

Development and Validation of a Source Test Method for
2,4-Toluene Diisocyanate

S.C. Foster and J.F. McGaughey
Radian Corporation
Research Triangle Park, NC 27709
and

F.W. Wilshire and J.E. Knoll
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

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 the insecticide carbaryl (i.e., Sevin®dust).

To support projected regulations, a study is under way to produce a source sampling and analysis method for the four pollutants cited above. In the procedure under development, the isocyanates are collected in an absorbing solution and derivatized with 1-(2-pyridyl)piperazine and analyzed by HPLC with UV detection. A system was developed in the laboratory to generate 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 following the procedures outlined in EPA Method 301.

A field test of the isocyanate method, following EPA Method 301 procedures, was performed at a flexible foam manufacturer in the Greensboro-High Point, North Carolina area. Results were excellent, with analyte spike recoveries of $91\% \pm 6\%$. The method's limit of quantitation (LOQ) was determined to be 351 ng of TDI/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 the production of flexible foam products, synthetic rubber products, insecticides, enamel wire coatings, and in the pressed board industry. Foam materials alone are widely used for such diverse items as toys, bedding, seat cushions, packing material, flotation devices, and as sorbents in the environmental field. 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 An example of the concerns expressed about human exposure to the isocyanates is demonstrated by the NIOSH IDLH level (concentration considered Immediately Dangerous to Life or Health) for 2,4-toluene diisocyanate, which is listed at 10 ppm.³

Several critical problems exist when sampling for isocyanates. They polymerize in the presence of concentrated alkaline compounds, decompose upon exposure to 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 one of the isocyanates of interest; 2,4-toluene diisocyanate. In this method, samples are collected at the source using a modified EPA Method 5 sampling train. 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. 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. The 2,4-toluene diisocyanate reacts with the derivatizing reagent to form a stable TDI/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 (TDI/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 High-Performance Liquid Chromatography (HPLC with 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, midway through the laboratory study, budget constraints required the focus to be shifted to only one of the isocyanates of interest. After discussions with personnel in the EPA's Office of Air Quality Planning and Standards, it was decided to focus our efforts on 2,4-toluene diisocyanate. The seven objectives originally planned for all of the isocyanates were followed for TDI and are listed in Table 1. Some of the objectives were also met for the other isocyanates of interest 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. An absorption solution was prepared by adding 1 gram of KOH to 500 mL of 99.9% ethanol. Standard solutions of each of the isocyanates were prepared by adding the isocyanate directly to 5 mL each of the ethanol/KOH solution as follows: 30 mg of MDI; 10 uL of MI, HDI, and TDI. Solid derivatives for MDI, HDI, and TDI were obtained, but formation of a derivative for MI was unsuccessful. Chromatograms for the derivatized and underivatized isocyanates were compared. No chromatographic peaks were observed for MI or HDI either derivatized or underivatized, however, peaks were detected for TDI and MDI.

Previous work by Goldberg, et al.⁴, using 1-(2-pyridyl)piperazine as the derivatizing agent, investigated collecting ambient air samples in midget impingers. Since no current source method for isocyanates exists, the secondary amine, 1-(2-pyridyl)piperazine [1,2PP] was investigated as a possible alternative derivatizing reagent for ethanol. Using the 1,2PP as the derivatizing reagent resulted in the formation of solid derivatives for all of the isocyanates of interest. Each isocyanate was prepared in a separate 200 mL flask. Approximately 0.2 grams of TDI, HDI, MDI was added to separate solutions of 0.3 mL of 1,2PP and 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 derivative was then 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 uL of MI to 1 mL of ACN and adding 300 uL of 1,2PP. The solution was shaken for five minutes and then diluted 1:1000 for analysis by HPLC. A 1,2-PP solution was prepared as previously mentioned for blank analysis on the HPLC. Also, a solution of the 1,2-PP with MI, HDI, MDI, and TDI was prepared to determine the retention time of each derivative. The results were excellent, demonstrating that a mixture of the four isocyanates could be analyzed with good chromatographic separation and quantitation.

Isocyanate Generator

An isocyanate atmosphere generator was constructed to provide a source of isocyanates as a simulated source, for testing within the laboratory. It is expected that this generator will 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.

A modified Method 5 sampling train (without the in-line filter) was set up in the laboratory. Attached to the end of the probe was a piece of heated 0.5 inch quartz tubing with a stainless

steel tee and septum (for introduction of the isocyanate(s) standard). The temperature of the probe and quartz tubing were maintained at 120° C. Five impingers were connected in series for this study. The first impinger was a Greenberg-Smith impinger and the four following impingers were modified Greenberg-Smith impingers (straight stem- no tip). Room air was pulled through a charcoal scrubber into the heated quartz tubing and subsequently into two impingers containing the 1,2-PP absorbing solution. Following the two impingers containing the absorbing solution were one empty impinger (trap), a silica gel impinger, and an impinger containing charcoal (scrubber). A TDI standard in methylene chloride (MeCl₂), prepared as described earlier, was introduced by a motor driven syringe pump, through the septum and into a heated air stream. Room air was sampled at a rate of 0.5 ft³/min for 40 minutes. This flow rate was chosen to test collection efficiencies at a flow rate expected to be used during the field testing. Cleanup and analysis procedures were as previously described, using toluene and ACN rinses and HPLC-UV analysis. Sample breakthrough, as measured by the recovery in the second impinger, was less than 8 percent. Mean recoveries for seven sample runs were 77 percent (see Table 2).

When the data in Table 2 was reevaluated, by eliminating the obvious outliers (Grubbs t-test for multiple outliers)⁵, the mean recovery is 98 +/- 15%. An obvious cause for the two outliers was not determined, since all operating parameters were standardized for the seven sample runs. As stated by Snedecor and Cochran in their chapter on regression analysis and outliers⁶, " when no explanation is found [for the outliers] the situation is perplexing. It is usually best to examine the conclusions obtained with the suspect (i) included, (ii) excluded. If these conclusions differ materially, as they sometimes do, it is well to note that either may be correct." Even though the Grubbs test for multiple outliers indicates that both of the outliers are suspect it is important to note that should one choose to include the suspect outliers, the recovery data would still be acceptable according to EPA Method 301 criteria.⁷

Method Validation

A field test of the method was performed in February, 1993, at a flexible foam manufacturer in the High Point, North Carolina area. 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 vent (see Figure 1). The sample gas stream was passed through a heated glass-lined/stainless steel probe and through two impingers containing the 1,2-PP absorbing solution, one empty impinger (carryover trap), one silica gel impinger, and one impinger containing charcoal (to trap any toluene vapors before they could enter the meter box). Sampling was non-isokinetic at 0.5 ft³/min for 60 minutes. Non-isokinetic sampling was performed since a presurvey indicated the analyte of

interest was present in the gas phase. Two of the quad trains for each sample run were spiked with a TDI derivatized standard (22.5 mg TDI/urea derivative in 15 mL of ACN). This standard spike was the equivalent of 8 mg of underivatized TDI, which was the amount 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 Table 3). The mean recovery of the spikes was 91 +/- 6%. Breakthrough, as measured by the recoveries in the second impingers, were all less than 2 percent, indicating near complete recovery in the first impinger. Background or emissions concentrations (as determined by analysis of the unspiked trains) ranged from 2000 ug/M³ to 7700 ug/M³. The method's Limit of Quantitation (L_q) for TDI, calculated as outlined in EPA Method 301⁷, was determined to be 351 ng/M³. The L_q of the method is defined as ten times the standard deviation of the mean of the data set whereas the method Limit of Detection (L_d) 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. Method validation procedures are still underway, but preliminary results from the first field test indicate that the method can be applied with a great degree of confidence to source emissions for TDI. Other isocyanate compounds (MI, MDI, HDI) have been or are being studied, and it is hoped that this method can be successfully applied to them as well. Current plans are for another field test in the near future, at another flexible foam manufacturer or other end user. Conditions not experienced in the sampling of source emissions during the first field test (i.e., higher humidity, particulate loadings, and/or warmer stack gas temperatures) will be investigated in the next field test.

REFERENCES

1. Clean Air Act Amendments of 1990, Public Law 101-549, U.S. Congress, November 15, 1990, 104 STAT., pp. 2533-2535.
2. Material Safety Data Sheet, No. 331, Genium Publishing Corporation, Schenectady, NY, Nov. 1978.
3. IDLH Levels, National Institute for Occupational Safety and Health (NIOSH), Publication No. 78-210, 5th Printing.
4. Goldberg, P.A., R.F. Walker, P.A. Ellwood, and H.L. Hardy, "Determination of Trace Atmospheric Isocyanate Concentrations by Reversed-Phase High-Performance Liquid Chromatography Using 1-(2-pyridyl)piperazine Reagent", Journal of Chromatography, 212, 1981, pp 93-104.
5. Grubbs, F.E., "Sample Criteria for Testing Outlying Observations", Annals of Mathematical Statistics, Vol. 21, 1950, pp. 27-58.
6. Snedecor, G.W. and W.G. Cochran, Statistical Methods, Sixth Edition, Iowa State University Press, 9th Printing, p. 158.
7. "Field Validation of Emission Concentrations from Stationary Sources," Method 301 Federal Register, U.S. Government Printing Office, Washington, D.C., December 1992.

DISCLAIMER

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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	no	no	yes
5	construct an isocyanate generator	no	no	no	yes
6	Determine recoveries from spiked Method 5 train	no	no	no	yes
7	Field test of method and validation	no	no	no	yes

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

Table 2. Recoveries of Isocyanate (TDI) Spikes

Run No.	Spike Amount (ug)	Spike Recovery (ug)	Recovery (%)
1	2.5	3.05	122
2	2.5	0.60	24
3	2.5	2.30	92
4	2.5	0.65	26
5	2.5	2.13	85
6	2.5	2.53	101
7	2.5	2.23	89
Mean w/outliers			77 +/- 38
Mean wo/outliers			98 +/- 15

Table 3. Field Test Spike Recoveries

Sample Train Identification ¹	Spike Amount (ug)	Spike Recovery (ug)	Recovery (%)
1A	7828	7436	95
1B	7828	6654	85
2C	7828	6732	86
2D	7828	7280	93
3A	7828	6810	87
3B	7828	7280	93
4C	7828	7436	95
4D	7828	7593	97
5A	7828	6888	88
5B	7828	7436	95
6C	7828	7515	96
6D	7828	7671	98
7A	7828	7826	100
7B	7828	6575	84
8C	7828	6732	86
8D	7828	6419	82
Mean			91 +/- 6

¹- Sample trains A&B are paired trains, as are sample trains C&D.

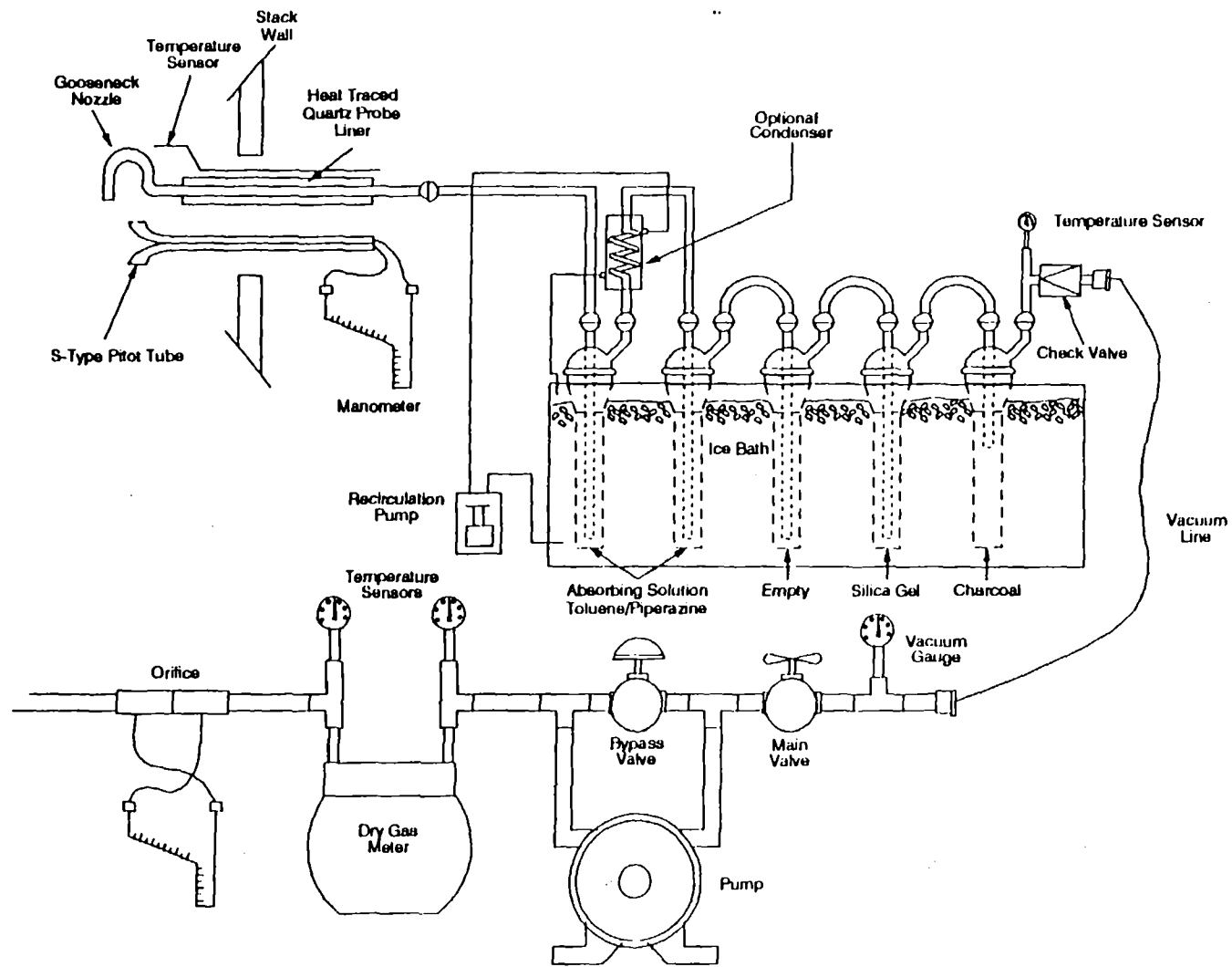


Figure 1. Isocyanate Sampling Train Configuration

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before com.)

1. REPORT NO. EPA/600/A-93/124		2.	
4. TITLE AND SUBTITLE Development and Validation of a Source Test Method for 2,4-Toluene Diisocyanate		5. REPORT DATE	
7. AUTHOR(S) F. Wilshire and J. Knoll, EPA/AREAL/MRDD, RTP, NC 27711 and S. Foster and J. McGaughey, Radian Corp., RTP, NC		6. PERFORMING ORGANIZATION CODE	
9. PERFORMING ORGANIZATION NAME AND ADDRESS U.S. Environmental Protection Agency Atmospheric Research and Exposure Assessment Laboratory MRDD/SMRB (MD-77A) Research Triangle Park, NC 27711		8. PERFORMING ORGANIZATION REPORT NO.	
12. SPONSORING AGENCY NAME AND ADDRESS U.S. Environmental Protection Agency AREAL/MRDD/SMRB (MD-77A) Research Triangle Park, NC 27711		10. PROGRAM ELEMENT NO.	
		11. CONTRACT/GRANT NO.	
		13. TYPE OF REPORT AND PERIOD COVERED	
		14. SPONSORING AGENCY CODE EPA/600/09	
15. SUPPLEMENTARY NOTES			

16. 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 the insecticide carbaryl (i.e., Sevin^R dust).

To support projected regulations, a study is under way to produce a source sampling and analysis method for the four pollutants cited above. In the procedure under development, the isocyanates are collected in an absorbing solution and derivatized with 1-(2-pyridyl)piperazine and analyzed by HPLC with UV detection. A system was developed in the laboratory to generate 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 following the procedures outlined in EPA Method 301.

A field test of the isocyanate method, following EPA Method 301 procedures was performed at a flexible foam manufacturer in the Greensboro-High Point, NC area. Results were excellent, with analyte spike recoveries of 91% ± 6%. The method's limit of quantitation (LOQ) was determined to be 351 ng of TDI/M³.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (This Report)	21. NO. OF PAGES 11
	20. SECURITY CLASS (This page)	22. PRICE