

Alternative Test Method for the Emission Measurement of Isocyanates

The Diisocyanates Panel of the Chemical Manufacturers Association (now the American Chemistry Council) worked for several years to develop reliable and cost-effective test methods for measuring emissions of diisocyanates, including methylene diphenyl diisocyanate (MDI) and toluene diisocyanate (TDI). As part of this effort, the Panel has developed an alternative to EPA's proposed Test Method 207 that we believe will be more reliable than Method 207 and less costly to use.

The enclosed paper discusses the alternative method and outlines the Panel's proposed approach for validating this method pursuant to EPA's Method 301. The method was approved by EPA on January 29, 1999 and was posted on the EPA Web site on March 17, 1999. http://www.polyurethane.org/mdi_2000/mdi_intro.html

Proposal to Validate Alternative Sampling Method

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Phase 1: Methylene Diphenyl Diisocyanate (MDI)

Phase 2: Toluene Diisocyanate (TDI)

Introduction

Over the last several years, the Environmental Protection Agency has been developing a test method for measuring emissions of isocyanate compounds. The Agency recently validated Method 207 for this purpose and published the proposed method in the Federal Register for public comment. See 62 Fed. Reg. 64532 (Dec. 8, 1997). During the comment period, the Diisocyanates Panel of the Chemical Manufacturers Association (CMA) submitted written comments raising two major concerns about the proposed method.

First, the Panel noted that Method 207 was only designed to sample vapor emissions and might therefore understate actual emissions of methylene diphenyl diisocyanate (MDI), which has a very low vapor pressure and is likely to be emitted to some extent as an aerosol. Second, the Panel expressed concern about the cost and feasibility of using Method 207 in many cases. Method 207 employs a Method 5-based sampling train operated at isokinetic conditions. It is very cumbersome to use on the vast majority of process vents from which diisocyanates may be emitted, primarily due to the physical constraints of the venting systems. It is also very costly. It generally takes two or three individuals two full days to set up the apparatus and conduct the measurements. The Panel recently used proposed Method 207 to conduct emissions tests at two facilities, at a cost of approximately \$25,000 per facility.

Even before the publication of proposed Method 207, the Panel had been working to develop reliable and cost-effective test methods for measuring emissions of all diisocyanates, including MDI. The purpose of this paper is to discuss an alternative to Method 207 and present the Panel's proposed approach for validating this method pursuant to EPA's Method

301. As discussed further below, Phase 1 of the proposal is designed specifically to validate the alternative method for measuring emissions of 2,4'-MDI and 4,4'-MDI. In Phase 2, the validation program would address 2,4-toluene diisocyanate (2,4-TDI) and 2,6-toluene diisocyanate (2,6-TDI). The Panel expects that the data from these two phases will be sufficient to validate the proposed test method for measuring emissions of all isocyanate compounds.

Summary of Proposed Test Method

Several methods are currently being used for workplace monitoring of MDI. The methods are summarized in Table 1 below. All of these methods utilize high-pressure liquid chromatography with UV (diode array), electrochemical or fluorescence detectors or a combination for the analysis of the derivatives formed in the collection media.

Table 1

Methods Commonly used for MDI Emission Measurements

Method Number	Collection Mechanism
OSHA 47	37 mm Glass-fiber filter impregnated with 1-(2-pyridyl)piperazine
Bayer 1.7.7	13 mm Glass-fiber filter impregnated with 1-(2-pyridyl)piperazine
MDHS 25/2	Midget impinger charged with 1-(2-methoxyphenyl)piperazine
Bayer 1.4.3	Midget impinger charged with N-4-nitrobenzyl-N-n-propylamine in toluene
NIOSH 5521	Midget impinger charged with 1-(2-pyridyl)piperazine

As the Panel has previously discussed with EPA, these methods have the potential to be used in a screening approach for evaluating stack emissions. See Letter from Carol Stack, Manager, Diisocyanates Panel, to Gary McAlister, EPA Office of Research and Development (Aug. 25, 1998). These methods, however, are not properly sampling the vent stream for particulates; they over sample particulates since they run at sub-isokinetic flow rates. The Diisocyanates Panel is proposing to validate an alternate method that addresses both particulate and vapor but does not present the operational difficulties that exist with Method 207. A detailed description of this method is attached as Appendix 1. It can be summarized as follows:

A 90-mm glass fiber filter is treated with 1-(2-methoxyphenyl) piperazine or 1-(2-pyridyl)piperazine and diethyl phthalate. The filter is held in a conventional Method 5 filter holder and a glass nozzle with a 90° bend is attached to the unit. A high volume pump equipped with a flow controller is attached to other fitting of the holder and the flow is set, based on nozzle and vent velocity, to be ± 10% of isokinetic conditions. Upon completion of the sample collection phase, the filter is field desorbed and returned to the laboratory for analysis by high-pressure liquid chromatography.

Note that a recent study by the Roy F. Weston, Inc. firm showed that, for purposes such as this, personnel sampling pumps are as accurate as the more complex trains that use dry gas meters. See David L. Elam, Jr. and Jeffrey W. Burdette, "Advances in Toluene

Diisocyanate Emission Measurement Methodology," presented at the Polyurethane World Congress, September, 1998, Amsterdam, The Netherlands (attached as Appendix 2).

Method 301

The Panel plans to conduct a validation study of this method pursuant to EPA's Method 301, "Field Validation of Pollutant Measurement Methods From Various Waste Media." Method 301 offers three options for validation purposes:

1. Isotopic (stable label) spiking
2. Comparison with an existing method
3. Analyte spiking

The Panel believes that Option 3, analyte spiking, is the most appropriate approach in this case. Option 1 is not feasible because it would require the use of liquid chromatography/mass spectrometry as the tool for quantification. It would be possible to use Option 2 and rely on a comparisons with Method 207 measurements. However, Method 207 has not yet been formally approved by EPA.

To be considered validated in accordance with EPA Method 301, the method must meet the following minimum criteria:

1. The bias (if any) must lead to a correction factor between 0.7 and 1.3. The test for statistically significant bias is performed by calculating the t-statistic and comparing it with the two-sided t-distribution at the 95% confidence level. If the calculated t-value is less than the critical value from the t-distribution, the bias is not statistically significant and no correction factor is required. If the calculated t-value is greater than the critical value from the t-distribution, a correction factor must be applied to the data. For analyte spiking, the correction factor must be within 0.7 to 1.3 for the method to be acceptable.
2. The precision, measured as the relative standard deviation (RSD) for both the spiked and unspiked train pairs, must be less than 50%. The number of samples required to be collected and analyzed is dictated by the following precision level:

Validated RSD $\leq \pm 15\%$ 3 replicate samples

Validated RSD $\leq \pm 30\%$ 6 replicate samples

Validated RSD $\leq \pm 50\%$ 9 replicate samples

Thus, for example, a method with a RSD of 20% would require the use of six runs to yield acceptable emission data.

Test Program Design

As noted above, the objective of the Panel's proposed test program is to conduct the work required to validate the proposed method in accordance with the requirements of EPA Method 301. Employing a version of the analyte spiking option, the program will include six quadruplicate sampling runs of a carefully controlled emission source. During each run, two of the trains will be spiked with MDI at predetermined concentrations (~ 2.5 times the anticipated concentration of MDI in the emission gas stream). The other two trains would be

left unspiked. Consequently, the precision, bias, and accuracy (see below) can be determined following the standard statistical formulae described in Method 301.

Vent System

The vent system consists of the following items:

1. An 8 inch galvanized duct ~ 90 inches tall
2. Flow straightener located directly above the blower plenum
3. Blower Model 2C889, Dayton
4. Model 100 Syringe Metering System, KD Scientific (Fisher Cat. No. 14-831-1)
5. Heated vaporization zone consisting of a "T" containing a glass wool bundle and heat tape connected to a temperature controller. One branch of the "T" is used as the needle inlet. One branch is used as a gas inlet and the third branch is inserted into a section of nine-inch ID duct connected to the suction side of the blower.
6. Four ports, 1 inch in diameter are located at 64 inches from the top of the flow straightener and are 90° apart. The stack extends an additional two diameters from the sampling ports.

Appendix 1 includes detailed information about velocity and volumetric flow data, as well as a picture of the vent system.

Analyte Spiking

Since this is a controlled system, the analyte spiking option will consist of six runs of quadruplicate trains that will yield 24 samples. In the case of MDI, pure 4,4'-MDI will be metered into the vent stream at a controlled rate so that the concentration in mg/ft³ will be known. Two of the four trains will be spiked with 2,4'-MDI derivative, either 1,2-MP or 1,2-PP. All four probes (see Method for details of the train) will be co-located within a 2.5 inch square inside the vent. The square plane is chosen such that wall effects are minimized. After addition of MDI is initiated, the vent will be allowed to stabilize for ~ 30 minutes, and then sampling is started. Sampling is continued for 1 hour. The resulting samples are processed as described in the method and analyzed for 2,4'-MDI and 4,4'-MDI. The data obtained from the six quadruplicate trains will be analyzed as described in Method 301.

Phase 2

In Phase 2, 2,4-TDI and 2,6-TDI will be substituted for the MDI. Since, in actual process sampling, the dominant isomer of TDI being emitted is 2,6-TDI, 2,4-TDI will be used as the spiking compound and 2,6-TDI will be metered into the vent system. Other conditions of sampling, analysis and data processing will be the same as for MDI.

Estimated Costs of the Proposed Test Method

As noted above, one of the primary drawbacks of Method 207 is cost. The Panel believes that its proposed alternative method will be much more cost effective, as shown on the following table:

Charge per Event

Item	Charge
Travel Costs*	
Time/Materials	\$2,000
Laboratory Analysis	\$3,000
Data Analysis and Report Generation	\$1,000

*Variable depending on contractor

APPENDIX 1

METHOD FOR THE MEASUREMENT OF ISOCYANATES FROM STATIONARY SOURCES

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 4.

1.0 Scope and Application.

1.1 This method is applicable to the collection of Methylene Diphenyl Diisocyanate (MDI) and Toluene Diisocyanate (TDI) from the emissions associated with manufacturing processes.

Compound Name	CAS No.	Detection Limits (mg/M3) ^a	Examples of Manufacturing Processes
Methylene Diphenyl Diisocyanate (MDI)	101-68-8	0.200	Pressed Board Production, Headliner Production
Toluene Diisocyanate (TDI)	584-84-9	0.200	Flexible Foam Production

^aEstimated detection limit is based on a sample volume of 0.5 M3 and a 5 mL sample extraction volume.

2.0 Summary of Method.

2.1 Gaseous and/or aerosolized isocyanates are withdrawn from an emission source at sub-kinetic sampling rate and are collected on a 90-mm glass fiber filter coated with ~50 mg of 1-(2-methoxyphenyl)piperazine (1,2-MP) or 1-(2-pyridyl)piperazine (1,2-PP). The

primary components of the train include a glass nozzle with 90° bend, filter cassette, and a personnel sampling pump.

2.2 The collected samples are analyzed by high performance liquid chromatography (HPLC) as described in OSHA Method 47.

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). 1-(2-Methoxyphenyl)piperazine (1,2-MP or MOPP) may reduce or eliminate these interferences.

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

5.1 The toxicity of each reagent has been precisely defined. 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 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 sampling train consists of the components detailed below.

Probe Nozzles. Glass, ~ 8 inches in length with a 90° angle. Several internal diameters, e.g., 0.269, 0.180, should be available to allow for approximating isokinetic conditions.

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 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).

Pumping System. Aircon-2 high volume air sampler or equivalent. Verify calibration of flowmeter using a Model M-5 Buck calibrator or equivalent.

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). 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).

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. Electronic notebooks may be used provided backups are preformed regularly, i.e., after each run minimum.

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

Wash Bottles. 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.

Glass Sample Storage Containers. Chemically resistant, borosilicate amber glass bottles, 40-mL VOA vials or 1 ounce. Bottles should be tinted to inhibit UV degradation. 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 fewer tendencies toward leakage.

Forceps. To handle filters after collection.

7.0 Reagents and Standards.

7.1 Filter Preparation

7.1.1 Weigh 2.00 mg of derivatizing reagent in a 100 mL volumetric flask, add 5 mL of diethyl phthalate and dilute to the mark with toluene. Mix well.

7.1.2 Transfer the solution to a crystallizing dish. Immerse 90-mm glass-fiber filters, one at a time for 20-30 seconds in the solution and place the filters on a nickel wire gauze to air dry (complete drying takes several hours). Minimize exposure to light during drying. Alternatively, a number filters can be placed in the coating solution and gently shaken to thoroughly wet all the filters (about 5-10 minutes). The filters are then air dried individually on a nickel wire gauze.

7.1.3 Load the dry coated filters into the filter holders, seal, and store in a cool, dark place until use.

7.2 Sample Recovery Reagents.

7.2.1 Dimethyl Sulfoxide (DMSO). 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.

7.2.3 Acetonitrile/DMSO Solution: Prepare a quantity of 90:10 (v/v) of acetonitrile/DMSO rinse solution to meet needs of the sampling event.

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 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 determine the stack pressure and temperature 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 isokinetic sampling-rate settings, i.e., probe ID and L/min to sampled. 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 stack velocity so that isokinetic sampling rates can be insured based on the sampling range of the sampling pump. During the run, do not change the nozzle.

8.2.3 A typical sample volume to be collected is 450 to 700 L. 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.

8.2.4 In some circumstances (e.g., batch cycles) it may be necessary to sample for shorter times and to obtain smaller gas-sample volumes.

8.3 Preparation of Sampling Train.

8.3.1 During preparation and assembly of the sampling train(s), 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 Monitor 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 approximately 50°- 75° C (122°-170° F), thus minimizing the loss of reagent from the filter.

8.4 Sampling-Train Operation.

8.4.1 During the sampling run, maintain isokinetic sampling.

8.4.2 For each run, record the data required on a data sheet such as the one shown in Figure 1.

8.4.3 With the full train constructed, set pump at the required flow rate and put the pump in hold mode.

8.4.4 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.

8.4.5 Start pump by pressing Hold/Run switch and record start time (Aircon-2 pumps have a built-in timer that displays actual run time).

8.4.6 A single train shall be used for the entire sample run

8.4.7 At the end of the sample run, record the final time.

8.4.8 Calculate percent isokineticity to determine whether the run was valid i.e., $100 \pm 10\%$ of the isokinetic rate or whether another test run should be performed.

8.6 Sample Recovery.

8.6.1 Preparation.

8.6.1.1 Transfer the probe and the filter holder assembly to the cleanup area. This area should be clean and protected from the weather to minimize sample contamination or loss.

8.6.1.2 Transfer approximately 20 mL of 90:10 (v/v) acetonitrile/DMSO directly from the wash bottle being used and place in a separate, pre-labeled glass sample container for use as a blank.

8.6.1.3 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. Separate the filter housing and place the filter in the container. The nozzle is rinsed with approximately 20 mL of 90:10 (v/v) acetonitrile/DMSO and the rinsate is add directly to the container containing the filter. The container is sealed and properly labeled.

8.6.3 Sample Preparation for Shipment.

8.6.3.1 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, using the proper shipping materials as prescribed for hazardous materials.

9.0 Quality Control.

9.1 Sampling.

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 unexposed filters processed as a normal sample.

9.1.2 Reagent Blanks. An aliquot, approximately 20 mL of 90:10 (v/v) acetonitrile/DMSO acetonitrile and the reagent solution used to prepare the filters must be included in the analytical scheme.

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.).

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 Personnel Sampling System.

10.3.1 Before its initial use in the field, the flow meter of the pumping system shall be calibrated using a Model M-5 Buck calibrator or equivalent.

10.3.2 After each field use, the calibration of the flow meter of the pumping system shall be checked using a Model M-5 Buck calibrator or equivalent. Initial and final rates should be with $\pm 10\%$ of each other.

11.0 Procedures.

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

11.2 Analytical. See OSHA Method 47.

12.0 Method Performance.

12.1 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.

12.2 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.

13.0 Pollution Prevention. Not Applicable.

14.0 Waste Management. Not Applicable.

15.0 References.

1. U.S. Environmental Protection Agency, 40 CFR Part 60, Appendix A, Methods 1-4.
 2. OSHA Method 47, Revised March, 1989, Carcinogen and Pesticide Branch, OSHA Analytical Laboratory, Salt Lake City, Utah.
 3. Bayer Corporate Industrial Hygiene Laboratory, Bayer CIHL Method No: 1.7.7.
- 16.0 Tables, Diagrams, Flowcharts, and Validation Data. Not Applicable.