Conditional Test Method 036

METHOD FOR MEASUREMENT OF ISOCYANATE COMPOUNDS IN STACK EMISSIONS

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 Toluene Diisocyanate (TDI), Methylenediphenyl Diisocyanate (MDI), Hexamethylene Diisocyanate (HDI), HDI Biuret, HDI Trimer, and isophorone diisocyanate (IPDI) from the emissions associated with manufacturing processes.

Compound Name	CAS No.	Detection Limits ($\mu g/M^3$)[a]	Examples of Manufacturing Processes
1,6-Hexamethylene Diisocyanate (HDI)	822-06-0	0.043	Paint Spray Booth
1,6-Hexamethylene Diisocyanate Biuret[b]	4035-89-6	0.48	Paint Spray Booth
1,6-Hexamethylene Diisocyanate Trimer[c]	28182-81-2	0.30	Paint Spray Booth
Isophorone Diisocyanate (IPDI)	4098-71-9	0.27	Coatings
2,4-Toluene Diisocyanate (TDI)	584-84-9	0.18	Flexible Foam
2,6-Toluene Diisocyanate (TDI)	91-08-7	0.036	Flexible Foam
2,4'-Methylenediphenyl Diisocyanate	5873-54-1	0.64	Oriented Strand Board
4,4'-Methylenediphenyl Diisocyanate	101-68-8	0.64	Oriented Strand Board

[a]Estimated method detection limit is based on a sample volume of 0.25 M^3 and a 5 mL sample extraction volume. [b]N,N'-2-Tris(6-isocyanatohexyl)imidodicarbonic diamide. [c]1,3,5-Tris(6-isocyanatohexyl)-1,3,5-triazine-2,4,6(1H,3H,5H)-trione; HDI isocyanurate.

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2.1 Gaseous and/or aerosolized isocyanates are withdrawn from an emission source at an isokinetic sampling rate and are collected on a 90 mm glass fiber filter coated with 10-12 $\mu g/mm^2$ of 1-(2-pyridyl)piperazine (1,2-PP). The primary components of the train include a filter cassette, and a sampling pump.

2.2 The collected samples are analyzed by high performance liquid chromatography (HPLC).

2.3 A correction factor of 1.19 was determined for each TDI isomer during Method 301 validation using 1,2-PP (3 replicates are required).

2.4 No correction factor is required for MDI (three replicates are required).

2.5 No correction factor is required for HDI (three replicates are required).

2.6 No correction factor is required for HDI Biuret (three replicates are required).

2.7 No correction factor is required for HDI Trimer (three replicates are required).

2.8 No correction factor is required for IPDI (three replicates are required).

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).

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 co-elute with one or more of the derivatized isocyanates.

5.0 Safety.

5.1 The toxicity of each reagent has been 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. The laboratory should provide additional references for laboratory safety.

6.0 Equipment and Supplies.

6.1 **Sample Collection**. The sampling train consists of the components detailed below.

Probe Nozzle. Approximately 8-12 inches x 0.125 inch ID Teflon® tubing sealed in a stainless steel tube with a 90° bend. A glass or similar type probe may also be used. The actual length and ID of the probe are dictated by the stack diameter and the ACFM.

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 15.0, 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. Gilian AirCon-2 air sampling pump or equivalent. Calibrate the pumps with a Gilian Gilibrator-2 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). **This determination is necessary only if the effluent stream is other than normal room air.**

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:

Glass Sample Storage Containers. Chemically resistant, borosilicate amber glass bottles, 20-mL VOA vials or 1 ounce. Bottles should be tinted to inhibit UV degradation of the contents or stored in the dark. Screw-cap liners shall be either Teflon® or constructed to be leak-free and resistant to chemical attack by organic recovery solvents.

Forceps. To handle filters before and after collection.

7.0 Reagents and Standards.

7.1 Filter Preparation

7.1.1 Weigh 1.2g of 1-(2-pyridyl)piperazine (1,2-PP) in a 50 mL volumetric flask, and dilute to the mark with acetone. Mix well.

7.1.2 Transfer the solution to a Petri dish. Immerse 90-mm glass-fiber filters (Gelman Sciences No. 61664 Type A/E Glass Fiber Filter or equivalent), 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 of filters (up to 15) can be placed in the coating solution and gently shaken to thoroughly wet all the filters (about 5 minutes). The filters are then air dried individually on a nickel wire gauze.

7.1.3 Store the dry, coated filters 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 below).

7.2.2 *Acetone.* Distilled-in-glass grade is required for preparation of filters.

7.2.3 *Acetonitrile.* Distilled-in-glass grade is required if used for sample recovery and cleanup.

7.2.4 *Toluene.* Distilled-in-glass grade is required if used for sample recovery and cleanup.

7.2.5 *Acetonitrile/DMSO Solution*: Prepare a quantity of 90:10 (v/v) or 70:30 (v/v) of acetonitrile/DMSO sample preparation solution to meet needs of the sampling event. Store the prepared reagent in a dark bottle containing 4A Molecular Sieves.

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. 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 necessary for molecular weight determination, i.e. **if other then room air**, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the sample run.

8.2.2 Calculate the stack velocity using the data collected.

8.2.3 Select a nozzle size based on the above calculated stack velocity so that isokinetic sampling rates can be achieved with the available pumps. For the AirCon-2, a typical rate is 8-15 L/min. During the run, do not change the nozzle.

8.2.4 A typical sample volume to be collected is 250 - 350L. 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 In some circumstances (e.g., batch cycles) it may be necessary to sample for shorter times and to obtain smaller gas-sample volumes.

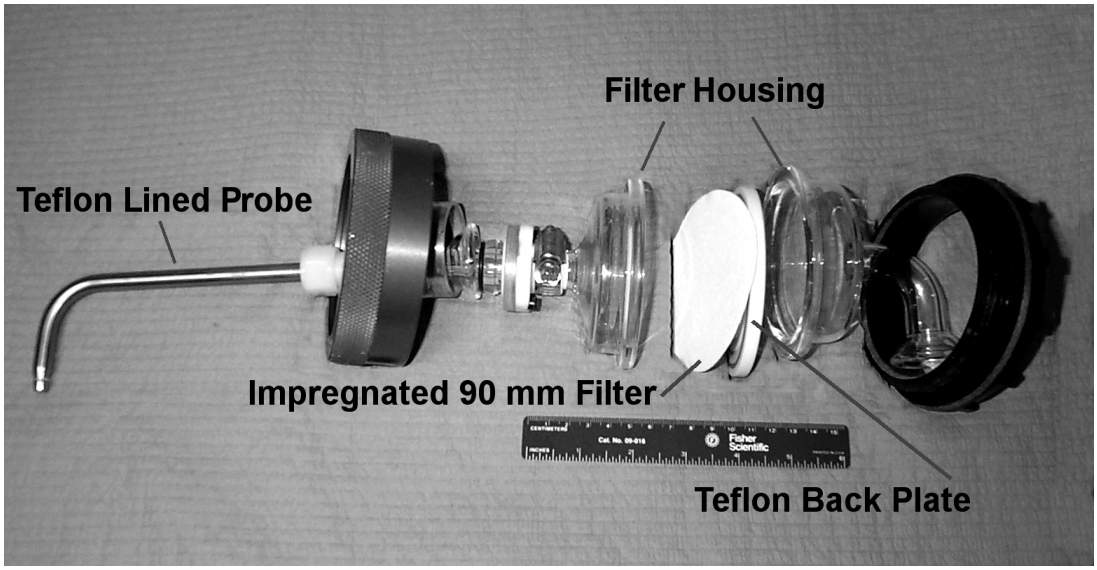
8.3 **Preparation of Sampling Train.**

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 (see picture).

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 125°C (257°F), thus minimizing the loss of reagent from the filter.

8.3.3 Just prior to sample collection, the flow rate through the train is set to meet isokinetic conditions using a Gilibrator-2 flow calibrator or preparing a calibration curve plotting the rotameter setting versus the actual flow rate through the train prior to the sampling event.

Sampling Train


Filter Housing
Teflon Lined Probe
Impregnated 90 mm Filter
Teflon Back Plate

Sampling-Train Operation.

8.4.1 During each of the three (3) sampling runs, maintain an isokinetic sampling rate.

8.4.2 For each run, record the data required on a data sheet such as the one shown in Figure 1. Be sure to record the initial start time.

8.4.3 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.

8.4.4 A single train shall be used for the entire sample run.

8.4.5 During the course of the sample collection, monitor the flow by observing the flow meter to ensure that the desired flow rate is maintained.

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

8.5 **Sample Recovery**.

8.5.1 Preparation.

8.5.2.1 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.

8.5.2.2 Transfer approximately 5 mL of 90:10 (v/v) or 70:30 (v/v) acetonitrile/DMSO, acetonitrile, or toluene directly from the reagent bottle being used and place in a separate, pre-labeled glass sample container for use as a reagent blank.

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

8.5.2 Sample Containers.

8.5.2.1 Separate the filter housing and place the filter in the container. Add 5.0 mL of 90:10 (v/v) [TDI or MDI] or 70:30 (v/v) [HDI/IPDI] acetonitrile/DMSO directly to the vial containing the filter. The vial is sealed and properly labeled.

8.5.2.2 At the end of the 3 runs, rinse the probes with acetone. Combine the rinses and add 2-4 drops of 1-(2-pyridyl)piperazine. Alternatively, one of the treated filters could be added. Prior to analysis, the sample is evaporated to dryness and 5 mL of 90:10 (v/v) [TDI or MDI] or 70:30 (v/v) [HDI/IPDI] acetonitrile/DMSO is added directly to the vial. The vial is sealed and properly labeled.

8.5.2.3 At the end of the 3 runs, wipe the inside of the front glass filter housing with a 1,2-PP treated filter moistened with acetone or 90:10 (v/v) [TDI or MDI] or 70:30 (v/v) [HDI/IPDI] acetonitrile/DMSO. Place the filter in a vial and add 5 mL of 90:10 (v/v) [TDI or MDI] or 70:30 (v/v) [HDI/IPDI] acetonitrile/DMSO. The vial is sealed and properly labeled.

8.5.2.4 Place an unexposed filter in a container and add 5.0 mL of 90:10 (v/v) [TDI or MDI] or 70:30 (v/v) [HDI/IPDI] acetonitrile/DMSO directly to the container containing the filter. The container is sealed and labeled as the Field or Media Blank.

8.5.2.5 Sample Preparation for Shipment. Prior to shipment, recheck all sample containers to ensure that the caps are well secured. If necessary, 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 or Media Blanks*. Field or media blanks must be submitted with the samples collected at each sampling site. The field or media blanks include the sample bottles containing aliquots of sample recovery solvents, and unexposed filters processed as a normal sample.

9.1.2 *Reagent Blanks*. A 5 mL aliquot, of 90:10 (v/v) [TDI or MDI] or 70:30 (v/v) [HDI or IPDI] acetonitrile/DMSO, 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 0.84-0.85 if it is not visibly nicked, dented, or corroded and if it meets design and intercomponent spacing specifications.

10.3 *Sampling System*.

10.3.1 Before its initial use in the field, the pumping system shall be calibrated using a Gilian calibrator or equivalent.

11.0 Procedures.

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

11.2 *Analytical*. See Reference 15.2 for typical HPLC conditions.

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 (IDL, See Table). The method detection limit (MDL) 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.

Table 1 **Instrument Detection Limits**

Compound	Instrument Detection Limit	SD
1,6-Hexamethylene diisocyanate	0.00215 ng/μL	0.0020
1,6-Hexamethylene Diisocyanate Biuret	0.024 ng/μL	0.016
1,6-Hexamethylene Diisocyanate Trimer	0.015 ng/μL	0.010
Isophorone Diisocyanate (IPDI)	0.0135 ng/μL	0.011
2,4-Toluene diisocyanate	0.0092 ng/μL	0.0064
2,6-Toluene diisocyanate	0.0089 ng/μL	0.0012
2,4'-Methylenediphenyl diisocyanate	0.03178 ng/μL	0.0233
4,4'-Methylenediphenyl diisocyanate	0.03175 ng/μL	0.0233

12.3 *Method Precision and Bias*. The method bias is dependent upon the collection, retention, and extraction efficiency of the train components. Evaluation data show that a correction factor of 1.19 is required for both the 2,4- and 2,6-TDI and 3 replicates must be obtained. No correction factor is required for MDI, IPDI, HDI, HDI Biuret, and HDI Trimer.

13.0 **Pollution Prevention**. Not Applicable.

14.0 **Waste Management**. Not Applicable.

15.0 **References**.

15.1 U.S. Environmental Protection Agency, 40 CFR Part 60, Appendix A, Methods 1-4.

15.2 OSHA Method 47, Revised March, 1989, Carcinogen and Pesticide Branch, OSHA Analytical Laboratory, Salt Lake City, Utah.

15.3 OSHA Method PV2030, January 1988, Carcinogen and Pesticide Branch, OSHA Analytical Laboratory, Salt Lake City, Utah.

15.4 Bayer Materials Science, Industrial Hygiene, a Unit of HSE Testing Laboratory, Bayer CIHL Method No: 1.7.6.

15.5 Bayer Materials Science, Industrial Hygiene, a Unit of HSE Testing Laboratory, Bayer CIHL Method No: 1.7.7.

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

Field Sampling Log

Site Name:		**Stack size:**	
Location:		**ACFM:**	
Date:		**Nozzle size:**	

Sample Number	Sampling Period		Total Time	Pump Flow Rate	Volume Sampled Liters	Stack Location	Pump Number
	Start Time	End Time					

Comments:

Figure 1. Field Data Sheet.