Note: The following procedure is only a screening procedure. If the MDI emisions mesured with this method are high enough to cause concern with any State regulation, the measurement must be repeated using EPA Method 207 or some other approved alternative.

SCREENING METHOD FOR METHYLENE DIPHENYL DIISOCYANATE (MDI)

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) from the emissions associated with manufacturing processes.

Compound Name	CAS No.	Detection Limits ($\mu g/M^3$)[a]	Examples of Manufacturing Processes
Methylene Diphenyl Diisocyanate (MDI)	101-68-8	200	Pressed Board Production Headliner Production

[a]Estimated detection limit is based on a sample volume of 0.06 M^3 and a 2 mL sample extraction volume.

2.0 Summary of Method.

2.1 Gaseous and/or aerosolized isocyanates are withdrawn from an emission source at a sub-isokinetic sampling rate and are collected on a 13 mm glass fiber filter coated with 1.0 mg of 1-(2-methoxyphenyl)piperazine (1,2-MP or MOPP) 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.

5.0 Safety.

5.1 The toxicity of each reagent has been precisely defined. 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 Nozzle. Approximately 8 inches x 0.269 inch ID glass with a 90◦ bend.

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. DuPont 2500B air sampling pump or equivalent. Calibrate with 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 performed regularly.

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 Teflon® or otherwise 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 200 mg of derivatizing reagent in a 10 mL volumetric flask. Add 0.5 mL of diethyl phthalate and dilute to the mark with toluene. Mix well.

7.1.2 Transfer the solution to a Petri dish. Immerse 13 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 of 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 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 be performed, as described in promulgated EPA Method 2, Section 3.1 (Reformatted Draft EPA Method 2, Section 8.1). 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 stack velocity so that sub-isokinetic sampling rates can be insured assuming a sampling rate of 1 L/min. During the run, do not change the nozzle.

8.2.3 A typical sample volume to be collected is 20-80 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 Calibrate the pump at the desired flow rate using a nozzle, a previously prepared filter cassette, and a Model M-5 Buck calibrator or equivalent. Record the flow rate and pump identifier for each pump. Discard the filter cassette after post-run calibration check.

8.3.3 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 each of the three (3) sampling runs, maintain a sub-isokinetic sampling rate that is from 5% to 15% of the isokinetic 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 At the end of the sample run, record the final time and conduct a post-run calibration check of the sample pump as described in Section 8.3.2. Record the flow rate. Initial and final rates should be within ± 10% of each other. If not, discard the filter and repeat the test. If initial and final rates are within acceptable range, average the results of the two flow measurements and use the average for the calculations.

8.4.6 Calculate percent isokineticity to determine whether the run was valid (i.e., 5-15% of the isokinetic rate) or whether another test run should be performed.

8.5 **Sample Recovery**.

8.5.1 *Preparation.*

8.5.1.1 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.

8.5.1.2 Transfer approximately 10 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.

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

8.5.2 *Sample Containers.*

Sample Container. Separate the filter housing and place the filter in the container. Rinse the nozzle with approximately 2 mL of 90:10 (v/v) acetonitrile/DMSO and add the rinsate directly to the container containing the filter. The container must be sealed and properly labelled.

8.5.3 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, 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 10 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 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 pumping system shall be checked using a Model M-5 Buck calibrator or equivalent. Initial and final rates should be within ± 10% of each other.

11.0 Procedures.

11.1 *Sampling Operation*. Follow the sampling procedure outlined in Section 8.0.

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 instrumental minimum detection limits (MDLs). 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.

12.3 *Method Precision and Bias*. The method bias is dependent upon the collection, retention, and extraction efficiency of the train components. Evaluation studies to date show that the method bias leads to emission values equal to or greater than actual emissions when compared to isokinetic sampling protocols such as Method 207.

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 Bayer Corporate Industrial Hygiene 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:		**Velocity:**	
Date:		**Nozzle size:**	

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

Comments:

Figure 1. Field Data Sheet.