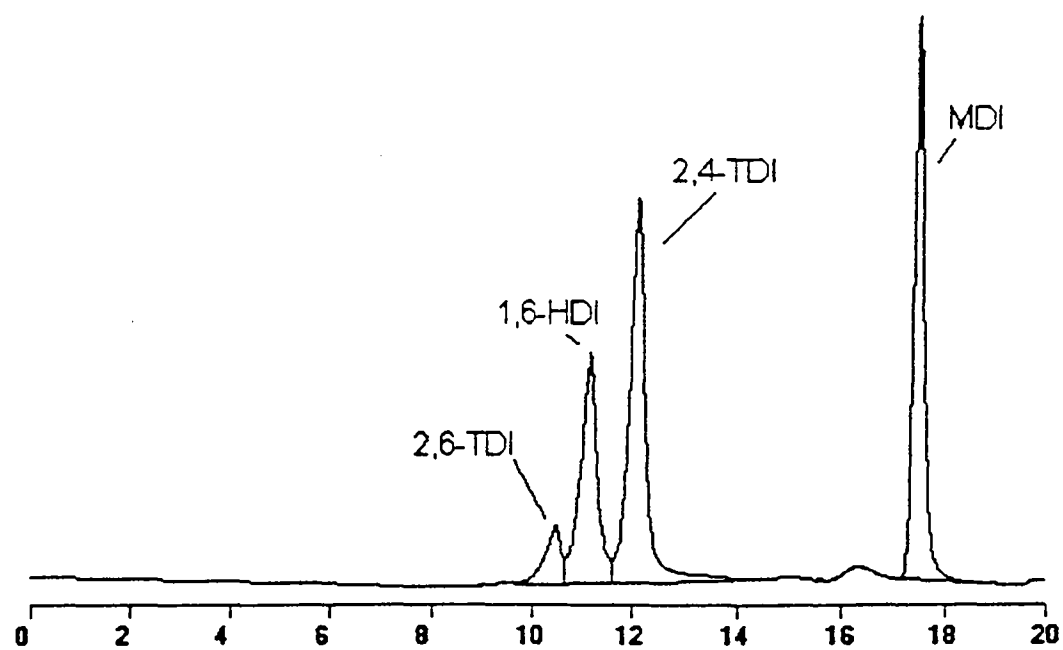


Figure 1. Chromatographic separation of HDI, TDI, and MDI.

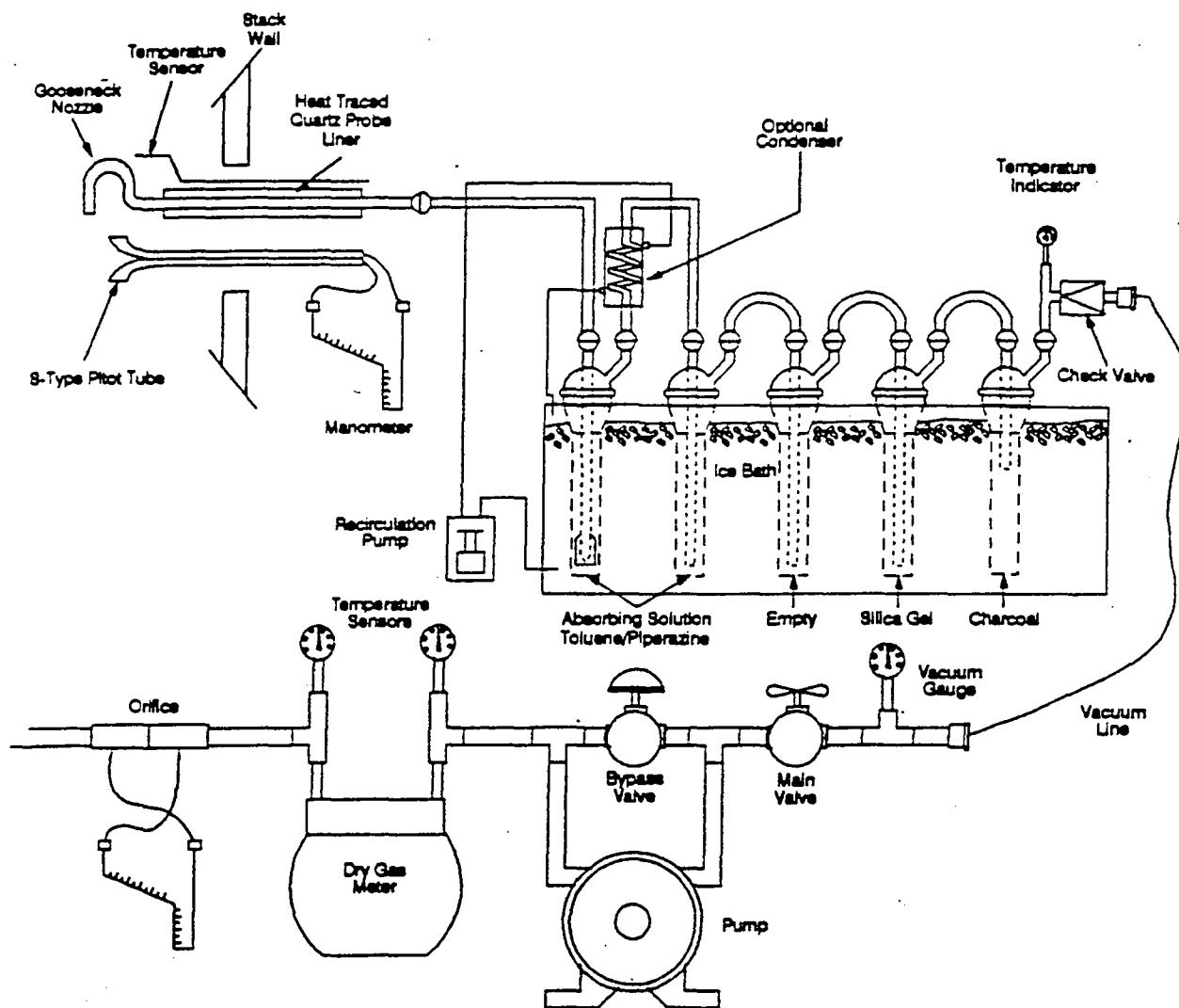


Figure 2. Isocyanate sampling train configuration.

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