METHOD 326 -- METHOD FOR DETERMINATION OF ISOCYANATES IN STATIONARY SOURCE EMISSIONS

1.0 Scope and Application

This method is applicable to the collection and analysis of isocyanate compounds from the emissions associated with manufacturing processes. 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 Method 1, Method 2, Method 3, and Method 5 found in Appendices A-1 and A-3 in Part 60 of this title.

1.1. Analytes. This method is designed to determine the mass emission of isocyanates being emitted from manufacturing processes. The following is a table (Table 1-1) of the isocyanates and the manufacturing process at which the method has been evaluated:

Table 1-1 Analytes

Compound's Name	CAS No.	Detection Limit (ng/m^3)[a]	Manufacturing Process
2,4-Toluene Diisocyanate (TDI)	584-84-9	106	Flexible Foam Production
1,6-Hexamethylene Diisocyanate (HDI)	822-06-0	396	Paint Spray Booth
Methylene Diphenyl Diisocyanate (MDI)	101-68-8	112	Pressed Board Production
Methyl Isocyanate(MI)	624-83-0	228	Not used in production

[a] Estimated detection limits are based on a sample volume of 1 m^3 and a 10-ml sample extraction volume.

1.2 Applicability. Method 326 is a method designed for determining compliance with National Emission Standards for Hazardous Air Pollutants (NESHAP). Method 326 may also be specified by New Source Performance Standards (NSPS), State Implementation Plans (SIPs), and operating permits that require measurement of isocyanates in stationary source emissions, to determine compliance with an applicable emission standard or limit.

1.3 Data Quality Objectives (DQO). The principal objective is to ensure the accuracy of the data at the actual emissions levels and in the actual emissions matrix encountered. To meet this objective, NIST-traceable calibration standards must be used.

2.0 Summary of Method.

2.1 Gaseous and/or aerosol isocyanates are withdrawn from an emission source at an isokinetic sampling rate and are collected in a multicomponent sampling train. The primary components of the train include a

heated probe, three impingers containing derivatizing reagent in toluene, an empty impinger, an impinger containing charcoal, and an impinger containing silica gel.

2.2 The impinger contents are concentrated to dryness under vacuum, brought to volume with acetonitrile (ACN) and analyzed with a high pressure liquid chromatograph (HPLC).

3.0 Definitions.

Reserved

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). This compound may interfere with the resolution of MI from the peak attributed to unreacted 1,2-PP.

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

4.3 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. All these materials must be routinely shown to be free from interferences under conditions of the analysis by preparing and analyzing laboratory method (or reagent) blanks.

4.3.1 Glassware must be cleaned thoroughly before using. The glassware should be washed with laboratory detergent in hot water followed by rinsing with tap water and distilled water. The glassware may be cleaned by baking in a glassware oven at 400 °C for at least one hour. After the glassware has cooled, it should be rinsed three times with methylene chloride and three times with acetonitrile. Volumetric glassware should not be heated to 400 °C. Instead, after washing and rinsing, volumetric glassware may be rinsed with acetonitrile followed by methylene chloride and allowed to dry in air.

4.3.2 The use of high purity reagents and solvents helps to reduce interference problems in sample analysis.

5.0 Safety.

5.1 The toxicity of each reagent has been precisely defined. Organizations performing this method are 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 performing the method. Additional references to laboratory safety are available.

6.0 Equipment and Supplies.

6.1 Sample Collection. A schematic of the sampling train used in this method is shown in Figure 207-1. This sampling train configuration is adapted from Method 5 procedures, and, as such, most of the required equipment is identical to that used in Method 5 determinations. The only new component required is a condenser.

6.1.1 Probe Nozzle. Borosilicate or quartz glass; constructed and calibrated according to Method 5, sections 6.1.1.1 and 10.1, and coupled to the probe liner using a Teflon union; a stainless steel nut is recommended for this union. When the stack temperature exceeds 210 °C (410 °F), a one-piece glass nozzle/liner assembly must be used.

6.1. 2 Probe Liner. Same as Method 5, section 6.1.1.2, except metal liners shall not be used. Water-cooling of the stainless steel sheath is recommended at temperatures exceeding 500 °C (932 °F). Teflon may be used in limited applications where the minimum stack temperature exceeds 120 °C (250 °F) but never exceeds the temperature where Teflon is estimated to become unstable [approximately 210 °C (410 °F)].

6.1.3 Pitot Tube, Differential Pressure Gauge, Filter Heating System, Metering System, Barometer, Gas Density Determination Equipment. Same as Method 5, sections 6.1.1.3, 6.1.1.4, 6.1.1.6, 6.1.1.9, 6.1.2, and 6.1.3.

6.1.4 Impinger Train. Glass impingers are connected in series with leak-free ground-glass joints following immediately after the heated probe. The first impinger shall be of the Greenburg-Smith design with the standard tip. The remaining five impingers shall be of the modified Greenburg-Smith design, modified by replacing the tip with a 1.3-cm (1/2-in.) I.D. glass tube extending about 1.3 cm (1/2 in.) from the bottom of the outer cylinder. A water-jacketed condenser is placed between the outlet of the first impinger and the inlet to the second impinger to reduce the evaporation of toluene from the first impinger.

6.1.5 Moisture Measurement. For the purpose of calculating volumetric flow rate and isokinetic sampling, you must also collect either Method 4 in Appendix A–3 to this part or other moisture measurement methods approved by the Administrator concurrent with each Method 326 test run

6.2 Sample Recovery

6.2.1 Probe and Nozzle Brushes. Polytetrafluoroethylene (PTFE) bristle brushes with stainless steel wire or PTFE handles are required. The probe brush shall have extensions constructed of stainless steel, PTFE, or inert material at least as long as the probe. The brushes shall be properly sized and shaped to brush out the probe liner and the probe nozzle.

6.2.2 Wash Bottles. Three. PTFE or glass wash bottles are recommended; polyethylene wash bottles must not be used because organic contaminants may be extracted by exposure to organic solvents used for sample recovery.

6.2.3 Glass Sample Storage Containers. Chemically resistant, borosilicate amber glass bottles, 500-mL or 1,000-ml. Bottles should be tinted to prevent the action of light on the sample. Screw-cap liners shall be either PTFE or constructed to be leak-free and resistant to chemical attack by organic recovery solvents. Narrow-mouth glass bottles have been found to leak less frequently.

6.2.4 Graduated Cylinder and/or Balances. To measure impinger contents to the nearest 1 ml or 1 g. Graduated cylinders shall have subdivisions not >2 ml.

6.2.5 Plastic Storage Containers. Screw-cap polypropylene or polyethylene containers to store silica gel and charcoal.

6.2.6 Funnel and Rubber Policeman. To aid in transfer of silica gel or charcoal to container (not necessary if silica gel is weighed in field).

6.2.7 Funnels. Glass, to aid in sample recovery.

6.3 Sample Preparation and Analysis.

The following items are required for sample analysis.

6.3.1 Rotary Evaporator. Buchii Model EL-130 or equivalent.

6.3.2 1000 ml Round Bottom Flask for use with a rotary evaporator.

6.3.3 Separatory Funnel. 500-ml or larger, with PTFE stopcock.

6.3.4 Glass Funnel. Short-stemmed or equivalent.

6.3.5 Vials. 15-ml capacity with PTFE lined caps.

6.3.6 Class A Volumetric Flasks. 10-ml for bringing samples to volume after concentration.

6.3.7 Filter Paper. Qualitative grade or equivalent.

6.3.8 Buchner Funnel. Porcelain with 100 mm ID or equivalent.

6.3.9 Erlenmeyer Flask. 500-ml with side arm and vacuum source.

6.3.10 HPLC with at least a binary pumping system capable of a programmed gradient.

6.3.11 Column Systems Column systems used to measure isocyanates must be capable of achieving separation of the target compounds from the nearest eluting compound or interferents with no more than 10 percent peak overlap.

6.5.12 Detector. UV detector at 254 nm. A fluoresence detector (FD) with an excitation of 240 nm and an emission at 370 nm may be also used to allow the detection of low concentrations of isocyanates in samples.

6.3.14 Data system for measuring peak areas and retention times.

7.0 Reagents and Standards.

7.1 Sample Collection Reagents.

7.1.1 Charcoal. Activated, 6-16 mesh. Used to absorb toluene vapors and prevent them from entering the metering device. Use once with each train and discard.

7.1.2 Silica Gel and Crushed Ice. Same as Method 5, sections 7.1.2 and 7.1.4 respectively

7.1.3 Impinger Solution. The impinger solution is prepared by mixing a known amount of 1- (2-pyridyl) piperazine (purity 99.5+ %) in toluene (HPLC grade or equivalent). The actual concentration of 1,2-PP should be approximately four times the amount needed to ensure that the capacity of the derivatizing solution is not exceeded. This amount shall be calculated from the stoichiometric relationship between 1,2-PP and the isocyanate of interest and preliminary information about the concentration of the isocyanate in the stack emissions. A concentration of 130 µg/ml of 1,2-PP in toluene can be used as a reference point. This solution shall be prepared, stored in a refrigerated area away from light, and used within ten days of preparation.

7.2 Sample Recovery Reagents.

7.2.1 Toluene. HPLC grade is required for sample recovery and cleanup (see NOTE to 7.2.2 below).

7.2.2 Acetonitrile. HPLC grade is required for sample recovery and cleanup. 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 before field use and only solvents with a low blank value. Should be used

7.3 Analysis Reagents. Reagent grade chemicals should be used in all tests. All reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.

7.3.1 Toluene, C6H5CH3. HPLC Grade or equivalent.

7.3.2 Acetonitrile, CH3CN (ACN). HPLC Grade or equivalent.

7.3.3 Methylene Chloride, CH2CL2. HPLC Grade or equivalent.

7.3.4 Hexane, C6H14. HPLC Grade or equivalent.

7.3.5 Water, H2O. HPLC Grade or equivalent.

7.3.6 Ammonium Acetate, CH3CO2NH4.

7.3.7 Acetic Acid (glacial), CH3CO2H.

7.3.8 1-(2-Pyridyl)piperazine, (1,2-pp), $\geq$99.5% or equivalent.

7.3.9 Absorption Solution. Prepare a solution of 1-(2-pyridyl)piperazine in toluene at a concentration of 40 mg/300 ml. This solution is used for method blanks and method spikes.

7.3.10 Ammonium Acetate Buffer Solution (AAB). Prepare a solution of ammonium acetate in water at a concentration of 0.1 M by transferring 7.705 g of ammonium acetate to a 1000 ml volumetric flask and diluting to volume with HPLC Grade water. Adjust pH to 6.2 with glacial acetic acid.

8.0 Sample Collection, Storage and Transport.

Note: Because of the complexity of this method, field personnel should be trained in and experienced with the test procedures in order to obtain reliable results.

8.1 Sampling

8.1.1 Preliminary Field Determinations. Same as Method 5, section 8.2.

8.1.2 Preparation of Sampling Train. Follow the general procedure given in Method 5, section 8.1.3, except for the following variations: Place 300 ml of the impinger absorbing solution in the first impinger and 200 ml each in the second and third impingers. The fourth impinger shall remain empty. The fifth and sixth impingers shall have 400 g of charcoal and 200-300 g of silica gel, respectively. Alternatively, the charcoal and silica gel may be combined in the fifth impinger. Setup the train as in Figure 326-1. During assembly, do not use any silicone grease on ground-glass joints.

Note: During preparation and assembly of the sampling train, keep all openings where contamination can occur covered with PTFE film or aluminum foil until just before assembly or until sampling is about to begin.

8.1.3 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, sections 8.4.2 (Pretest Leak-Check), 8.4.3 (Leak-Checks During the Sample Run), and 8.4.4 (Post-Test Leak-Check), with the exception that the pre-test leak-check is mandatory

8.1.4 Sampling Train Operation. Follow the general procedures given in Method 5, section 8.5. Turn on the condenser coil coolant recirculating pump and 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 50°C (122 °F), thus reducing the loss of toluene from the first impinger. For each run, record the data required on a data sheet such as the one shown in Method 5, Figure 5-3.

8.2 Sample Recovery. Allow the probe to cool. When the probe can be handled safely, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over the tip to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling down because this will create a vacuum in the train. Before moving the sample train to the cleanup site, remove the probe from the sample train and cap the open outlet, being careful not to lose any condensate that might be present. Cap the impinger inlet. Remove the umbilical cord from the last impinger and cap the impinger. Transfer the probe and the impinger/condenser assembly to the cleanup area. This area should be clean and protected from the weather to reduce sample contamination or loss. Inspect the train prior to and during disassembly and record any abnormal conditions. It is not necessary to measure the volume of the impingers for the purpose of moisture determination as the method is not validated for moisture determination. Treat samples as follows:

8.2.1 Container No. 1, Probe and Impinger Numbers 1 and 2. Rinse and brush the probe/nozzle first with toluene twice and then twice again with acetonitrile and place the wash into a glass container labeled with the test run identification and "Container No. 1". When using these solvents insure that proper ventilation is available. Quantitatively transfer the liquid from the first two impingers and the condenser into Container No. 1. Rinse the impingers and all connecting glassware twice with toluene and then twice again with acetonitrile and transfer the rinseates into Container No. 1. After all components have been collected in the container, seal the container, and mark the liquid level on the bottle.

8.2.2 Container No. 2, Impingers 3 and 4. Quantitatively transfer the liquid from each impinger into a glass container labeled with the test run identification and "Container No. 2". Rinse each impinger and all connecting glassware twice with toluene and twice again with acetonitrile and transfer the rinseates into Container No. 2. After all components have been collected in the container, seal the container, and mark the liquid level on the bottle and add the proper label.

Note: The contents of the fifth and sixth impinger (silica gel) can be discarded.

8.2.3 Container No. 3, Reagent Blanks. Save a portion of both washing solutions (toluene/acetonitrile) used for the cleanup as a blank. Transfer 200 ml of each solution directly from the wash bottle being used and combine in a glass sample container with the test identification and "Container No. 3". Seal the container, and mark the liquid level on the bottle and add the proper label.

8.2.4 Field Train Proof Blank. To demonstrate the cleanliness of sampling train glassware, you must prepare a full sampling train to serve as a field train proof blank just as it would be prepared for sampling. The field blanks include the sample bottles containing aliquots of sample recovery solvents, and impinger solutions. At a minimum, one complete sampling train will be assembled in the field staging area, taken to the sampling area, and leak-checked at the beginning and end of the testing (or for the same total number of times as the actual test train). The probe of the blank train shall be heated during the sample test. The train will be recovered as if it were an actual test sample. No gaseous sample will be passed through the sampling train. Field blanks are recovered in the same manner as sections 8.2.1 and 8.2.2 and must be submitted with the samples collected at each sampling site.

8.2.5 Field Train Spike. To demonstrate the effectiveness of the sampling train, field handling, and recovery procedures you must prepare a full sampling train to serve as a field train spike just as it would be prepared for sampling with the exception. The field spike is performed in the same manner as the field spike with the additional step of introducing the Field Spike Standard into the first impinger after the initial leak check. The train will be recovered as if it were an actual test sample. No gaseous sample will be passed through the sampling train. Field train spikes are recovered in the same manner as sections 8.2.1 and 8.2.2 and must be submitted with the samples collected for each test program.

8.3 Sample Transport Procedures. Containers must remain in an upright position at all times during shipment. Samples must also be stored at <4°C between the time of sampling and concentration. Each sample should be extracted and concentrated within 30 days after collection and analyzed within 30 days after extraction. The extracted sample must be stored at 4°C.

8.4 Sample Custody. Proper procedures and documentation for sample chain of custody are critical to ensuring data integrity. The chain of custody procedures in ASTM D4840-99 "Standard Guide for Sampling Chain-of-Custody Procedures" shall be followed for all samples (including field samples and blanks).

9.0 Quality Control.

9.1 Sampling. Sampling Operations. See Section 9.0 of Method 5 and the sampling quality control procedures and acceptance criteria are listed in Table 9-1.

9.2 Analysis. The quality assurance program required for this method includes the analysis of the field train proof blank, field train spike, reagent and method blanks. Analytical quality control procedures and acceptance criteria are listed in Table 9-2.

9.2.1 Check for Breakthrough. Recover and determine the isocyanate(s) concentration of the last impinger separately from the first three impingers.

9.2.2 Field Train Proof Blank. Field blanks must be submitted with the samples collected at each sampling site.

9.2.3 Reagent Blank and Field Train Spike. At least one reagent blank and a field train spike must be submitted with the samples collected for each test program.

9.2.4 Determination of Method Detection Limit. Based on your instrument's sensitivity and linearity, determine the calibration concentrations or masses that make up a representative low level calibration range. The MDL must be determined at least annually for the analytical system using an MDL study such as that found in section 15.0 to Method 301 of appendix A to part 63 of this chapter.

Table 9-1 Sampling Quality Assurance and Quality Control

QA/QC Criteria	Acceptance Criteria	Frequency	Consequence if not met
Sampling Equipment Leak Checks	≤0.00057 m3/min (0.020 cfm) or 4% of sampling rate, whichever is less.	Prior to, during (optional) and at the completion to sampling	Prior to: Repair and repeat calibration. During/Completion: None, testing should be considered invalid.
Dry Gas Meter Calibration – Pre-Test (individual correction factor – Yi)	within ±2% of average factor (individual)	Pre-test	Repeat calibration point
Dry Gas Meter Calibration – Pre-Test (average correction factor –Yc)	1.00 ± 1%	Pre-test	Adjust the dry gas meter and recalibrate.
Dry Gas Meter Calibration – Post-test	Average dry gas meter calibration factor agrees with ±5% Yc	Each Test	Adjust sample volumes using the factor that gives the smallest volume.
Temperature sensor calibration	Absolute temperature measures by sensor within ±1.5% of a reference sensor	Prior to initial use and before each test thereafter	Recalibrate; sensor may not be used until specification is met.
Barometer calibration	Absolute pressure measured by instrument within ±10 mm Hg of reading with a mercury barometer or NIST traceable barometer	Prior to initial use and before each test thereafter	Recalibrate; instrument may not be used until specification is met.

Table 9-2 Analytical Quality Assurance and Quality Control

QA/QC Criteria	Acceptance Criteria	Frequency	Consequence if not met
Calibration – Method Blank	<5% level of expected analyte	Each Analytical Blank	Locate source of contamination; reanalyze
Calibration – Calibration Points	At least six calibration point bracketing the expected range of analysis	Each Analytical Batch	Incorporate additional calibration points to meet criteria
Calibration – Linearity	Correlation Coefficient >0.995	Each Analytical Batch	Verify integration, reintegrate. If necessary, recalibrate
Calibration – secondary standard verification	Within ±10% of true value	After each initial calibration	Repeat secondary standard verification, recalibrate if necessary

Calibration – continual calibration verification	Within ±10% of true value	Daily and after every ten samples	Invalidate previous ten sample analysis, recalibrate and repeat independent standard analysis, reanalyze samples until successful.
Sample Analysis	Within the valid calibration range	Each Sample	Invalidate the sample if greater than the calibration range and dilute the sample so that it is within the calibration range. Appropriately flag any value below the calibration range.
Replicate Samples	Within ±10% of RPD	Each Sample	Evaluate integrations and repeat sample analysis as necessary
Field Train Proof Blank	<10% level of expected analyte	Each Test	Evaluate source of contamination.
Field Train Spike	Within ±30% of true value	Each Test	Evaluate Performance of the method and consider invalidating results.
Breakthrough	Final Impinger Mass collected is >5% of the total mass or >20% of the total mass when the measured results are 20% of the applicable standard. Alternatively, there is no breakthrough requirement when the measured results are 10% of the applicable standard	Each Run	Invalidate Test Run

10.0 Calibration and Standardization.

NOTE: Maintain a laboratory log of all calibrations.

10.1 Probe Nozzle, Pitot Tube Assembly, Dry Gas Metering System, Probe Heater, Temperature Sensors, Leak-Check of Metering System, and Barometer. Same as Method 5, sections 10.1, 10.2, 10.3, 10.4, 10.5, 8.4.1, and 10.6, respectively.

10.2 High Performance Liquid Chromatograph. Establish the retention times for the isocyanates of interest will depend on the chromatographic conditions. The retention times provided in Table10-1 are provided as a guide to relative retention times when using a C18, 250 mm x 4.6 mm ID, 5µm particle size

column, a 2 ml/min flow rate of a 1:9 to 6:4 Acetonitrile/Ammonium Acetate Buffer, a 50 µl sample loop, and a uv detector set at 254 nm.

Table 10-1. Retention Times

TCompound	Retention Time (minutes)
MI	10.0
1,6-HDI	19.9
2,4-TDI	27.1
MDI	27.3

10.3 Preparation of Isocyanate Derivatives.

10.3.1 HDI, TDI, MDI. Dissolve 500 mg of each isocyanate in individual 100 ml aliquots of MeCl2, except MDI which requires 250 ml of MeCl2. Transfer a 5-ml aliquot of 1,2-pp (see section 7.3.8) to each solution, stir and allow to stand overnight at room temperature. Transfer 150 ml aliquots of hexane to each solution to precipitate the isocyanate-urea derivative. Using a Buchner funnel, vacuum filter the solid-isocyanate-urea derivative and wash with 50 ml of hexane. Dissolve the precipitate in a minimum aliquot of MeCl2. Repeat the hexane precipitation and filtration twice. After the third filtration, dry the crystals at 50 EC and transfer to bottles for storage. The crystals are stable for at least 21 months when stored at room temperature in a closed container.

10.3.2 MI. Prepare a 200 µg/ml stock solution of methyl isocyanate-urea, transfer 60 mg of 1,2-pp to a 100- ml volumetric flask containing 50 ml of MeCl2. Carefully transfer 20 mg of methyl isocyanate to the volumetric flask and shake for 2 minutes. Dilute the solution to volume with MeCl2 and transfer to a bottle for storage. Methyl isocyanate does not produce a solid derivative and standards must be prepared from this stock solution.

10.4 Preparation of calibration standards. Prepare a 100 µg/ml stock solution of the isocyanates of interest from the individual isocyanate-urea derivative as prepared in sections 10.3.1 and 10.3.2. This is accomplished by dissolving 1 mg of each isocyanate-urea derivative in 10 ml of Acetonitrile. Calibration standards are prepared from this stock solution by making appropriate dilutions of aliquots of the stock into Acetonitrile.

10.5 Preparation of Method Blanks. Prepare a method blank for every ten samples by transferring 300 ml of the absorption solution to a 1000-ml round bottom flask and concentrate as outlined in section 11.2.

10.6 Preparation of Field Spike Solution. Prepare a field spike for every test program is the same manner as calibration standards (see Section 10.4). The spike solution used for the field spike train shall be equivalent to the level that matches the source concentration for each compound, alternatively you may also prepare a solution that represents half the applicable standard.

10.6 HPLC Calibrations. See Section 11.1

11.0 Analytical Procedure.

11.1 Analytical Calibration. Perform a multipoint calibration of the instrument at six or more upscale points over the desired quantitative range (multiple calibration ranges shall be calibrated, if necessary). The field samples analyzed must fall within at least one of the calibrated quantitative ranges and meet the performance criteria specified below. The lowest point in your calibration curve must be at least 5, and preferably 10, times the MDL . For each calibration curve, the value of the square of the linear correlation

coefficient, i.e., r^2, must be ≥0.995, and the analyzer response must be within 10 percent of the reference value at each upscale calibration point. Calibrations must be performed on the day of the analysis, before analyzing any of the samples. Following calibration, a secondary standard shall be analyzed. The measured value of this independently prepared standard must be within ±10 percent of the expected value. Report the results for each calibration standard and the conditions of the HPLC. The reports should include at least the peak area, height, and retention time for each isocyanate compound measured as well chromatogram for each standard.

11.2 Concentration of Samples. Transfer each sample to a 1000-ml round bottom flask. Attach the flask to a rotary evaporator and gently evaporate to dryness under vacuum in a 65 °C water bath. Rinse the round bottom flask three times each with 2 ml of acetonitrile and transfer the rinse to a 10-ml volumetric flask. Dilute the sample to volume with Acetonitrile and transfer to a 15- ml vial and seal with a PTFE lined lid. Store the vial ≤ 4 °C until analysis.

11.3 Analysis. Analyze replicative samples by HPLC, using the appropriate conditions established in section 10.2. The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of the chromatograms. If the peak area exceeds the linear range of the calibration curve, the sample must be diluted with Acetonitrile and reanalyzed. Average the replicate results for each run. For each sample you must report the same information required for analytical calibrations (Section 11.1). For Non-Detect or values below the detection limit of the method, you shall report the value as "<" numerical detection limit.

12.0 Data Analysis and Calculations.

Same as in Method 5, section 6, with the following additions.

12.1 Nomenclature. Same as Method 5, section 6.1 with the following additions:

AS = Response of the sample, area counts.
b = Y-intercept of the linear regression line, area counts.
BR = Percent Breakthrough
C_A = Concentration of a specific isocyanate compound in the initial sample, µg/ml.
C_B = Concentration of a specific isocyanate compound in the replicate sample, µg/ml.
C_I = Concentration of a specific isocyanate compound in the sample, µg/ml.
C_{rec} = Concentration recovered from spike train, µg/ml.
C_S = Concentration of isocyanate compound in the stack gas, µg/dscm
C_T = Concentration of a specific isocyanate compound (Impingers 1-4), µg/dscm
C_{spike} = Concentration spiked, µg/ml.
C_4 = Concentration of a specific isocyanate compound (Impingers 14), µg/dscm
FI_m = Mass of Free Isocyanate
FTS_{rec} = Field Train Spike Recovery
I_m = Mass of the Isocyanate
I_{mw} = MW of the Isocyanate
IU_m = Mass of Isocyanate-urea derivative
IU_{mw} = MW of the isocyanate-urea
M= Slope of the linear regression line, area counts-ml/µg.
m_I = Mass of isocyanate in the total sample MW = Molecular weight
RPD = Relative Percent Difference
VF = Final volume of concentrated sample, typically 10 ml.

Vm_{std} = Volume of gas sample measured by the dry-gas meter, corrected to standard conditions, dscm (dscf).

12.3 Conversion from Isocyanate to the Isocyanate-urea derivative. The equation for converting the amount of free isocyanate to the corresponding amount of isocyanate-urea derivative is as follows:

$$IU_m = I_m \frac{IU_{mw}}{I_{mw}} \qquad \text{Eq. 207-1}$$

The equation for converting the amount of IU derivative to the corresponding amount of FI_m is as follows:

$$I_m = IU_m \frac{I_{mw}}{IU_{mw}} \qquad \text{Eq. 207-2}$$

12.4 Calculate the correlation coefficient, slope, and intercepts for the calibration data using the least squares method for linear regression. Concentrations are expressed as the x-variable and response is expressed as the y-variable.

12.5 Calculate the concentration of isocyanate in the sample:

$$C_I = \frac{As - b}{M} \qquad \text{Eq. 207-3}$$

12.6 Calculate the total amount collected in the sample by multiplying the concentration (µg/ml) times the final volume of Acetonitrile (10 ml).

$$m_I = CI \times V_f \qquad \text{Eq. 207-4}$$

12.7 Calculate the concentration of isocyanate (µg/dscm) in the stack gas.

$$C_s = \frac{M_I}{Vm_{std}} K \qquad \text{Eq. 207-5}$$

12.8 Calculate Relative Percent Difference (RPD) for each replicative sample

$$\%RPD = \left| \frac{(C_A - C_B)}{(C_A + C_B)/2} \right| x\ 100 \qquad \text{Eq. 207-5}$$

12.9 Calculate Field Train Spike Recovery

$$FTS_{rec} = \left[\frac{C_{rec}}{C_{spike}} \right] \text{ x } 100$$

12.10 Calculate Breakthrough Percentage

$$Br = \left[\frac{C_4}{C_T} \right] \text{ x } 100$$

Where as : K = 35.314 ft3/m3 if Vm(std) is expressed in English units. = 1.00 m3/m3 if Vm(std) is expressed in metric units.

13.0 Method Performance.

Evaluation of sampling and analytical procedures for a selected series of compounds must meet the quality control criteria (See Section 9) for each associated analytical determination. The sampling and analytical procedures should be challenged by the test compounds spiked at appropriate levels and carried through the procedures.

14.0 Pollution Prevention.

Reserved

15.0 Waste Management. =

Reserved

16.0 Alternative Procedures

Reserved

17.0 References

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18.0 Diagrams

Figure 326-1 Method 326 Sampling Train