indexed securities are different from interest components stripped from fixed-principal securities and, accordingly, are not interchangeable for reconstitution purposes.

(e) *Applicable regulations.* Unless otherwise provided in this part, notes and bonds stripped into their STRIPS components are governed by subparts A, B, and D of part 357 of this chapter.

4. Appendix B to part 356 is amended by revising the list of section headings at the beginning of the appendix to read as follows:

Appendix B to Part 356—Formulas and Tables

I. Computation of Interest on Treasury Bonds and Notes.
II. Formulas for Conversion of Fixed-Principal Security Yields to Equivalent Prices.
III. Formulas for Conversion of Inflation-Indexed Security Yields to Equivalent Prices.
IV. Computation of Adjusted Values and Payment Amounts for Stripped Inflation-Indexed Interest Components.
V. Computation of Purchase Price, Discount Rate, and Investment Rate (Coupon-Equivalent Yield) for Treasury Bills.

* * * * *

5. Appendix B to Part 356 is amended by redesignating Section IV as Section V and adding a new Section IV to read as follows:

* * * * *

IV. Computation of Adjusted Values and Payment Amounts for Stripped Inflation-Indexed Interest Components

Note: Valuing an interest component stripped from an inflation-indexed security at its adjusted value enables this interest component to be interchangeable (fungible) with other interest components that have the same maturity date, regardless of the underlying inflation-indexed security from which the interest components were stripped. The adjusted value provides for fungibility of these various interest components when buying, selling, or transferring them, or when reconstituting an inflation-indexed security.

Definitions

C=the regular annual interest rate, payable semiannually, e.g., 3.625% (the decimal equivalent of a 3–⅝% interest rate)
Par=par amount of the security to be stripped
Ref $CPI_{Issue\ Date}$=reference CPI for the original issue date (or dated date, when the dated date is different from the original issue date) of the underlying (unstripped) security
Ref CPI_{Date}=reference CPI for the maturity date of the interest component
AV=adjusted value of the interest component
PA=payment amount at maturity by Treasury

Formulas

AV=Par (C/2)(100/Ref $CPI_{Issue\ Date}$) (rounded to 2 decimals with no intermediate rounding)
PA=AV (Ref CPI_{Date}/100) (rounded to 2 decimals with no intermediate rounding)

Example. A 10-year inflation-indexed note paying 3½% interest is issued on January 15, 1999, with the second interest payment on January 15, 2000. The Ref CPI on January 15, 1999 (Ref $CPI_{Issue\ Date}$) is 174.62783, and the Ref CPI on January 15, 2000 (Ref CPI_{Date}) is 179.86159. Calculate the adjusted value and the payment amount at maturity of the interest component.

Definitions

C=3.50%
Par=$1,000,000
Ref $CPI_{Issue\ Date}$=174.62783
Ref CPI_{Date}=179.86159

Resolution

For a par amount of $1 million, the adjusted value of each stripped interest component is $1,000,000 (.035/2)(100/174.62783), or $10,021.31 (no intermediate rounding).

For an interest component maturing on January 15, 2000, the payment amount is $10,021.31×(179.86159/100), or $18,024.49 (no intermediate rounding).

* * * * *

6. Exhibit C to Part 356 is amended by revising the heading to read as follows:

Exhibit C to Part 356—Minimum Par Amounts for Fixed-Principal STRIPS

* * * * *

[FR Doc. 97–31953 Filed 12–5–97; 8:45 am]
BILLING CODE 4810–39–P

ENVIRONMENTAL PROTECTION AGENCY

40 CFR Part 51

[FRL–5930–6]

RIN 2060–AG88

Preparation, Adoption, and Submittal of State Implementation Plans; Appendix M, Test Method 207

AGENCY: Environmental Protection Agency (EPA).

ACTION: Proposed rule and notice of public hearing.

SUMMARY: The purpose of this proposed rule is to add a validated stationary source test method for the measurement of isocyanate emissions from stationary sources to the Code of Federal Regulations. This method, validated according to EPA Method 301 criteria, would be used to reliably collect and analyze gaseous isocyanate emissions from stationary sources such as flexible foam manufacturers, automobile paint spray booths, and the pressed board industry. Specifically, methylene diphenyl diisocyanate (MDI), methyl isocyanate (MI), hexamethylene 1,6-diisocyanate (HDI), and 2,4-toluene diisocyanate (TDI) are the gaseous pollutants in source emissions to be measured. The test method is entitled, ''A Method for Measuring Isocyanates in Stationary Source Emissions,'' and will be added to 40 CFR Part 51, Appendix M, as Test Method 207. This method will provide a tool for state and local governments, representatives of private industry, and the U.S. Government to reliably monitor stationary sources for isocyanate emissions with a validated stationary source method. Additionally, this method will allow the U.S. Environmental Protection Agency to comply with the requirements of the Clean Air Act Amendments of 1990 for monitoring these hazardous air pollutants. Prior to the development of this method, no other ''validated'' method has been available to monitor these highly reactive hazardous emissions. Isocyanates are used extensively in the production of polyurethane materials such as flexible foam, enamel wire coatings, paint formulations, and in binders for the pressed board industry. A public hearing will be held, if requested, to provide interested persons an opportunity for oral presentation of data, views, or arguments concerning the proposed method.

DATES: *Comments.* Comments must be received on or before February 23, 1998.

Public Hearing. If anyone contacts EPA requesting to speak at a public hearing by December 29, 1997, a public hearing will be held January 22, 1998 beginning at 10:00 a.m. Persons interested in attending the hearing should call the contact mentioned under **ADDRESSES** to verify that a meeting will be held.

Request to Speak at Hearing. Persons wishing to present oral testimony must contact EPA by December 29, 1997.

ADDRESSES: *Comments.* Comments should be submitted (in duplicate if possible) to: Central Docket Section (Mail Code: 6102), Attention: Docket Number A–96–06, U.S. Environmental Protection Agency, Room M–1500, First Floor, Waterside Mall, 401 M Street, S.W., Washington, D.C. 20460.

Public Hearing. If anyone contacts EPA requesting a public hearing, it will be held at EPA's Emission Measurement Center, Research Triangle Park, North Carolina. Persons interested in attending the hearing or wishing to present oral testimony should notify Frank Wilshire, Methods Branch (MD–44), Air

Measurements Research Division, National Exposure Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, telephone number (919) 541–2785.

Docket. Docket No. A–96–06, containing materials relevant to this rulemaking, is available for public inspection and copying between 8:00 a.m. and 5:30 p.m., Monday through Friday, at EPA's Air Docket Section, Room M–1500, First Floor, Waterside Mall, 401 M Street, S.W., Washington, D.C. 20460. A reasonable fee may be charged for copying.

FOR FURTHER INFORMATION CONTACT: Frank Wilshire, at the address listed under *Public Hearing,* or Gary McAlister, Source Characterization Group B (MD–19), Emissions Monitoring and Analysis Division, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, telephone number (919) 541–1062.

SUPPLEMENTARY INFORMATION:

I. The Rulemaking

A. Summary of Proposed Method

The U.S. Environmental Protection Agency, under the authority of Title III of the Clean Air Act Amendments of 1990, requires the development of a validated (per EPA Method 301 criteria) stationary source sampling and analysis method for the following isocyanates: methyl isocyanate, methylene diphenyl diisocyanate, hexamethylene 1,6-diisocyanate, and 2,4-toluene diisocyanate. The isocyanate sampling method developed is a modification of the EPA Method 5 sampling train (no filter and the addition of impingers), employing impingers and a derivatizing reagent [1-(2-pyridyl)piperazine in toluene] to immediately stabilize the isocyanates upon collection. Collected samples are analyzed under laboratory conditions sufficient to separate and quantify the isocyanates, using high performance liquid chromatography with ultra violet detection.

B. Comments and Responses on Draft

The proposed method is available by request. Requests should be made to: Frank Wilshire (MD–44), Methods Branch, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711. To date, over thirty-five copies of the isocyanate method have been requested by representatives of the private sector, state and local governments, industry trade associations, and the Canadian Government.

On June 7, 1995 a presentation was made before members of the Analytical and Environmental Subcommittee of the International Isocyanate Institute to review the method and address the timetable and procedure for including the isocyanate method in the Code of Federal Regulations (CFR). Members of the Subcommittee were enthusiastic about the method and inquired when it might be included in the Code of Federal Regulations. To date, no technical comments have been received from other sources. Oral comments have been received by many of those requesting copies of the method, suggesting publication of the method in the CFR. This action would establish a reference method for the collection and analysis of isocyanates from stationary sources and aid in standardizing monitoring of isocyanate emissions from these sources.

II. Administrative Requirements

A. Public Hearing

A public hearing will be held, if requested, to discuss the proposed rulemaking in accordance with Section 307(d)(5) of the Clean Air Act. Persons wishing to make oral presentations should contact EPA at the address given in the **ADDRESSES** section of this preamble. Oral presentation will be limited to 15 minutes each. Any member of the public may file a written statement with the EPA before, during, or within 30 days after the hearing. Written statements should be addressed to the Central Air Docket Section address given in the **ADDRESSES** section of this preamble.

A verbatim transcript of the hearing and written statements will be available for public inspection and copying during normal working hours at EPA's Central Air Docket Section in Washington, D.C. (see **ADDRESSES** section of this preamble).

B. Docket

The docket is an organized and complete file of all the information submitted to or otherwise considered by the EPA in the development of this proposed rulemaking. The principal purposes of the docket are to: (1) Allow interested parties to identify and locate documents so that they can effectively participate in the rulemaking process, and (2) serve as the record in case of judicial review except for interagency review materials [Section 307(d)(7)(A)].

C. Office of Management and Budget Review

Under Executive Order 12866 (58 FR 51735, October 4, 1993), the EPA is required to judge whether a regulation is ''significant'' and therefore subject to Office of Management and Budget (OMB) review and the requirements of this Executive Order to prepare a regulatory impact analysis. The Order defines ''significant regulatory action'' as one that is likely to result in a rule that may: (1) Have an annual effect on the economy of $100 million or more or adversely affect in a material way the economy, a sector of the economy, productivity, competition, jobs, the environment, public health or safety, or State, local, or tribal governments or communities; (2) create a serious inconsistency or otherwise interfere with an action taken or planned by another agency; (3) materially alter the budgetary impact of entitlements, grants, user fees, or loan programs, or the rights and obligation of recipients thereof; or (4) raise novel legal or policy issues arising out of legal mandates, the President's priorities, or the principles set forth in the Executive Order. Pursuant to the terms of the Executive Order, this action has been determined to be ''not significant.''

D. Regulatory Flexibility Act Compliance

The Regulatory Flexibility Act (RFA) generally requires an agency to conduct a regulatory flexibility analysis of any rule subject to notice and comment rulemaking requirements unless that Agency certifies that the rule will not have a significant economic impact on a substantial number of small entities. Small entities include small businesses, small not-for-profit enterprises, and small governmental jurisdictions. This proposed rule would not have a significant impact on a substantial number of small entities because the overall impact of these amendments is a net decrease in requirements on all entities including small entities. Therefore, I certify that this action will not have a significant economic impact on a substantial number of small entities.

E. Paperwork Reduction Act

The rule does not change any information collection requirements subject of Office of Management and Budget review under the Paperwork Reduction Act of 1980, 44 U.S.C. 3501 *et seq.*

F. Unfunded Mandates

Under Section 202 of the Unfunded Mandates Reform Act of 1995 (''Unfunded Mandates Act''), signed into law on March 22, 1995, EPA must prepare a budgetary impact statement to accompany any proposed or final rule

that includes a Federal mandate that may result in estimated costs to State, local, or tribal governments in the aggregate; or to the private sector, of $100 million or more. Under Section 205, EPA must select the most cost-effective and least burdensome alternative that achieves the objectives of the rule and is consistent with statutory requirements. Section 203 requires EPA to establish a plan for significantly or uniquely impacted by the rule.

EPA has determined that the action proposed today does not include a Federal mandate that may result in estimated costs of $100 million or more to either State, local, or tribal governments in the aggregate, or to the private sector, nor does this action significantly or uniquely impact small governments, because this action contains no requirements that apply to such governments or impose obligations upon them. Therefore, the requirements of the Unfunded Mandates Act do not apply to this action.

List of Subjects in 40 CFR Part 51

Environmental protection, Air pollution control, Hazardous air pollutants, Polyurethane production, Flexible foam manufacturing, Enamel wire coatings, Manufactured wood products, Isocyanates.

Dated: November 25, 1997.

Carol M. Browner,

Administrator.

It is proposed that 40 CFR part 51 be amended to read as follows:

1. The authority citation for part 51 continues to read as follows:

Authority: 42 U.S.C. 7401, 7411, 7412, 7413, 7414, 7470–7479, 7501–7508, 7601, and 7602.

2. Appendix M to part 51 is amended by adding Method 207 in numerical order to read as follows:

Appendix M to Part 51—Recommended Test Methods for State Implementation Plans

* * * * *

Method 207—A Method for Measuring Isocyanates in Stationary Source 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 Method 1, Method 2, Method 3, and Method 5 found in Part 60 of this title.

1.0 Scope and Application.

1.1 This method is applicable to the collection and analysis of isocyanate compounds from the emissions associated with manufacturing processes. The following is a list of the isocyanates and the manufacturing process at which the method has been evaluated:

Compound name	CAS No.	Detection limits [a] (ng/m³)	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)	624–83–9	228	Not used in production.

[a] Estimated detection limits are based on a sample volume of 1 m³ and a 10-ml sample extraction volume.

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 the 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. 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). 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 coelute 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, the glassware 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 ACN 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. Each isocyanate can produce dangerous levels of hydrogen cyanide (HCN). 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 following items are required for sample collection:

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

6.1.2 Construction details for the basic train components are given in APTD–0581 (see Martin, 1971, in Section 16.0, References); commercial models of this equipment are also available. Additionally, the following subsections list changes to APTD–0581 and identify allowable train configuration modifications.

6.1.3 Basic operating and maintenance procedures for the sampling train are described in APTD–0576 (see Rom, 1972, in Section 16.0, References). As correct usage is important in obtaining valid results, all users

should refer to APTD–0576 and adopt the operating and maintenance procedures outlined therein unless otherwise specified. The sampling train consists of the components detailed below.

6.1.3.1 Probe Nozzle. Glass with sharp, tapered (30° angle) leading edge. The taper shall be on the outside to preserve a constant internal diameter. The nozzle shall be buttonhook or elbow design. A range of nozzle sizes suitable for isokinetic sampling should be available in increments of 0.16 cm (1/16 in.), e.g., 0.32–1.27 cm (1/8–1/2 in.), or larger if higher volume sampling trains are used. Each nozzle shall be calibrated according to the procedures outlined in Paragraph 10.1.

6.1.3.2 Probe liner. Borosilicate or quartz-glass tubing with a heating system capable of maintaining a probe gas temperature of 120±14 °C (248±25 °F) at the exit end during sampling. (The tester may opt to operate the equipment at a temperature lower than that specified.) Because the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD–0581 and using the calibration curves of APTD–0576 (or calibrated according to the procedure outlined in APTD–0576) are considered acceptable. Either borosilicate or quartz glass probe liners may be used for stack temperatures up to about 480 °C (900 °F). Quartz glass liners shall be used for temperatures between 480 and 900 °C (900 and 1650 °F). (The softening temperature for borosilicate is 820 °C (1508 °F), and for quartz glass 1500 °C (2732 °F).) Water-cooling of the stainless steel sheath will be necessary at temperatures approaching and exceeding 500 °C.

6.1.3.3 Pitot tube. Type S, as described in Section 2.1 of promulgated EPA Method 2 or other appropriate devices (see Vollaro, 1976 in Section 16.0, References). The pitot tube shall be attached to the probe to allow constant monitoring of the stack-gas velocity. The impact (high-pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see EPA Method 2, Figure 2–6b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 4.0 of promulgated EPA Method 2.

6.1.3.4 Differential Pressure Gauge. Inclined manometer or equivalent device as described in Section 2.2 of promulgated EPA Method 2. One manometer shall be used for velocity-head (delta P) readings and the other for orifice differential pressure (delta H) readings.

6.1.3.5 Impinger Train. Six 500 mL 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. The first, second and third impingers shall contain known quantities of the derivatizing reagent in toluene with the first impinger containing 300 mL and 200 mL in the second and third. The fourth impinger remains empty. The fifth impinger is filled with a known amount (2/3 full) of activated charcoal and the sixth with a known amount of desiccant. 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.

6.1.3.6 Metering System. The necessary components are a vacuum gauge, leak-free pump, temperature sensors capable of measuring temperature to within 3 °C (5.4 °F), dry-gas meter capable of measuring volume to within 1%, and related equipment, as shown in Figure 207–1. At a minimum, the pump should be capable of four cubic feet per minute (cfm) free flow, and the dry-gas meter should have a recording capacity of 0–999.9 cubic feet (cu ft) with a resolution of 0.005 cu ft. Other metering systems capable of maintaining sampling rates within 10% of isokineticity and of determining sample volumes to within 2% may be used. The metering system must be used with a pitot tube to enable checks of isokinetic sampling rates. Sampling trains using metering systems designed for flow rates higher than those described in APTD–0581 and APTD–0576 may be used, if the specifications of this method are met.

6.1.3.7 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). Often 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).

6.1.3.8 Gas density determination equipment. Temperature sensor and pressure gauge (as described in Sections 2.3 and 2.4 of EPA Method 2, and gas analyzer, if necessary (as described in EPA Method 3). The temperature sensor ideally should be permanently attached to the pitot tube or sampling probe in a fixed configuration such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just before use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see promulgated EPA Method 2, Figure 2–7. As a second alternative, if a difference of no more than 1% in the average velocity measurement is to be introduced, the temperature sensor need not be attached to the probe or pitot tube.

6.1.3.9 Calibration/Field-Preparation Record. A permanent 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 (i.e., silica gel tare weights, quality assurance/quality control check results, dry-gas meter, and thermocouple calibrations, etc.). The duplicate copies should be detachable and should be stored separately in the test program archives.

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

6.2.1 Probe Liner. Probe and nozzle brushes; Teflon® bristle brushes with stainless steel wire or Teflon® handles are required. The probe brush shall have extensions constructed of stainless steel, Teflon®, 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. 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.

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 Teflon® 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. Laboratory balances capable of weighing to ±0.5 g or better are required.

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 Crushed Ice. Quantities ranging from 10–50 lb may be necessary during a sampling run, depending on ambient air temperature.

6.4 Stopcock Grease. The use of silicone grease is not permitted. Silicone grease usage is not necessary if screw-on connectors and Teflon® sleeves or ground-glass joints are used.

6.5 Sample Analysis. The following items are required for sample analysis.

6.5.1 Rotary Evaporator. Buchii Model EL–130 or equivalent.

6.5.2 1000 ml round bottom flask for use with a rotary evaporator.

6.5.3 Separatory Funnel. 500-ml or larger, with Teflon® Stopcock.

6.5.4 Glass Funnel. Short stemmed or equivalent.

6.5.5 Vials. 15-ml capacity with Teflon® lined caps.

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

6.5.7 Filter Paper. Scientific Products Grade 370 Qualitative or equivalent.

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

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

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

6.5.11 Column. Alltech Altima C18, 250 mm × 4.6 mm ID, 5µm particle size (or equivalent).

6.5.12 Guard Column. Alltech Hypersil ODS C18, 10 mm × 4.6 mm ID, 5µm particle size (or equivalent).

6.5.13 UV detector at 254 nm.

6.5.14 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. Indicating type, 6–16 mesh. If previously used, dry at 175 °C (350 °F) for 2 hours before using. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

7.1.3 Impinger Solution. The impinger solution is prepared in the laboratory 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 should be prepared in the laboratory, stored in a refrigerated area away from light, and used within ten days of preparation.

7.2 Sample Recovery Reagents.

7.2.1 Toluene. 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.

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 (<0.001%) shall be used.

7.3 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, $C_6H_5CH_3$. HPLC Grade or equivalent.

7.3.2 Acetonitrile, CH_3CN (ACN). HPLC Grade or equivalent.

7.3.3 Methylene Chloride, CH_2CL_2. HPLC Grade or equivalent.

7.3.4 Hexane, C_6H_{14}. Pesticide Grade or equivalent.

7.3.5 Water, H_2O. HPLC Grade or equivalent.

7.3.6 Ammonium Acetate, $CH_3CO_2NH_4$.

7.3.7 Acetic Acid (glacial), CH_3CO_2H.

7.3.8 1-(2-Pyridyl) piperazine, (1,2-pp). Aldrich, 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, Preservation, Storage and Transport.

8.1 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.

8.2 Preliminary Field Determinations.

8.2.1 Select the sampling site and the minimum number of sampling points according to EPA Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and range of velocity heads using EPA Method 2. It is recommended that a leak-check of the pitot lines (see promulgated EPA Method 2, Section 3.1) be performed. 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. 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 the range of velocity heads so that changing the nozzle size in order to maintain isokinetic sampling rates is not necessary. During the run, do not change the nozzle. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of promulgated EPA Method 2).

8.2.3 Select a suitable probe liner and probe length so that all traverse points can be sampled. For large stacks, to reduce the length of the probe, consider sampling from opposite sides of the stack.

8.2.4 A typical sample volume to be collected is 1 dscm (35.31 dscf). The sample volume can be adjusted as required 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 Determine the total length of sampling time needed to obtain the identified minimum volume by comparing the anticipated average sampling rate with the volume requirement. Allocate the same time to all traverse points defined by EPA Method 1. To avoid timekeeping errors, the length of time sampled at each traverse point should be an integer or an integer plus one-half min.

8.2.6 In some circumstances (e.g., batch cycles) sampling for shorter times at the traverse points may be necessary and to obtain smaller gas-sample volumes. In these cases, the Administrator's approval must first be obtained.

8.3 Preparation of Sampling Train.

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

8.3.2 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 preweighed charcoal and 200–300 g of silica gel, respectively.

8.3.3 When glass probe liners are used, install the selected nozzle using a Viton®-A O-ring when stack temperatures are <260 °C (500 °F) and a woven glass-fiber gasket when temperatures are higher. See APTD–0576 (Rom, 1972) for details. Other connecting systems using Teflon® ferrules may be used. Mark the probe with heat-resistant tape or by another method to denote the proper distance into the stack or duct for each sampling point.

8.3.4 Set up the train as shown in Figure 207–1. During assembly, do not use any silicone grease on ground-glass joints. Connect all temperature sensors to an appropriate potentiometer/display unit. Check all temperature sensors at ambient temperature.

8.3.5 Place crushed ice around the impingers.

8.3.6 Turn on the condenser coil coolant recirculating pump and begin monitoring 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.

8.3.7 Turn on and set the probe heating systems at the desired operating temperatures. Allow time for the temperature to stabilize.

8.4 Leak-Check Procedures.

8.4.1 Pre-test leak-check.

8.4.1.1 Because the additional connection in the train (over the EPA Method 5 Train) increases the possibility of leakage, a pre-test leak-check is required.

8.4.1.2 After the sampling train has been assembled, turn on and set the probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton® A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 381-mm Hg (15-in. Hg) vacuum. Leakage rates greater than 4% of the average sampling rate or >0.00057 m^3/min (0.020 cfm), whichever is less, are unacceptable.

Note: A lower vacuum may be used, if it is not exceeded during the test.

8.4.1.3 The following leak-check instructions for the sampling train described in APTD–0576 and APTD–0581 may be helpful. Start the pump with the fine-adjust valve fully open and the coarse-adjust valve completely closed. Partially open the coarse-adjust valve and slowly close the fine-adjust valve until the desired vacuum is reached. Do *not* reverse direction of the fine-adjust valve; this will cause impinger contents to back up in the train. If the desired vacuum is exceeded, either leak-check at this higher

vacuum or end the leak-check, as shown below, and start over.

8.4.1.4 When the leak-check is completed, first slowly remove the plug from the inlet to the probe. When the vacuum drops to 127 mm (5 in.) Hg or less, immediately close the coarse-adjust valve. Switch off the pumping system and reopen the fine-adjust valve. Do not reopen the fine-adjust valve until the coarse-adjust valve has been closed. This prevents the reagent in the impingers from being forced backward into the probe and silica gel from being entrained backward into the fifth impinger.

8.4.2 Leak-Checks During Sampling Run.

8.4.2.1 If, during the sampling run, a component change becomes necessary, a leak-check shall be conducted immediately after the interruption of sampling and before the change is made. The leak-check shall be done according to the procedure outlined in Paragraph 8.4.1, except that it shall be done at a vacuum greater than or equal to the maximum value recorded up to that point in the test. If the leakage rate is no greater than 0.00057 m^3/min (0.020 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered. If a higher leakage rate is obtained, the tester shall void the sampling run.

Note: Any ''correction'' of the sample volume by calculation reduces the integrity of the pollutant concentration data generated and must be avoided.

8.4.2.2 Immediately after a component change, and before sampling is restarted, a leak-check similar to a pre-test leak-check must also be conducted.

8.4.3 Post-Test Leak-Check.

8.4.3.1 A leak-check of the sampling train is mandatory at the conclusion of each sampling run. The leak-check shall be performed with the same procedures as those with the pre-test leak-check, except that it shall be conducted at a vacuum greater than or equal to the maximum value reached during the sampling run. If the leakage rate is no greater than 0.00057 m^3/min (0.020 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate, correct the sample volume (as shown in Section 6.3 of Method 5), and consider the data obtained of questionable reliability, or void the sampling run.

8.5 Sampling-Train Operation.

8.5.1 During the sampling run, maintain an isokinetic sampling rate to within 10% of true isokinetic, unless otherwise specified by the Administrator.

8.5.2 For each run, record the data required on a data sheet such as the one shown in Figure 207–2. Be sure to record the initial dry-gas meter reading. Record the dry-gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made before and after each leak-check, and when sampling is halted. Take other readings shown by Figure 207–2 at least once at each sample point during each time increment and additional readings when significant changes (20% variation in velocity-head readings) require additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

8.5.3 Clean the stack access ports before the test run to eliminate the chance of collecting deposited material. To begin sampling, verify that the probe heating system is at the specified temperature, remove the nozzle cap, and verify that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point, with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations, are available. These nomographs are designed for use when the Type S pitot-tube coefficient is 0.84±0.02 and the stack-gas equivalent density (dry molecular weight) is equal to 29±4. APTD–0576 details the procedure for using the nomographs. If the stack-gas molecular weight and the pitot-tube coefficient are outside the above ranges, do not use the nomographs unless appropriate steps (Shigehara, 1974, in Section 16.0, References) are taken to compensate for the deviations.

8.5.4 When the stack is under significant negative pressure (equivalent to the height of the impinger stem), take care to close the coarse-adjust valve before inserting the probe into the stack, to prevent the impinger solutions from backing into the probe. If necessary, the pump may be turned on with the coarse-adjust valve closed.

8.5.5 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.

8.5.6 Traverse the stack cross section, as required by EPA Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the access port, in order to reduce the chance of extracting deposited material.

8.5.7 During the test run, make periodic adjustments to keep the temperature of the condenser at the proper levels; add more ice and, if necessary, salt to maintain the temperature. Also, periodically check the level and zero of the manometer.

8.5.8 A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or in cases where equipment failure requires a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

8.5.9 At the end of the sample run, close the coarse-adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry-gas meter reading, and conduct a post-test leak-check. Also, leak-check the pitot lines as described in EPA Method 2. The lines must pass this leak-check in order to validate the velocity-head data.

8.5.10 Calculate percent isokineticity (see Section 6.11 of Method 5) to determine whether the run was valid or another test run should be performed.

8.6 Sample Recovery.

8.6.1 Preparation.

8.6.1.1 Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. 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.

8.6.1.2 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.

8.6.1.3 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.

8.6.1.4 Save a portion of all 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 place each in a separate, prelabeled glass sample container.

8.6.1.5 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. With the aid of an assistant, rinse the probe/nozzle first with toluene and then with acetonitrile by tilting and rotating the probe while squirting the solvent into the upper end of the probe so that all of the surfaces are wetted with solvent. When using these solvents insure that proper ventilation is available. Let the solvent drain into the container. If particulate is visible, use a Teflon® brush to loosen/remove the particulate and follow with a second rinse of each solvent. After weighing the contents of the first impinger, add it to container No. 1 along with the toluene and acetonitrile rinses of the impinger. (Acetonitrile will always be the final rinse.) If two liquid layers are present add both to the container. After all components have been collected in the container, seal the container, mark the liquid level on the bottle and add the proper label.

8.6.2.2 Container No. 2. After weighing the contents of the second, third and fourth impingers, add them to container No. 2 along with the toluene and acetonitrile rinses of the impingers, the condenser and all connecting glassware. After all components have been collected in the container, seal the container, mark the liquid level on the bottle and add the proper label.

8.6.3 The contents of the fifth and sixth impingers (charcoal and silica gel) can be discarded after they have been weighed.

8.6.4 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, packed in ice, using the proper shipping materials as prescribed for hazardous materials. The samples must 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.

9.0 Quality Control.

9.1 Sampling. See EPA Manual 600/4–77–027b for Method 5 quality control.

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 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.

9.1.2 Reagent Blanks. An aliquot of toluene, acetonitrile and the impinger solution will be collected in the field as separate samples and returned to the laboratory for analysis to evaluate artifacts that may be observed in the actual samples.

9.2 Analysis.

9.2.1 The correlation coefficient for the calibration curve must be 0.995 or greater. If the correlation coefficient is less than 0.995, the HPLC system should be examined for problems, and a new calibration curve should be prepared and analyzed.

9.2.2 A solvent blank should be analyzed daily to verify that the system is not contaminated.

9.2.3 A calibration standard should be analyzed prior to any samples being analyzed, after every 10 injections and at the end of the sample set. Samples must be bracketed by calibration standards that have a response that does not vary by more than 10% of the target value. If the calibration standards are outside the limit, the samples must be reanalyzed after it is verified that the analytical system is in control.

9.2.4 A method blank should be prepared and analyzed for every 10 samples concentrated (Section 11.4).

9.2.5 A method spike should be prepared and analyzed for every 20 samples. The response for each analyte should be within 20% of the expected theoretical value of the method spike (Section 11.3).

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.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

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, 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 Metering System.

10.3.1 Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD–0576. Instead of physically adjusting the dry-gas meter dial readings to correspond to the wet-test meter readings, calibration factors may be used to correct the gas meter dial readings mathematically to the proper values. Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: Make a 10-min calibration run at 0.00057 m^3/min (0.020 cfm); at the end of the run, take the difference of the measured wet-test and dry-gas meter volumes and divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.020 cfm).

10.3.2 After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single intermediate orifice setting (based on the previous field test). The vacuum shall be set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet-test meter and the inlet of the metering system. Calculate the average value of the calibration factor. If the calibration has changed by more than 5%, recalibrate the meter over the full range of orifice settings, as outlined in APTD–0576.

10.3.3 Leak-check of metering system. That portion of the sampling train from the pump to the orifice meter (see Figure 207–1) should be leak-checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13–18 cm (5–7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for 1 min. A loss of pressure on the manometer indicates a leak in the meter box. Leaks, if present, must be corrected.

Note: If the dry-gas-meter coefficient values obtained before and after a test series differ by >5%, either the test series shall be voided or calculations for test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

10.4 Probe Heater. The probe-heating system shall be calibrated before its initial use in the field according to the procedure outlined in APTD–0576. Probes constructed according to APTD–0581 need not be calibrated if the calibration curves in APTD–0576 are used.

10.5 Temperature Sensors. Each thermocouple must be permanently and uniquely marked on the casing; all mercury-in-glass reference thermometers must conform to ASTM E–1 63 specifications. Thermocouples should be calibrated in the laboratory with and without the use of extension leads. If extension leads are used in the field, the thermocouple readings at ambient air temperatures, with and without the extension lead, must be noted and recorded. Correction is necessary if the use of an extension lead produces a change >1.5%.

10.5.1 Dry-gas meter thermocouples. For the thermocouples used to measure the temperature of the gas leaving the impinger train three-point calibration at ice-water, room-air, and boiling-water temperatures is necessary. Accept the thermocouples only if the readings at all three temperatures agree to ±2°C (3.6°F) with those of the absolute value of the reference thermometer.

10.5.2 Probe and stack thermocouples. For the thermocouples used to indicate the probe and stack temperatures, a three-point calibration at ice-water, boiling-water, and hot-oil-bath temperatures must be performed; it is recommended that room-air temperature be added, and that the thermometer and the thermocouple agree to within 1.5% at each of the calibration points. A calibration curve (equation) may be constructed (calculated) and the data extrapolated to cover the entire temperature range suggested by the manufacturer.

10.6 Barometer. Adjust the barometer initially and prior to each test series to agree to within ±2.5 mm Hg (0.1 in. Hg) of the mercury barometer or the corrected barometric pressure value reported by a nearby National Weather Service Station (same altitude above sea level).

10.7 Balance. Calibrate the balance before each test series, using Class-S standard weights; the weights must be within ±0.5% of the standards, or the balance must be adjusted to meet these limits.

10.8 High Performance Liquid Chromatograph. Establish the retention times for each of the isocyanates of interest using the chromatographic conditions provided in Section 11.5.1. The retention times provided in Table 11.5.1–1 are provided as a guide to relative retention times. Prepare derivatized calibration standards (concentrations expressed in terms of the free isocyanate, Section 12.4) according to the procedure in Section 10.8.1. Calibrate the chromatographic system using the external standard technique (Section 10.8.2)

10.8.1 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 11.1.1 and 11.1.2. This is accomplished by dissolving 1 mg of each isocyanate-urea derivative in 10 ml of ACN. Calibration standards are prepared from this stock solution by making appropriate dilutions of aliquots of the stock into ACN. Calibrate the instrument from 1 to 20 µg/ml for HDI, TDI and MDI, and from 1 to 80 µg/ml for MI using at least six calibration points.

10.8.2 External standard calibration procedure. Analyze each derivatized

calibration standard using the chromatographic conditions listed in Section 11.5.1 and tabulate peak area against concentration injected. The working calibration curve must be verified on each working day by the measurement of one or more calibration standards. If the response for any analyte varies from the target response by more than 10%, the test must be repeated using a fresh calibration standard(s) after it is verified that the analytical system is under control. Alternatively, a new calibration curve may be prepared for that compound.

11.0 Analytical Procedure.

11.1 Preparation of isocyanate derivatives.

11.1.1 HDI, TDI, MDI.

11.1.1.1 Dissolve 500 mg of each isocyanate in individual 100 ml aliquots of $MeCl_2$, except MDI which requires 250 ml of $MeCl_2$. 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 $MeCl_2$. Repeat the hexane precipitation and filtration twice. After the third filtration, dry the crystals at 50 °C and transfer to bottles for storage. The crystals are stable for at least 21 months when stored at room temperature in a closed container.

11.1.2 MI.

11.1.2.1 To 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 $MeCl_2$. Carefully transfer 20 mg of methyl isocyanate to the volumetric flask and shake for 2 minutes. Dilute the solution to volume with $MeCl_2$ and transfer to a bottle for storage. Methyl isocyanate does not produce a solid derivative and standards must be prepared from this stock solution.

11.2 Concentration of Samples.

11.2.1 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 two ml of ACN and transfer the rinse to a 10-ml volumetric flask. Dilute the sample to volume with ACN and transfer to a 15-ml vial and seal with a Teflon® lined lid. Store the vial at 4 °C until analysis.

11.3 Preparation of Method Spikes.

11.3.1 Prepare a method spike for every twenty samples. Transfer 300 ml of the absorption solution to a 1000-ml round bottom flask. Transfer 1 ml of a 100 µg/ml standard containing the isocyanate-urea derivatives of interest. Follow the procedure outlined in Section 11.2.1 for sample concentration. This will result in a method spike with a theoretical concentration of 10 µg/ml.

11.4 Preparation of Method Blanks.

11.4.1 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 11.2.1.

11.5 Chromatographic Analysis.

11.5.1 Chromatographic Conditions.

Column	C18, 250 mm x 4.6 mm ID, 5µm particle size.
Mobile Phase	Acetonitrile/Ammonium Acetate Buffer.
Gradient	10:90 (v/v) ACN:AAB to 60:40 (v/v) ACN:AAB over 30 minutes.
Flow Rate	2 ml/min.
UV Detector	254 nm.
Injection Volume	50 µl.

11.5.2 Analysis.

11.5.2.1 Analyze samples by HPLC, using conditions established in Section 11.5.1.

11.5.2.2 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.

11.5.2.3 If the peak area exceeds the linear range of the calibration curve, the sample should be diluted with ACN and reanalyzed.

12.0 Data Analysis and Calculations.

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

12.1 Perform Calculations. Round off figures after the final calculation to the correct number of significant figures.

12.2 Nomenclature. Same as Method 5, Section 6.1 with the following additions:

A_S = Response of the sample, area counts.

b = Y-intercept of the linear regression line, area counts.

C_I = Concentration of a specific isocyanate compound in the sample, µg/ml.

M = Slope of the linear regression line, area counts-ml/µg.

m_I = Mass of isocyanate in the total sample.

V_F = Final volume of concentrated sample, typically 10 ml.

$$\text{Amount of the isocyanate-urea} = \text{Amount of free isocyanate} * \left(\frac{\text{Molecular weight of the isocyanate-urea}}{\text{Molecular weight of the isocyanate}} \right) \qquad \text{Eq. 207-1}$$

$V_{m(std)}$ = 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:

The equation for converting the amount of isocyanate-urea derivative to the corresponding amount of free isocyanate is as follows:

$$\text{Amount of the isocyanate} = \text{Amount of isocyanate-urea} * \left(\frac{\text{Molecular weight of the isocyanate}}{\text{Molecular weight of the isocyanate-urea}} \right) \qquad \text{Eq. 207-2}$$

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:

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

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

$$m_I = C_I V_F \qquad \text{Eq. 207-4}$$

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

$$C_S = K \frac{m_I}{V_{m(std)}} \qquad \text{Eq. 207-5}$$

Where:

K = 35.31 ft^3/m^3 if $V_{m(std)}$ is expressed in English units.

= 1.00 m^3/m^3 if $V_{m(std)}$ is expressed in metric units.

13.0 Method Performance.

13.1 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.

13.2 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.

13.3 Method Precision and Bias. The overall method precision and bias must be determined on a compound-by-compound basis at a given concentration level. The method precision value would include a combined variability due to sampling, sample preparation, and instrumental analysis. The method bias would be dependent upon the collection, retention, and extraction efficiency of the train components. From evaluation studies to date using a dynamic spiking system, acceptable method biases (per EPA Method 301) have been determined for all four isocyanates. A precision of less than 10% relative standard deviation (RSD) has been calculated from field test data sets which resulted from a series of paired, unspiked and spiked trains.

14.0 Pollution Prevention. Not Applicable.

15.0 Waste Management. Not Applicable.

16.0 References.

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2. Rom, J.J., Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment, Research Triangle Park, NC, U.S. Environmental Protection Agency, March 1972, PB–209 022/BE, APTD–0576, 39 pp.

3. Schlickenrieder, L.M., Adams, J.W., and Thrun, K.E., Modified Method 5 Train and Source Assessment Sampling System: Operator's Manual, U.S. Environmental Protection Agency, EPA/600/8–85/003 (1985).

4. Shigehara, R.T., Adjustments in the EPA Nomograph for Different Pitot Tube Coefficients and Dry Molecular Weights, Stack Sampling News, 2:4–11 (October 1974).

5. U.S. Environmental Protection Agency, 40 CFR Part 60, Appendix A, Methods 1–5.

6. Vollaro, R.F., A Survey of Commercially Available Instrumentation for the Measurement of Low-Range Gas Velocities, Research Triangle Park, NC, U.S. Environmental Protection Agency, Emissions Measurement Branch, November 1976 (unpublished paper).

17.0 Tables, Diagrams, Flowcharts, and Validation Data.

TABLE 1.—MOLECULAR WEIGHT OF THE FREE ISOCYANATES AND THE ISOCYANATE-UREA DERIVATIVE

Analyte	MW (free Isocyanate)	MW (Derivative)
1,6–HDI	168	494.44
2,4–TD	174.16	500.56
MDI	250.25	576.65

TABLE 2.—MOLECULAR WEIGHT OF FREE METHYL ISOCYANATE AND METHYL ISOCYANATE-UREA DERIVATIVE

Analyte	MW (free Isocyanate)	MW (Derivative)
MI	57.1	220.32

TABLE 3.—RETENTION TIMES OF THE FOUR ISOCYANATES

Compound	Retention time (minutes)
MI	10.0
1,6–HDI	19.9
2,4–TDI	27.1
MDI	27.3

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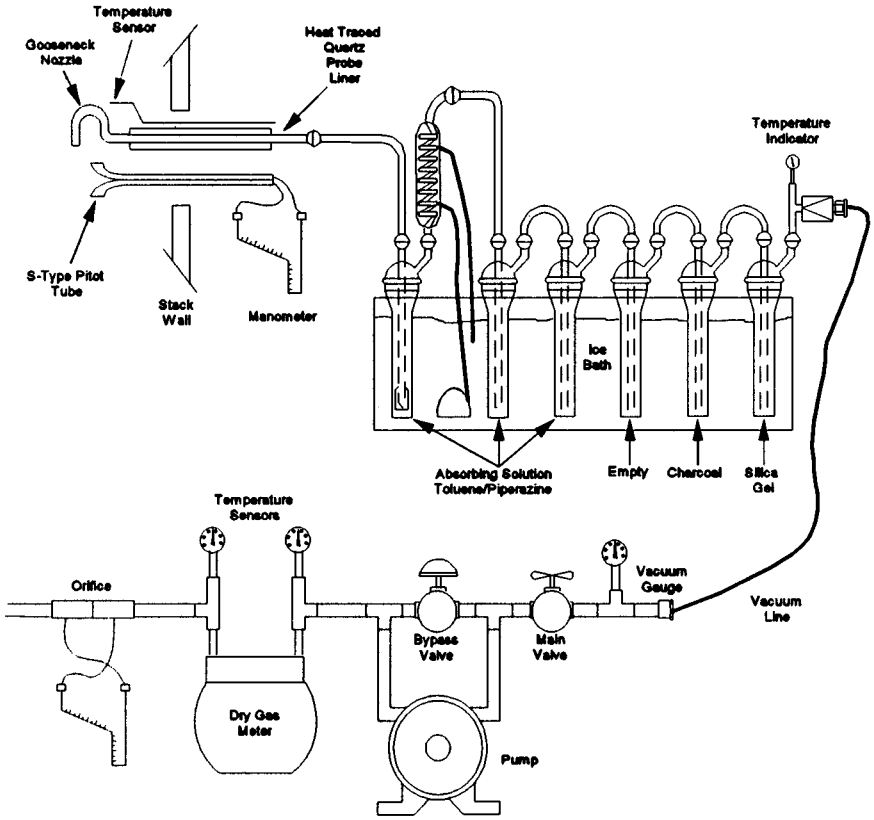

Figure 207-1-1. Sampling Train Configuration for Isocyanates

FIELD DATA

Run _____
Page 1 of _____

Plant		Probe Length and Type		Height of Location (ft)		
Date		Nozzle ID (In.)		Duct Dimensions (In)		
Sampling Location		Meter Box Number		Filter Number		
Sample Type		Meter ΔH@		Assumed Moisture (%)		
Run Number		Yd		O2 (%)		
Operator		K Factor		CO2 (%)		
Ambient Temperature (°F)		Probe Heater Setting (°F)		O2/CO2 Method		
Barometric Pressure (in)		Heater Box Setting (°F)		Moisture Collected (g)		
Static Pressure (in H2O)		Initial Leak Check		Final Leak Check		

Diagram of Duct

Read and Record all Data Every _____ Minutes

Traverse Point Number	Sampling Time (min)	Clock Time (24-hr)	Gas Meter Reading Vm (ft^3)	Velocity Head ΔP (in H2O)	Orifice Pressure Differential ΔH (in H2O)	Flue Gas Temperature (°F)	Probe Temperature (°F)	Filter Temperature (°F)	Dry Gas Meter Temperature		Impinger Exit (°F)	Pump Vacuum (in. Hg)
									Inlet (°F)	Outlet (°F)		

Comments:

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