Appendix A

Draft Method XPHS

Sampling and Analysis
for
Phosgene Emissions from Stationary Sources

DRAFT METHOD XPHS

Draft Method XPHS - Sampling and Analysis for Phosgene Emissions from Stationary Sources

1.0 SCOPE AND APPLICATION.

1.1 Method XPHS is applicable to the collection and analysis of phosgene from the emissions associated with manufacturing processes and incineration. Table XPHS-1 lists the CAS number, matrices evaluated, and method sensitivity. 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 methods in the sampling and analytical procedures. Therefore, to obtain reliable results, testers using this method should have a thorough knowledge of at least the following test methods: EPA Method 1, EPA Method 2, EPA Method 3, EPA Method 4, and EPA Method 5, and SW 846 Method 8270.

1.2 The method sensitivity is listed in Table XPHS-1. The method sensitivity for a specific matrix may differ from the method sensitivity listed in Table XPHS-1 depending on the nature of interferences in the sample matrix.

TABLE XPHS-1. CAS NUMBER, MATRICES, AND METHOD SENSITIVITY

			Method Sensitivity	
Compound	CAS No.[a]	Matrix	Total µg[b]	ppbv[c]
Phosgene	75-44-5	Air, 0-20% Moisture	400	100

[a]Chemical Abstract Services Registry Number.
[b]Based on the slope of the calibration curve, the standard deviation in response for the internal standard, and 600 mL of reagent.
[c]For an 849 liter (30 cubic foot) sample, based on the slope of the calibration curve, the standard deviation in response for the internal standard, and 600 mL of reagent.

1.3 Sample collection under this method must be performed by testers trained and experienced with isokinetic sampling techniques. The analytical procedures in this method are restricted to use by, or under the supervision of, analysts experienced in the use of chromatography and in the interpretation of chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF THE METHOD.

2.1 Gaseous and particulate pollutants are withdrawn from an emission source at an isokinetic sampling rate and are collected in a multicomponent sampling train. Sampling is conducted isokinetically because of the significant solubility of phosgene in water droplets which may be present in combustion device stacks, especially those equipped with wet scrubber systems. The volume of sample collected is dependent on the type of source sampled, the estimated level of analyte in the source, and the detection limit required for the application. Customarily, 1.0±0.2 cubic meters (35.3±7.1 cubic feet) of sample is collected.

2.2 Phosgene present in the source gas stream is collected in a 4M diethylamine in toluene solution. The phosgene reacts with the diethylamine to form the tetraethylurea derivative and a reaction byproduct, diethylamine hydrochloride.

2.3 The primary components of the sampling train include a heated probe and four impingers. The first two impingers have vertical inlet and outlet water-cooled condensers. These two impingers contain the derivatizing reagent in toluene. A peristaltic pump with an adjustable spray nozzle is used to recirculate the reagent through the coils of the condenser above the first impinger. The third impinger contains silica gel. A fourth impinger contains charcoal.

2.4 The volume of the toluene layer collected in each impinger is measured. An aliquot of each impinger sample is dried with anhydrous sodium sulfate and submitted for analysis. Alternatively, to obtain lower detection limits, a water-free aliquot of the sample may be carefully concentrated,using proven concentrating techniques, before being submitted for analysis. The analyst should demonstrate that the technique chosen is capable of yielding the desired concentration without unacceptable analyte losses.

2.5 An aliquot of the dried sample is then analyzed by gas chromatography/mass spectrometry (GC/MS). GC/MS analytical conditions are described in Section 11.3. The analytical conditions permit the chromatographic separation and quantitative analysis of the phosgene derivative in the reagent which may contain large quantities of unreacted reagent and siloxane plasticizers extracted from the train construction materials.

3.0 DEFINITIONS.

Calibration Check Standard - Calibration standard used to verify the calibration curve before analyzing samples.

Field Reagent Blank - Aliquots of the reagent used in the impinger train and the solvents used to recover the train that are collected in the field and returned to the laboratory for analysis.

Field Spike - An aliquot of reagent that is spiked with a known amount of analyte in the field.

Field Train Blank - A sampling train that is assembled, taken to the sampling area, leak checked, and recovered as though it were a normal train sample although no gaseous sample is collected.

Isokinetic Variation - Measure of how proportional the sampling rate is to the source gas velocity.

Laboratory Method Blank - Blank reagent that is carried through the sample preparation procedures with the samples and that is used to evaluate whether any contamination occurred in the laboratory.

Matrix Spike - An aliquot of sample that is spiked with a known amount of analyte in the laboratory and then carried through the sample preparation procedures with the samples.

Replicate Analysis - A second injection of a prepared sample into the analytical system.

Replicate Sample - A second aliquot of sample that is carried through the sample preparation procedures with the samples.

4.0 INTERFERENCES.

4.1 Water may interfere with the collection and derivatization of phosgene. Sampling sources containing high (20%) moisture may affect phosgene recoveries when using DEA as the derivatizing reagent. Siloxanes leached from the peristaltic pump tubing will also interfere if mass spectrometry is not used as the analysis method. The reagent must be stored in an uncontaminated environment both before and after sampling to minimize blank problems.

4.2 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other sample processing hardware. These method interferences lead to discrete artifacts and/or elevated baselines in the chromatograms. All reagents and glassware must be routinely demonstrated to be free from interferences under the conditions of the analysis by analyzing laboratory reagent blanks.

4.2.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used. This rinse should be followed by washing with hot water and detergent, and rinsing with tap water and distilled water. Glassware should then be drained and heated in a laboratory oven at 130°C (266°F) for several hours before use. Solvent rinses using methanol and methylene chloride may be substituted for the oven heating. After drying and cooling, glassware should be stored in a clean environment to prevent any accumulation of dust or other contaminants.

4.2.2 The use of high purity reagents and solvents helps to minimize interference problems. Purification of solvents by distillation in all-glass systems may be required.

4.3 Matrix interferences may be caused by contaminants that are absorbed from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the matrix being sampled. If interferences occur in subsequent samples, some cleanup of the solution may be necessary.

4.4 The extent of interferences that may be encountered using gas chromatography/ mass spectrometry techniques has not been fully assessed. Although the GC/MS conditions described allow for a resolution of the phosgene from the siloxanes leached from the peristaltic pump tubing, other matrix components may interfere.

5.0 SAFETY.

5.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. However, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means are available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety & Health Administration (OSHA) regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available.

5.2 Phosgene is toxic, capable of causing severe eye and respiratory irritation and injury and death. It can enter the body via inhalation and skin absorption. The occupational safety and health administration standard for phosgene is 0.1 ppmv averaged for an 8-hour shift.

5.3 Diethylamine is flammable and toxic by inhalation. Diethylamine vapor is 2.5 times denser than air and may travel a considerable distance to a source of ignition and flash back. The explosion limits in air are 1.8 to 10.1% and the flashpoint is -20°F. Because it is volatile with a low boiling point (55°C [131°F]) and high vapor pressure (183 mm Hg at 20°C [3.51 PSI at 68°F]), efforts must be made to ensure that diethylamine is not emitted from the train. Symptoms of exposure may include burning sensation, coughing, wheezing, laryngitis, shortness of breath, headache, nausea and vomiting. If the sampler suspects that diethylamine vapors are being emitted from the train, the sampler may add an additional impinger containing activated charcoal to the train, decrease the exit temperature from the impinger train, or decrease the sampling rate.

6.0 EQUIPMENT AND SUPPLIES.

6.1 The following items are required for sample collection.

6.1.1 A schematic diagram of the sampling train used in this method is shown in Figure XPHS-1. This sampling train configuration is adapted from the EPA Method 5 procedures. The majority of the required equipment is identical to that used in EPA Method 5 train.

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. 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). Correct usage is important in obtaining valid results. All users of this methodology should therefore 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. Quartz or glass with a sharp leading edge at a tapered 30° angle. 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 Section 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 utilizing 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 (Section 6.1 of Reformatted Draft 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 6-2b) 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 (Section 10.0 of Reformatted Draft EPA Method 2).

6.1.3.4 Differential Pressure Gauge. Two inclined manometers or equivalent device as described in Section 2.2 of promulgated EPA Method 2 (Section 10.0 of Reformatted Draft EPA Method 2). One manometer shall be used for velocity-head readings and the other for orifice differential pressure (ΔH) readings.

6.1.3.5 Temperature Sensor. A temperature sensor capable of measuring temperature to within ± 3 °C (± 5.4 °F) shall be installed so that the temperature at the impinger outlet can be regulated and monitored during sampling.

6.1.3.6 Impinger Train. The sampling train requires four impingers connected in series. The first and second impingers are 1000-mL impingers with specially constructed condensers that contain two vertical inlet and outlet condensers within a common water jacket. The third and fourth impingers are 500-mL impingers of the modified Greenburg-Smith design, modified by replacing the tip with a 1.3-cm (½-inch) inside diameter glass tube extending to 1.3 cm (½ inch) from the bottom of the outer cylinder. The first and second impingers shall contain 600 mL of diethylamine reagent. The third impinger is filled with a known amount (2/3 full) of desiccant and the fourth impinger contains a known amount (2/3) full of charcoal.

6.1.3.6.1 First Impinger. The first impinger is shown in Figure XPHS-2. The 1000-mL impinger has a port on the top of the impinger with a 1.3-cm (½-inch) glass tube extending to 1.3 cm (½ inch) from the bottom of the outer cylinder which allows the derivatizing reagent to be pulled out and recirculated through the coils of the condenser.

6.1.3.6.2 Second Impinger. The second impinger has the same dimensions as the first impinger and differs from the first impinger only in that it does not have a port with an internal tube for removing solution.

6.1.3.6.3 First Impinger Condenser. The first impinger condenser is shown in Figure XPHS-3. The inlet vertical condenser is a condenser coil with a straight 1.3-cm (½-inch) glass tube with a Greenburg-Smith impaction plate at the end that extends into the impinger to within 1.3 cm (½ inch) of the impinger bottom. The outlet vertical condenser is a straight tube extending about 2.54 cm (1 inch) into the impinger. The inlet of the coiled condenser contains a second port so that the impinger solution can be sprayed into the condenser through an adjustable nozzle, shown in Figure XPHS-4, consisting of a 0.65-cm (1/4-inch) glass tube with a single hole.

6.1.3.6.4 Second Impinger Condenser. The second impinger condenser, shown in Figure XPHS-5, has the same dimensions as the first impinger. The inlet vertical condenser is a straight Liebig condenser. The Liebig condenser has a long fragile glass tail that inserts into the impinger body. The glass tail has a Greenburg-Smith impaction plate at the end that extends into the impinger to within 1.3 cm (½ inch) of the impinger bottom. The outlet vertical condenser is a coil type Graham condenser with a straight tube extending about 2.54 cm (1 inch) into the impinger. The inlet of the condenser contains only one port.

6.1.3.7 Reagent Pump. A chemically inert liquid pump capable of pumping 90 mL/min to ±5% accuracy and capable of performing continously against a back pressure of 10 psi is needed for circulating the reagent through the first impinger. All tubing must be inert and contamination free.

6.1.3.8 Metering System. The necessary components of the metering system are a vacuum gauge, leak-free pump, temperature sensors capable of measuring temperature within 3 °C (5.4 °F), dry-gas meter capable of measuring volume to within 1%, and related equipment as shown in Figure XPHS-1. At a minimum, the pump should be capable of 113 liters per minute (4 cubic feet per minute [cfm]) free flow, and the dry-gas meter should have a recording capacity of 0-28.36 cubic meters (0-999.9 cubic feet) with a resolution of 0.14 Liters (0.005 cubic feet). Other metering systems capable of maintaining sample rates within 10% of isokineticity and of determining sample volumes to within 2% of the actual value may be used. The metering system must be used in conjunction 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, provided that the specifications of this method are met.

6.1.3.9 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). The barometric pressure reading may be obtained from a nearby National Weather Service Station. In this case, the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point be made at a rate of minus 2.5 mm (0.1 in.) Hg per 30 meters (100 ft.) elevation increase or plus 2.5 mm (0.1 in.) Hg per 30 meters (100 ft.) elevation decrease.

6.1.3.10 Gas Density Determination Equipment. Temperature sensor and pressure gauge (as described in Sections 2.3 and 2.4 of Promulgated EPA Method 2 as well as Sections 6.3 and 6.4 of Reformatted Method 2), and gas analyzer, if necessary, as described in EPA Method 3. The temperature sensor shall, preferably, be permanently attached to the pitot tube or sampling probe in a

fixed configuration so 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 prior to 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 well as Reformatted Method 2, Figure 2-4). As a second alternative, if a difference of no more than 1% in the average velocity measurements is to be introduced, the temperature sensor need not be attached to the probe or pitot tube (subject to the approval of the Administrator).

6.1.3.11 Calibration/Field Preparation Record. A permanently bound laboratory notebook, in which duplicate copies of data may be made as they are being recorded, is required for documenting and recording calibrations and preparation procedures (i.e., silica gel tare weights, quality assurance/ quality control check results, dry-gas meter readings, and thermocouple calibrations, etc.). The duplicate copies should be detachable and should be stored separately in the test program archives.

6.1.3.12 Viton® A O-ring.

6.1.3.13 Heat Resistant Tape.

6.1.3.14 Teflon® Tape.

6.1.3.15 Flexible Teflon® Tubing.

6.1.3.16 Solvirel® Fittings.

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

6.2.1 Probe Liner and Probe 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 must be properly sized and shaped to brush out the probe liner and the probe nozzle.

6.2.2 Wash Bottles. Three wash bottles are required. 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 1000-mL amber glass bottles. Bottles should be tinted to prevent photochemical reactions. Screw-cap liners shall be either Teflon® or constructed to be leak-free and

resistant to chemical attack by organic solution. Narrow-mouth glass bottles have been found to exhibit less tendency toward leakage.

6.2.4 Graduated Cylinder and/or Balance. 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.

6.2.6 Glass Funnel and Rubber Policeman. To aid in the transfer of silica gel and charcoal into and out of containers in the field. These items are unnecessary when the silica gel and charcoal are weighed in the field.

6.2.7 Funnels. Glass, to aid in sample recovery.

6.2.8 Coolers. To store and ship sample containers.

6.2.9 Crushed Ice. Quantities ranging from 10-50 lb may be necessary during a sampling run, depending upon the temperature of ambient air and the moisture content of the gas stream.

6.2.10 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.

6.3 Reagent Preparation

6.3.1 Bottles/Caps. Amber 1- or 4-L bottles with Teflon®-lined caps are required for storing the diethylamine solution.

6.3.2 Volumetric Flask. A large (2- or 4-L) volumetric flask is required for preparing the 4 M diethylamine solution.

6.3.3 Graduated Cylinder. At least one large (1- or 2-L) graduated cylinder is required for measuring the diethylamine when preparing the reagent solution.

6.4 Analysis

6.4.1 Vials. 2 and 15 mL, glass with Teflon® -lined screw caps or crimp tops.

6.4.2 Analytical Balance. Capable of accurately weighing to the nearest 0.1 mg.

6.4.3 Gas Chromatograph and Mass Spectrometer. A capillary gas chromatograph interfaced to a mass spectrometer with an appropriate data system is required for analyzing the samples. The gas chromatograph should have a heated injection port capable of handling 1 µL injections of sample in toluene.

6.4.4 Column. 60 m x 0.32 mm ID, 1.0 µ film thickness, DB-1 (or equivalent).

6.4.5 Glass funnel. Short-stemmed or equivalent.

6.4.6 Silanized Glass Wool or Glass-Fiber Filter Paper.

6.4.7 Pipets. Disposable, 10 or 25 mL.

6.4.8 Rotary Evaporator.

6.4.9 Round Bottom Flasks. 100 to 1000 mL for use with rotary evaporator.

7.0 REAGENTS AND STANDARDS.

7.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided that the reagent is of sufficiently high purity to use without jeopardizing accuracy.

7.2 Impinger Solution. The impinger solution is prepared by adding 800 mL of diethylamine to a 2-L volumetric flask and diluting to volume with toluene. This solution can be prepared in the laboratory or in the field and should be stored in amber glass bottles at room temperature and used within six months of preparation.

7.3 Silica Gel. Indicating type, 6-16 mesh. If previously used, dry at 180°C (350°F) for two hours before using. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent to silica gel or better) may be used, subject to the approval of the Administrator.

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

7.5 Field Spike Standard Preparation. The field spike standard is prepared at 420 µg/mL. Use a 500 µL gas-tight syringe to transfer 450 µL of 20% by weight phosgene in toluene solution into a 200 mL volumetric flask filled half full with toluene. Dilute to the line with toluene, cap the flask, and mix the solution well by inverting the flask three times. Transfer the solution to an amber glass bottle with a Teflon®-lined cap, seal and label the bottle, and store the solution at 4±2°C (39.2±3.6°F). Use within one month of preparation.

7.6 Diethylamine, $N(CH_2CH_3)_2$. Reagent grade diethylamine is required for preparing the impinger solution used to derivatize the phosgene.

7.7 Toluene, $CH_3C_6H_5$. Toluene (HPLC grade or equivalent) is required for preparing the impinger solution, recovering the samples, making standard solutions, and rinsing glassware.

7.8 Phosgene, $COCl_2$. A 20% by weight phosgene in toluene solution is required for preparing the field spike standard.

7.9 Methanol, CH_3OH. Methanol (HPLC grade or equivalent) is required for rinsing glassware.

7.10 Methylene Chloride, CH_2Cl_2. Methylene chloride (HPLC grade or equivalent) is required for rinsing glassware.

7.11 Tetraethylurea, $CO(CH_2CH_3)_4$. Tetraethylurea (98% or greater) is required for preparation of analytical standards.

7.12 Napththalene-d_8, $C_{10}D_8$. Naphthalene-d_8 is required for use as an internal standard.

7.13 Calibration Standard Solutions.

7.13.1 Calibration Standards Preparation.

7.13.1.1 Stock Standard. Prepare a tetraethylurea stock standard at a concentration of 2 mg/mL by weighing 200 mg (±0.01 mg) of tetraethylurea into a 100 mL volumetric flask and diluting to the line with toluene.

7.13.1.2 Calibration Standards. Prepare calibration standards by diluting 0.25, 0.50, 1.0, 2.0, and 4.0 mL of stock standard to 50 mL with toluene to provide a standard curve with calibration points at 10, 20, 40, 80, and 160 µg/mL.

7.13.1.3 Internal Standard. Prepare an internal standard solution at a concentration of 1,000 µg/mL by weighing 100 mg (±0.01 mg) of naphthalene-d_8 into a 100 mL volumetric flask and diluting to the line with toluene or use a commercially prepared standard.

7.14 Standard solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

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 Laboratory Preparation.

8.2.1 All the components must be maintained and calibrated according to the procedure described in APTD-0576 (Reference 1 in Section 16.0), unless otherwise specified.

8.2.2 Weigh several 200 to 300 g portions of silica gel to the nearest 0.5 g and place the silica gel in airtight containers. Record on each container the total weight of the silica gel plus container. As an alternative to preweighing the silica gel, the silica gel may be weighed directly in the impinger just prior to assembly of the sampling train.

8.2.3 Weigh several 400 g portions of charcoal to the nearest 0.5 g and place the charcoal in airtight containers. Record on each container the total weight of charcoal plus container. As an alternative to preweighing the charcoal, the charcoal may be weighed directly in the impinger just prior to assembly of the sampling train.

8.3 Preliminary Field Determinations.

8.3.1 Select the sampling site and the minimum number of sampling points according to EPA Method 1 or other relevant criteria. Determine the stack pressure, temperature, and range of velocity heads using EPA Method 2. Check the pitot lines for leaks according to Promulgated EPA Method 2, Section 3.1 (Reformatted EPA Method 2, Section 8.1). Determine the stack gas moisture content using EPA Approximation Method 4 or its alternatives to establish estimates of isokinetic sampling-rate settings. Determine the stack gas dry molecular weight, as described in Promulgated EPA Method 2, Section 3.6 (Reformatted EPA Method 2, Section 8.6). If integrated EPA Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the sample run.

8.3.2 Select a nozzle size based on the range of velocity heads so that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the sampling 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, as well as Section 8.2 of Reformatted EPA Method 2).

8.3.3 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.

8.3.4 A typical sample volume to be collected is 1 dry standard cubic meter (dscm) (35.31 dry standard cubic feet [dscf]). The sample volume can be adjusted as necessitated by analytical detection limit constraints and/or estimated stack concentrations. A maximum limit should be determined to avoid exceeding the capacity of the reagent, estimated at 66 mg phosgene (19 ppmv for an 849 L [30 cubic feet] sample).

8.3.5 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 plus one-half minute.

8.3.6 In some circumstances (e.g., batch cycles) it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas-volume samples. In these cases, careful documentation must be maintained in order to allow accurate concentration calculation.

8.4 Preparation of Collection Train.

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

8.4.2 Place 600 mL of diethylamine derivatizing solution in each of the first two impingers. The third impinger shall have 200 to 300 g of pre-weighed silica gel. The fourth impinger shall have 400 g of preweighed charcoal. Be careful to ensure that the silica gel or charcoal is not entrained and carried out from the impinger during sampling. Place the silica gel containers in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger and charcoal plus impinger may be determined to the nearest 0.5 g and recorded. For moisture determination, weigh both of the impingers after filling them with reagent.

8.4.3 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 some other method to denote the proper distance into the stack or duct for each sampling point.

8.4.4 Assemble the train as shown in Figure XPHS-1. During assembly, do not use any silicone grease on the ground-glass joints of the impingers. Use Teflon® tape, if required. Check all temperature sensors at ambient temperatures.

8.4.5 Place crushed ice around the impingers.

8.4.6 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 minimizing the loss of toluene from the first impinger.

8.4.7 Turn on and set the probe heating and filter heating systems at the desired temperature. Allow time for the temperature to stabilize.

8.5 Leak-Check Procedures.

8.5.1 Pre-test Leak Check.

8.5.1.1 Because the number of additional intercomponent connections in the train (over the EPA Method 5 Train) increases the possibility of leakage, a pre-test check is required.

8.5.1.2 After the sampling train has been assembled, turn on and set the probe heating system to the desired operating temperature. Allow time for the temperature 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 in excess of 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, provided that it is not exceeded during the test.

8.5.1.3 The following leak check instructions for the sampling train described in APTD-0576 and APTD-0581 (References 1 and 2 of Section 16.0, respectively) may be helpful. Start the pump with the fine-adjust valve fully open and 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 <u>not</u> reverse direction of the fine adjust valve, as liquid will back up into the train. If the desired vacuum is exceeded, either perform the leak check at this higher vacuum or end the leak check, as shown below, and start over.

8.5.1.4 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 to prevent the liquid in the impingers from being forced backward in the sampling line and silica gel from being entrained backward into the third impinger.

8.5.2 Leak Checks During the Sampling Run.

8.5.2.1 If, during the sampling run, a component change becomes necessary, conduct a leak-check immediately after the interruption of sampling and before the change is made. Conduct the leak check according to the procedure described in Section 8.5.1, except conduct it at a vacuum greater than or equal to the maximum value recorded up to that point in the test. If the leakage rate is found to be 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, 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.

8.5.2.2 Immediately after a component change and before sampling is reinitiated, conduct a leak check similar to a pre-test leak check.

8.5.3 Post-Test Leak Check.

8.5.3.1 A leak check of the sampling train is mandatory at the conclusion of each sampling run. Conduct the leak check in accordance with the same procedures as the pre-test leak check, except conduct the post-test leak check at a vacuum greater than or equal to the maximum value reached during the sampling run. If the leakage rate is found to be 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. If, however, a higher leakage rate is obtained, record the leakage rate, correct the sample volume (as shown in Section 12.0 of this method), formally note that this correction has been made to the data, and consider the data obtained of questionable reliability, or void the sampling run.

8.6 Sampling Train Operation.

8.6.1 During the sampling run, maintain a isokinetic sampling rate to within 10% of true isokinetic, below 28 L/min (1.0 cfm). Maintain a probe temperature of 120° ± 14°C (248° ± 25°F).

8.6.2 For each run, record the data on a data sheet such as the one shown in Figure XPHS-6. 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 indicated by Figure XPHS-6 at least once at each sampling point during each time increment and additional readings when significant adjustments (20% variation

in velocity head readings) necessitate 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.

8.6.3 Clean the stack access ports prior to the test run to eliminate the chance of collecting deposited material. To begin sampling, verify that the probe heating systems are 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 with the Type S pitot tube with a coefficient of 0.84 ± 0.02 and the stack gas equivalent density (dry molecular weight) is equal to 29 ± 4. APTD-0576 (Reference 1 in Section 16.0) 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.

8.6.4 When the stack is under significant negative pressure, take care to close the coarse-adjust valve before inserting the probe into the stack in order to prevent the impinger solutions from backing up into the probe. If necessary, the pump may be turned on with the coarse-adjust valve closed.

8.6.5 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. Start the peristaltic pump and adjust the spray nozzle so that the reagent sprays into the probe, cascading from the top surface of the probe to the bottom surface as shown in Figure XPHS-7.

8.6.6 Traverse the stack cross-section, as required by EPA Method 1. To minimize the chance of extracting deposited material, be 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.

8.6.7 During the test run, make periodic adjustments to keep the temperature of the probe and condenser at the proper levels. Add more ice and, if necessary, salt, to

maintain a temperature of <20°C (68°F) at the silica gel outlet. Also, periodically check the level and zero of the manometer.

8.6.8 A single train shall be used for the entire sampling run, except in cases where simultaneous sampling is required in two or more separate ducts; at two or more different locations within the same duct; or, in cases where equipment failure necessitates a change of trains. Additional train(s) may also be used for sampling when the capacity of a single train is exceeded.

8.6.9 When two or more trains are used, components from each train shall be analyzed. If multiple trains have been used because the capacity of a single train would be exceeded, first impingers from each train may be combined, and second impingers from each train may be combined.

8.6.10 At the end of the sampling run, turn off the coarse adjust valve and the peristaltic pump, 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 as outlined in Section 8.5.3. Also, leak check the pitot lines as described in EPA Method 2 (Section 8.1 of Reformatted Method 2). The lines must pass this leak check in order to validate the velocity-head data.

8.6.11 Calculate percent isokinetic variation (as described in Section 6.11 of Method 5, as well as see Section 12.11 of Reformatted Method 5) to determine whether the run was valid or another test should be performed.

8.7 Sample Recovery.

8.7.1 Preparation.

8.7.1.1 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 because a vacuum will be created drawing liquid form the impingers back through the sampling train.

8.7.1.2 Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet, being careful not to lose any condensate that might be present. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used, let any condensed water or liquid drain into the impingers. Cap off any open impinger inlets and outlets. Ground glass stoppers, Teflon® caps, or caps of other inert materials may

be used to seal all openings. Remove the peristaltic pump tubing from the peristaltic pump.

8.7.1.3 Transfer the probe and impinger/condenser assembly to an area that is cleaned and protected from wind so that the chances of contaminating or losing the sample are minimized.

8.7.1.4 Inspect the train before and during disassembly, and note any abnormal conditions.

8.7.1.5 Save a portion of all washing solutions (toluene) used for cleanup as a reagent blank. Transfer 200 mL of each solution directly from the wash bottle and place each in a separate prelabeled sample "reagent blank" container (see Section 8.7.3).

8.7.2 Sample Containers

8.7.2.1 Container No. 1.

8.7.2.1.1 Using two people, rinse the probe/nozzle with toluene by tilting and rotating the probe while squirting solvent into the upper end so that all of the surfaces are wetted with the rinse solution. Let the solvent drain into the container. If particulate is visible, use a Teflon® brush to loosen and remove the particulate material and follow with a second rinse.

8.7.2.1.2 Disconnect the peristaltic pump tubing from the first impinger condenser inlet and hold the end of the tubing above the first impinger so that all of the contents drain out of the tubing into the impinger. Disconnect the peristaltic pump tubing from the first impinger. Rinse the tubing with toluene. Let the solvent drain into Container No. 1.

8.7.2.1.3 Weigh the contents of the first impinger. Then transfer the first impinger contents to Container No. 1 along with the toluene rinses of the impinger and the condenser. When two liquid layers are present, add both layers to the container. After all of the components and their rinses have been collected in the container, seal the container, mark the liquid level on the bottle, and add the proper label.

8.7.2.2 Container No. 2. After weighing the contents of the second impinger, pour the contents of Impinger No. 2 into Container No. 2 along with the toluene rinses of the impinger, the condenser, and all connecting tubing. After all of the components have been collected in the container, mark the liquid level, seal the container, and add the proper sample label.

8.7.3 Reagent Blanks. Prepare reagent blanks by transferring 200 mL of reagent and 200 mL of each wash solvent to separate amber glass jars. Process the reagent blanks in the same manner as the samples.

8.7.4 Moisture determination. If a moisture determination is to be made, measure the volume (or weight) gain of each impinger as well as the impingers containing the silica gel and charcoal before transferring the contents to the sample containers.

8.7.5 Sample preparation for shipment. Prior to shipment, recheck all sample containers to ensure that the caps are well secured. Seal the lids with Teflon® tape. Ship all samples upright, using the proper shipping materials as prescribed for hazardous materials.

9.0 QUALITY CONTROL.

9.1 Sampling. Sampling quality control procedures are listed in Table XPHS-2. See Reference 3 in Section 16.0 for additional Method 5 quality control.

9.1.1 Field Train Blanks. Field train blanks must be submitted with the samples collected at each sampling site. The field train blanks include the sample bottles containing aliquots of sample recovery solvents, and unused diethylamine reagent. At a minimum, assemble one complete sampling train in the field staging area, take it to the sampling area, and leak-check it at the beginning and end of the testing (or for the same total number of times as the actual sampling train). Heat the probe of the field blank train during the sample test. Recover the field blank train as if it were an actual test sample. Do not pass any gaseous sample through the field blank sampling train.

TABLE XPHS-2. SAMPLING QUALITY CONTROL PROCEDURES

Criteria	Control Limits[a]	Corrective Action
Isokinetic Variation	90% to 110%	None: If the results are low in comparison with the standard and the isokinetic variation is beyond the acceptable range or if the isokinetic variation is less than 90%, the Administrator may opt to accept the results.
Final Leak Rate	$\leq$0.00057 m^3/min or 4% of sampling rate, whichever is less.	None: Results are questionable and should be compared with other train results.
Dry Gas Meter Calibration	Post average factor agrees ±5% of pre-factor.	Adjust sample volumes using the factor that gives the smallest volume.
Individual Correction Factor (γ)	Agree within 2% of average factor.	Redo correction factor.
Average Correction Factor	1.00 ± 1%.	Adjust the dry gas meter and recalibrate.
Intermediate Dry Gas Meter	Calibrated every six months against EPA standard.	--
Analytical Balance (top loader)	±0.1 g of ASTM Class 1 (NIST Class S) Weights.	Repair balance and recalibrate.
Barometer	Within 2.55 mm Hg of mercury-in-glass barometer.	Recalibrate.

[a] Control limits are established based on previous test programs conducted by the EPA.

9.1.2 Reagent Blanks. Collect a 200 mL aliquot of toluene and diethylamine solution in the field as separate samples and return them to the laboratory for analysis to evaluate artifacts that may be observed in the actual samples.

9.1.3 Field Spike. Introduce 20 mL of the Field Spike Standard into an impinger containing 600 mL of diethylamine solution. Follow standard impinger recovery procedures and use the spike as a check on field handling and recovery procedures. Retain an aliquot of the Field Spike Standard in the laboratory for comparative analysis.

9.2 Analysis. The quality assurance program required for this method includes the analysis of the field train, field reagent, and laboratory method blanks, procedure validations, and analysis of field spikes.

The assessment of combustion data and positive identification and quantitation of phosgene depend on the integrity of the samples received and the precision and accuracy of the analytical methodology. Quality assurance procedures for this method are designed to monitor the performance of the analytical methodology and to provide the required information to take corrective action if problems are observed in laboratory operations or in field sampling activities. Table XPHS-3 lists laboratory quality control procedures.

9.2.1 Laboratory Method Blanks. Prepare a method blank for each set of analytical operations to evaluate contamination and artifacts that can be derived from glassware, reagents, and sample handling in the laboratory.

9.2.2 Preparation of Diethylamine Reagent. Take two aliquots of the diethylamine reagent. The size of the aliquots depends on the exact sampling procedure used, but 600 mL is reasonably representative. To ensure that the background in the reagent is acceptable for field use, analyze one aliquot of the reagent according to the procedure in Section 11. Save the other aliquot of aqueous diethylamine for use as a laboratory method blank when the analysis is performed.

TABLE XPHS-3. LABORATORY QUALITY CONTROL PROCEDURES FOR GC/MS ANALYSIS

Parameter	Quality Control Check	Frequency	Acceptance Criteria	Corrective Action
Linearity Check	Run 5-point curve.	At setup or when check standard is out-of-range	See Section 7.4.3 of Method 8270 and 7.17.3 of Draft Method 5041A	Check integration, reintegrate. If necessary recalibrate.
Retention Time	Analyze check standard	Every 12 hours	Within three standard deviations of average calibration relative retention time	Check instrument function. Adjust column temperature or carrier gas flow rate.
Tune	Analyze DFTPP	Every 12 hours	See Section 7.3.1 and 7.4.1 of Method 8270	Retune. Perform instrument maintenance or service.
Calibration Check	Analyze check standard	Every 12 hours	See Section 7.4.3 of Method 8270 and 7.17.3 of Method 5041A	Recalibrate.
Matrix Spike/Matrix Spike Duplicate	Analyze spiked sample	1/set or 1/20 samples	±20% of spiked amount	Check integration, check instrument function, reanalyze, reprepare if possible
Replicate Samples	Analyze duplicate sample aliquot	1/set or 1/20 samples	±20% of first aliquot	Check integration, check instrument function, reanalyze, reprepare if possible
Replicate Analyses	Re-inject sample	1/20 samples or 1/set	±15% of first injection	Check integration, check instrument function, reanalyze
Laboratory Method Blank	Analyze toluene	1/set or 1/20 samples	<20% of lowest standard	Locate source of contamination, reanalyze, reprepare if possible

10.0 CALIBRATION AND STANDARDIZATION.

NOTE: Maintain a laboratory log of all calibrations.

10.1 Probe Nozzle. Calibrate probe nozzles 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 the nozzles become nicked, dented, or corroded, replace them. Permanently and uniquely identify each nozzle.

10.2 Pitot Tube Assembly. Calibrate the Type S pitot tube assembly according to the procedure outlined in Section 4 of Promulgated EPA Method 2 (Section 10.1 of Reformatted Draft EPA Method 2), or assign a nominal coefficient of 0.84 if it is not visibly nicked or corroded, and, if it meets design and intercomponent spacing specifications.

10.3 Metering System.

10.3.1 Calibration Prior to Use. Before its initial use in the field, calibrate the metering system according to the procedure outlined in APTD-0576 (see Reference 1 of Section 16.0). 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, is it suggested that a leak-check be conducted. For metering systems having diaphragm pumps, a standard leak check procedure may not detect leakages within the pump. For these cases, use the following leak check procedure. Make a ten-minute 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 Calibration After Use. After each field use, check the calibration of the metering system by performing three calibration runs at a single intermediate orifice setting (based on the previous field test). Set the vacuum 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 value has changed by more the 5%, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576 (Reference 1 of Section 16.0).

10.3.3 Leak check of metering system. Leak check the portion of the sampling train from the pump to the orifice meter (see Figure XPHS-1) prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. Use the following procedure. 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 minute. 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 must be voided or calculations for the 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. Calibrate the probe heating system before its initial use in the field according to the procedure outlined in APTD-0576 (Reference 1 of Section 16.0). Probes constructed according to APTD-0581 (Reference 2 of Section 16.0) need not be calibrated if the calibration curves in APTD-0576 (Reference 1 of Section 16.0) are used.

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

10.5.1 Impinger and Dry-Gas Meter Temperature Sensors. For the temperature sensors used to measure the temperature of the gas leaving the impinger train, a three-point calibration at ice water, room air, and boiling water temperatures is necessary. Accept the temperature sensors 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 Temperature Sensor. For the temperature sensors used to indicate the probe and stack temperatures, conduct a three-point calibration at ice water, boiling water, and hot oil bath temperatures. Use of a point at room air temperature is recommended. The thermometer and thermocouple must 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 before each test series to agree to within ± 2.5 mm Hg (0.1 in. Hg) of the mercury barometer or the correct barometric pressure value reported by a nearby National Weather Service Station (same altitude above sea level).

10.7 Top-Loading Electronic Balance. Calibrate the balance before each test series, using ASTM Class 1 (NIST 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 Analytical Calibration.

10.8.1 Establish gas chromatography/mass spectrometry operating parameters to produce a retention time for tetraethylurea equivalent to suggested GC/MS conditions provided in Section 11.2. Prepare calibration standards according to the procedure in Section 7.13.1. Calibrate the chromatographic system using the internal standard technique (Section 10.8.2).

10.8.2 Internal Standard Calibration Procedure.

10.8.2.1 Analyze each calibration standard using the chromatographic conditions listed in Section 11.2, and tabulate peak area ratios against concentration injected ratios. The results may be used to prepare an average response factor for tetraethylurea.

10.8.2.2 The working calibration curve must be verified on each working day by the measurement of one or more calibration standards. If the response for tetraethylurea varies from the previously established response by more than acceptance criteria in Section 7.4.3 of Method 8270 and 7.17.3 of Draft Method 5041A, a new calibration curve must be prepared. If an autosampler is available, it is convenient to prepare a calibration curve daily by analyzing standards along with test samples.

10.8.2.3 Every 12 hours, use the check standard prepared in Section 7.13.1.3 to check the instrument response and calibration curve.

11.0 PROCEDURES

11.1 Analysis of Stack Gas Samples: Impinger Contents

11.1.1 Measure the sample volume. Decide whether the samples need to be concentrated or diluted. Perform the analysis. If analytes saturate, dilute the solution. If analytes are not observed, concentrate the solution.

11.1.2 If the sample does not need to be concentrated, remove a 20 mL aliquot and dry it by eluting it through anhydrous sodium sulfate. Place a small amount of sodium sulfate in a funnel using a small amount of glass wool or a glass fiber filter to retain the sodium sulfate. Elute the aliquot through the sodium sulfate and collect the eluent in a 15 mL vial.

11.1.3 If the sample needs to be concentrated, remove and dry an aliquot as described in 11.1.2. Place a measured amount of the dried aliquot into a round bottom flask. Use a rotary evaporator to reduce the volume to about 10 mL. Transfer the sample to a 25 mL (to contain) graduated cylinder. Measure and record the volume.

Alternatively, transfer the sample to a 10 mL volumetric flask and bring the volume up to 10 mL with toluene. Transfer the sample to a 15 mL vial.

11.1.4 Transfer a measured aliquot of the dried or dried and concentrated sample to an autosampler vial. Add 40 µL of internal standard for 1 mL of sample. Store the sample at 4±2°C (39±3.6°F) until it is analyzed.

11.2 Chromatographic Conditions.

Chromatographic Conditions	70°C for 1 min, then 20°C/min to 300°C and hold 3 min
Injector Temperature	280°C
Sweep Flow	10 mL/min
Carrier Gas	Helium
Flow Rate	1 mL/min
Mass Range	35 - 650 daltons
Electron Energy	70 ev (nominal)
Quantitation Ion	72 m/z 100% Abundance 100 m/z 60% Abundance 172 m/z 10% Abundance
Injection Volume	1 µL
Retention Times:	Tetraethylurea 10.74 minutes Naphthalene-d_8 10.84 minutes

11.3 GC/MS Analysis.

11.3.1 Analyze samples by GC/MS, using conditions established in Section 11.2. Other GC columns, chromatographic conditions, or detectors may be used if the requirements for Section 9.2. are met, or if the data are within the limits described in Table XPHS-1.

11.3.2 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.

11.3.3 If the peak area exceeds the linear range of the calibration curve, a smaller sample volume should be used. Alternatively, the final solution may be diluted with toluene and reanalyzed.

11.3.4 If the peak area measurement is prevented by the presence of observed interferences, use an alternate quantitation ion (See 11.2 for suggestions). If a suitable quantitation ion cannot be used, cleanup is required. However, no method has been evaluated for this procedure.

12.0 DATA ANALYSIS AND CALCULATIONS.

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures to the correct number of significant figures after final calculations.

12.1 Nomenclature:

A_n	=	Cross-sectional area of nozzle, m^2 (ft^2).
B_{ws}	=	Water vapor in the gas stream, proportion by volume.
C_d	=	Type S pitot tube coefficient (nominally 0.84 ±0.02), dimensionless.
C_f	=	Concentration of phosgene in stack gas (μg/dscm)
I	=	Percent of isokinetic sampling.
L_1	=	Individual leakage rate observed during the leak-check conducted prior to the first component change m^3/min (cfm).
L_a	=	Maximum acceptable leakage rate for a leak-check, either pre-test or following a component change; equal to 0.00057 m^3/min (0.020 cfm) or 4% of the average sampling rate, whichever is less.
L_i	=	Individual leakage rate observed during the leak-check conducted prior to the "i^{th}" component change (I = 1, 2, 3...n) m^3/min (cfm).
L_p	=	Leakage rate observed during the post-test leak-check, m^3/min (cfm).
M_d	=	Stack-gas dry molecular weight, g/g-mole (lb/lb-mole).
MVOL	=	Total volume of recovered sample (mL)
M_w	=	Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
P_{bar}	=	Barometric pressure at the sampling site, mm Hg (in. Hg).
P_C	=	Concentration of tetrethylurea in aliquot (μg/mL)
P_s	=	Absolute stack-gas pressure, mm Hg (in. Hg).
P_{std}	=	Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
P_T	=	Total phosgene in sample (μg)
R	=	Ideal gas constant, 0.06236 mm Hg-m^3/K-g-mole (21.85 in. Hg-ft^3/R-lb-mole).
T_m	=	Absolute average dry-gas meter temperature, K (°R).
T_s	=	Absolute average stack-gas temperature, K (°R).
T_{std}	=	Standard absolute temperature, 293 K (528°R).

V_{adj}	=	Volume of sample aliquot after concentration
V_{aliq}	=	Volume of aliquot used
V_{lc}	=	Total volume of liquid collected in the impingers and silica gel, mL.
V_m	=	Volume of gas sample as measured by dry-gas meter, dscm (dscf).
$V_{m(std)}$	=	Volume of gas sample measured by the dry-gas meter, corrected to standard conditions, dscm (dscf).
$V_{w(std)}$	=	Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).
V_s	=	Stack-gas velocity, calculated by EPA Method 2, Equation 2-9, using data obtained from EPA Method 5, m/sec (ft/sec).
γ	=	Dry-gas-meter calibration factor, dimensionless.
ΔH	=	Average pressure differential across the orifice meter, mm H_2O (in. H_2O).
ρ_w	=	Density of water, 0.9982 g/mL (0.002201 lb/mL).
Θ	=	Total sampling time, min.
Θ_1	=	Sampling time interval from the beginning of a run until the first component change, min.
Θ_i	=	Sampling time interval between two successive component changes, beginning with the interval between the first and second changes, min.
Θ_p	=	Sampling time interval from the final (n^{th}) component change until the end of the sampling run, min.
13.6	=	Specific gravity of mercury.
60	=	sec/min.
100	=	Conversion to percent.
0.574	=	Conversion from tetraethylurea to phosgene.

12.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See field data sheet.

12.3 Dry-Gas Volume. Correct the sample measured by the dry-gas meter to standard conditions (20°C, 760 mm Hg [68°F, 29.92 in. Hg]) by using Equation XPHS-1:

$$V_{m(std)} = V_m \gamma \frac{T_{std}}{T_m} \frac{P_{bar} + \Delta H/13.6}{P_{std}} = K_1 V_m \gamma \frac{P_{bar} + \Delta H/13.6}{T_m} \qquad \textbf{Eq. XPHS-1}$$

where:

K_1 = 0.3853 K/mm Hg for metric units, or

K_1 = 17.64 °R/in. Hg for English units.

It should be noted that Equation XPHS-1 can be used as written, unless the leakage rate observed during any of the mandatory leak-checks (i.e., the post-test leak-check or leak-checks conducted prior to component changes) exceeds L_a. If L_p or L_i exceeds L_a, Equation XPHS-1 must be modified as follows:

a. Case I (no component changes made during sampling run): Replace V_m in Equation XPHS-1 with the expression:

$$V_m - (L_p - L_a)\,\Theta$$

b. Case II (one or more component changes made during the sampling run): Replace V_m in Equation XPHS-1 by the expression:

$$V_m - (L_1 - L_a)\,\theta_1 - \sum_{i=2}^{N} (L_i - L_a)\,\theta_i - (L_p - L_a)\,\theta_p$$

and substitute only for those leakage rates (L_i or L_p) that exceed L_a.

12.4 Volume of Water Vapor Condensed.

$$V_{w(std)} = V_{1c}\,\frac{\rho_w}{M_w}\,\frac{RT_{std}}{P_{std}} = K_2\,V_{1c} \qquad \textbf{Eq. XPHS-2}$$

where:

K_2 = 0.001333 m^3/mL for metric units, or

K_2 = 0.04707 ft^3/mL for English units.

12.5 Moisture Content.

$$B_{WS} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad \textbf{Eq. XPHS-3}$$

NOTE: In saturated or water-droplet-laden gas streams, make two calculations of the moisture content of the stack gas: one from the impinger analysis (Equation XPHS-3) and a second from the assumption of saturated conditions. The lower of the two values of B_{ws} shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in the **NOTE** to Section 1.2 of Promulgated EPA Method 4 (Section 4.0 of Reformatted Draft EPA Method 4). For the purposes of this method, the average stack-gas temperature may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is ±1°C (2°F).

12.6 Conversion Factors.

From	To	Multiply by
scf	m^3	0.02832
g/ft^3	gr/ft^3	15.43
g/ft^3	lb/ft^3	2.205×10^{-3}
g/ft^3	g/m^3	35.31

12.7 Isokinetic Variation.

12.7.1 Calculation From Raw Data.

$$I = \frac{100\ T_s\ [K_3 V_{1c} + (V_m \gamma / T_m)\ (P_{bar} + \Delta H/13.6)]}{60 \theta V_s P_s A_n} \qquad \textbf{Eq. XPHS-4}$$

where:

K_3 = 0.003454 mm Hg-m^3/mL-K for metric units, or

K_3 = 0.002669 in. Hg-ft^3/mL-°R for English units.

12.7.2 Calculation For Intermediate Values.

$$I = \frac{T_s V_{m(std)}\ P_{std} 100}{T_{std}\ V_s \theta A_n P_s 60(1 - B_{ws})} = K_4 \frac{T_s V_{m(std)}}{P_s V_s A_n \theta (1 - B_{ws})} \qquad \textbf{Eq. XPHS-5}$$

where:

K_4 = 4.320 for metric units, or

K_4 = 0.09450 for English units.

12.8 Concentration of Tetraethylurea in Sample. Use an average response factor of the calibration standards to calculate the concentration (P_C) of tetraethylurea in the aliquot analyzed.

12.9 Calculation of Total Weight of Phosgene in the Sample. Determine the total phosgene using the following equation:

$$P_T = P_C \text{ x MVOL x } \frac{V_{adj}}{V_{aliq}} \text{ x } 0.574 \qquad \textbf{Eq. XPHS-6}$$

12.10 Phosgene Concentration in Stack Gas. Determine the phosgene concentration in the stack gas using the following equation:

$$C_f = \frac{K \times P_T}{V_{m(std)}} \qquad \textbf{Eq. XPHS-7}$$

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: The expected method performance parameters for precision, accuracy, and detection limits are provided in Table XPHS-4.

13.2 The Estimated Detection Limit concentrations listed in Table XPHS-4 were obtained using 1/5 of the lowest standard concentration.

14.0 POLLUTION PREVENTION. Reserved.

15.0 WASTE MANAGEMENT.

15.1 Disposal of Excess Diethylamine Reagent. Excess diethylamine reagent may be returned to the laboratory and recycled or treated as organic waste for disposal purposes.

15.2 Disposal of used Charcoal. Activated charcoal may be returned to the laboratory and reactivated or disposed of as hazardous waste.

TABLE XPHS-4. EXPECTED METHOD PERFORMANCE BASED ON LABORATORY STUDIES
TEST MATRIX: HOT MOIST AIR

Phosgene Concentration Level (ppmv, wet)	Percent Moisture (%)	Precision (% RSD)[a]	Recovery (%)[b]	Estimated Detection Limit (ppbv)[c]
1.7 ± 0.4	17 ± 1	9.2	75	200
0.17 ± 0.01	18 ± 4	25	85	200
1.9 ± 0.2	10 ± 5	5.4	86	200
2.7 ±0.2	0	6.6	92	200

[a] Relative Standard Deviation (%) for three spiked trains.
[b] Mean recovery for three spiked trains.
[c] Based on 1/5 the lowest standard for a 849 L (30 cubic foot) sample and 600 mL reagent volume.

15.3 Disposal of excess phosgene spiking solution. Excess spiking solution may be disposed of by reacting the solution with aqueous sodium hydroxide. Dispose of the resulting mixture as a hazardous mixed waste.

16.0 REFERENCES.

1. Rom, Jerome J, *Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment*, Environmental Protection Agency, Research Triangle Park, North Carolina 27711, APTD-0576, PB-209 022/BE, March 1972.

2. Martin, Robert M., *Construction Details of Isokinetic Source-Sampling Equipment*, Environmental Protection Agency, Research Triangle Park, North Carolina 27711, APTD-0581, PB-203 060/BE, April 1971.

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 Type 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, North Carolina, U.S. Environmental Protection Agency, Emissions Measurement Branch, November 1976 (unpublished paper).

7. Quality Assurance Handbook for Air Pollution Measurement Systems. Volume III: Stationary Sources of Specific Methods (Interim Edition). U.S. Environmental Protection Agency. Office of Research & Development, Washington D.C., 20460. EPA/600/R-94-038c. April 1994.

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9. EPA Method 8270 and Draft Method 5041A, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846, Third Edition. September 1988, Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, D.C. 20460

10. Steger, J.S., Bursey, J.T., and Merrill, R.G., “Research and Development of A Field-Ready Protocol for Sampling of Phosgene from Stationary Source Emissions: Diethylamine Reagent Studies,” EPA/600/R-98-xx, PB98-xxxxxx, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, April 1998.

11. Steger, J.L., Coppedge, E.A. and Johnson, L.D., "Research and Development of A Source Method for Phosgene," Proceedings of the EPA/A&WMA International Symposium: Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, May 1996, VIP-64, Air & Waste Management Association, Pittsburgh, PA, 1996, pp 285-289.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA.

17.1 See Section 13 and References 10 and 11 for method performance and evaluation data based on laboratory tests utilizing full scale sampling equipment, dynamic spiking, and a source emissions simulator. This method has not yet been field tested.

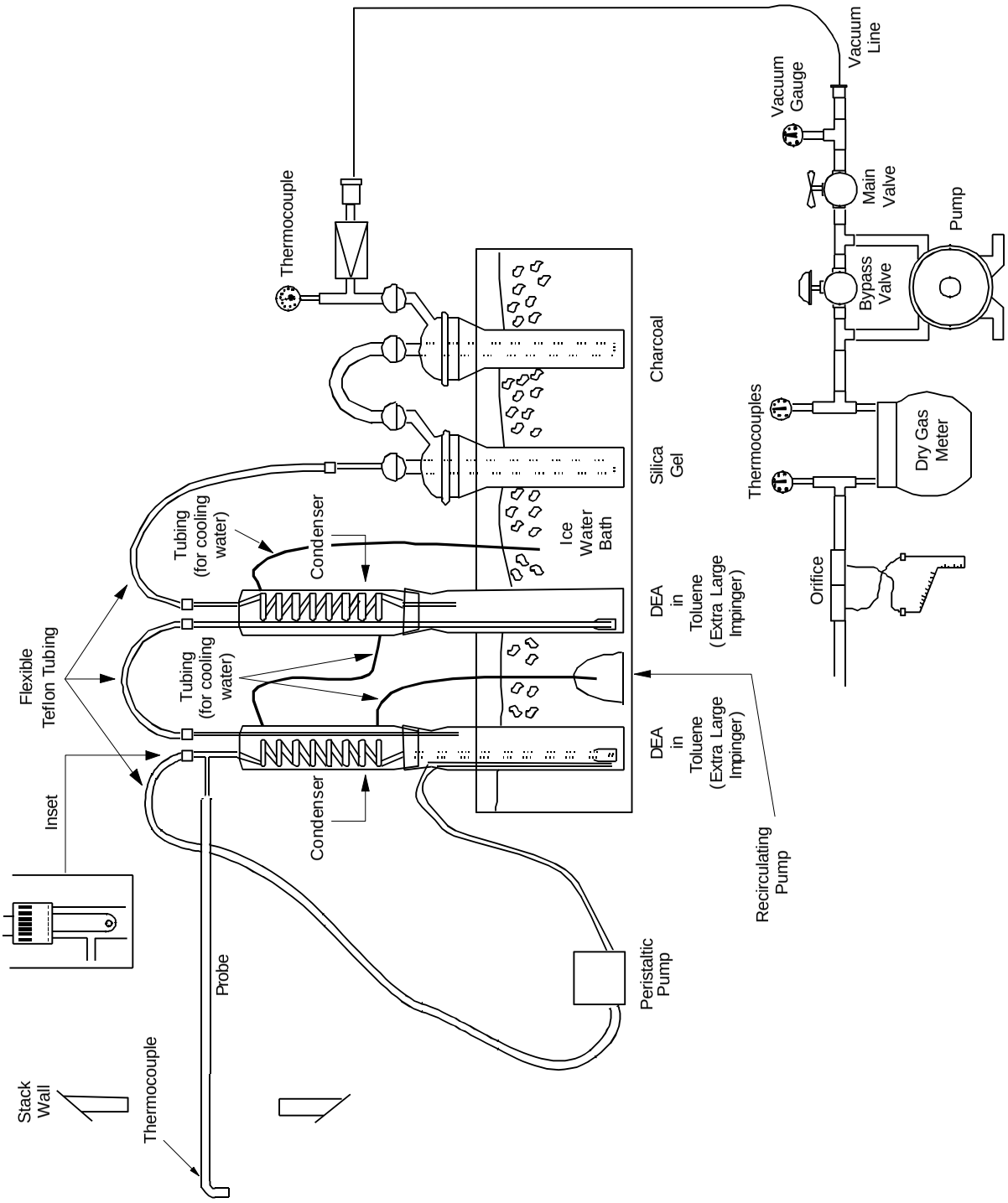

Figure XPHS-1. Sampling Train for Phosgene

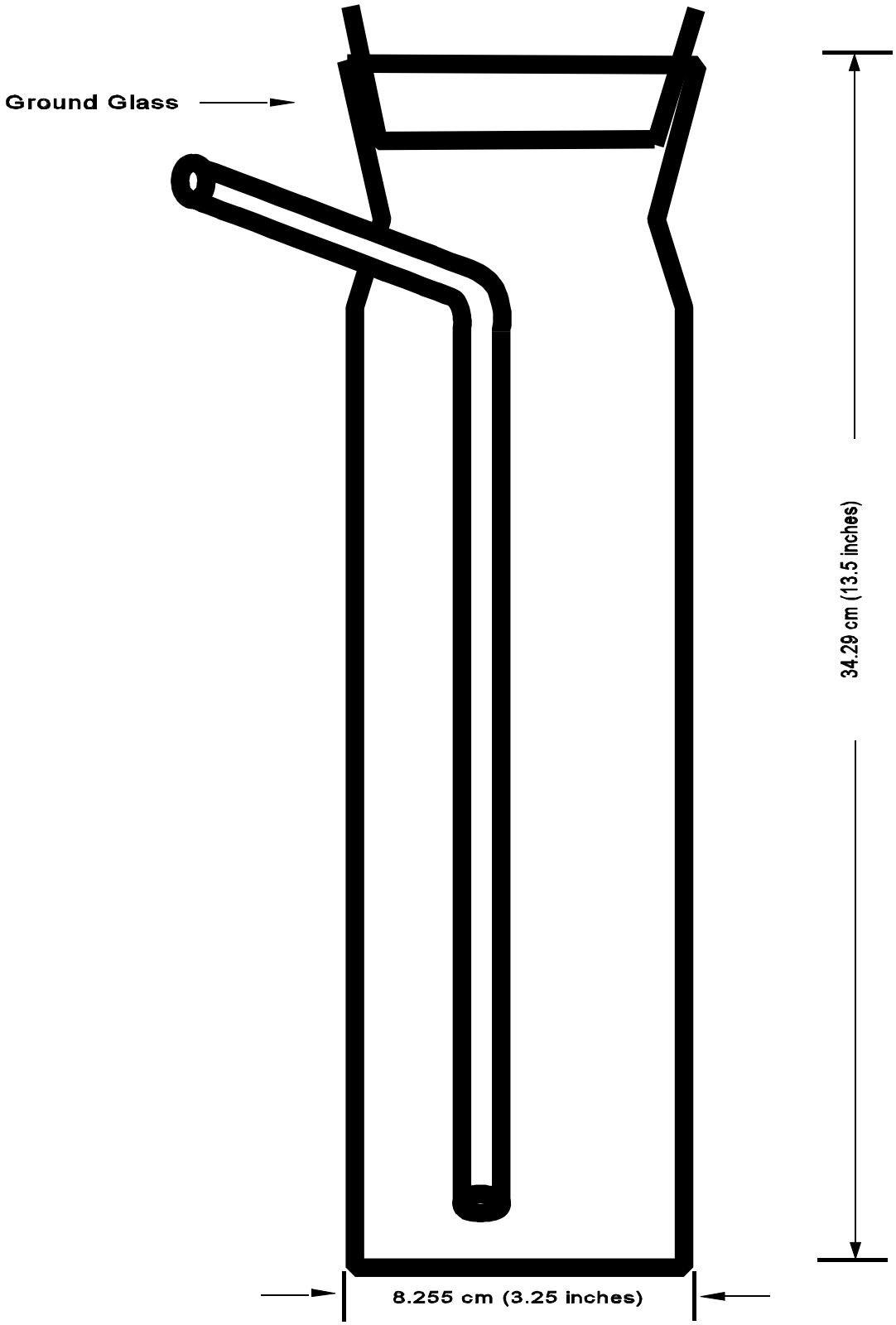

Figure XPHS-2. First Impinger

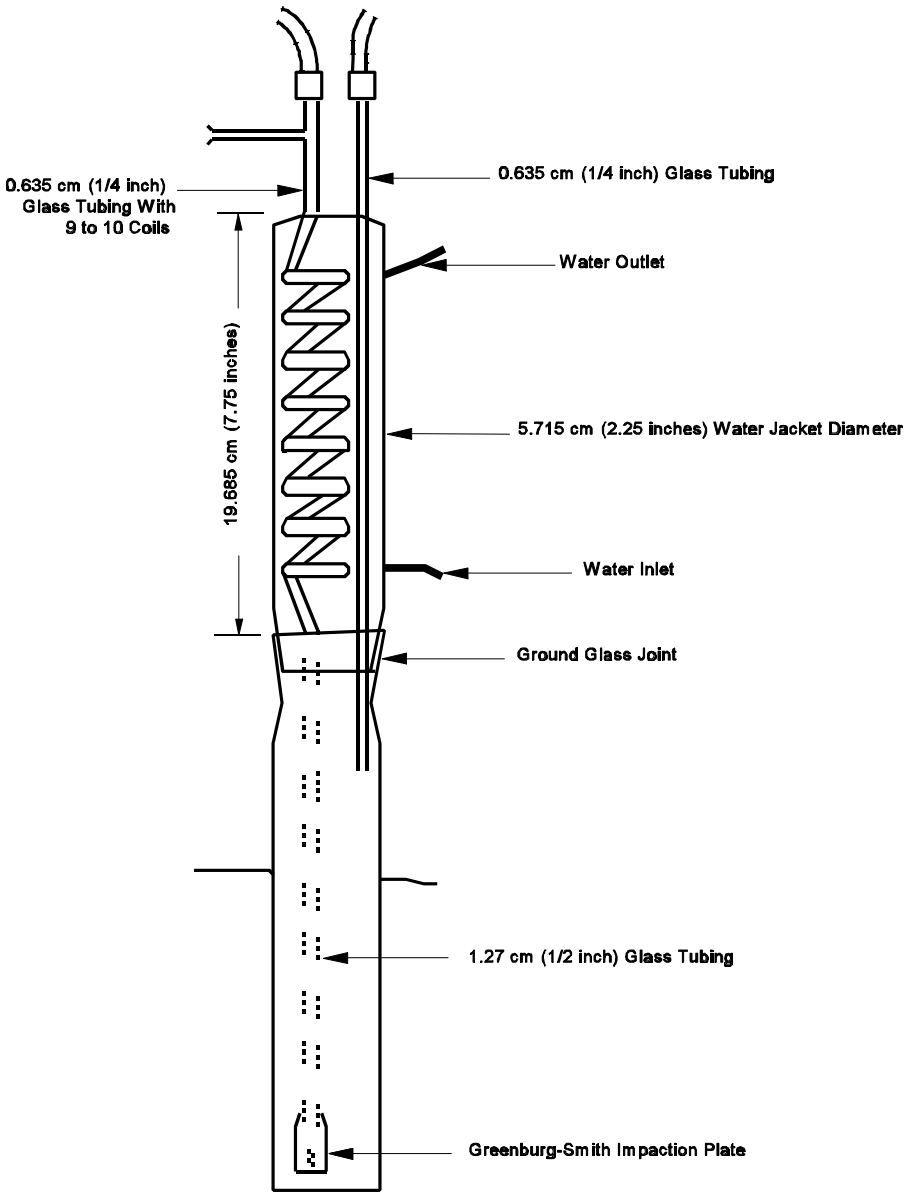

Figure XPHS-3. First Impinger Condenser

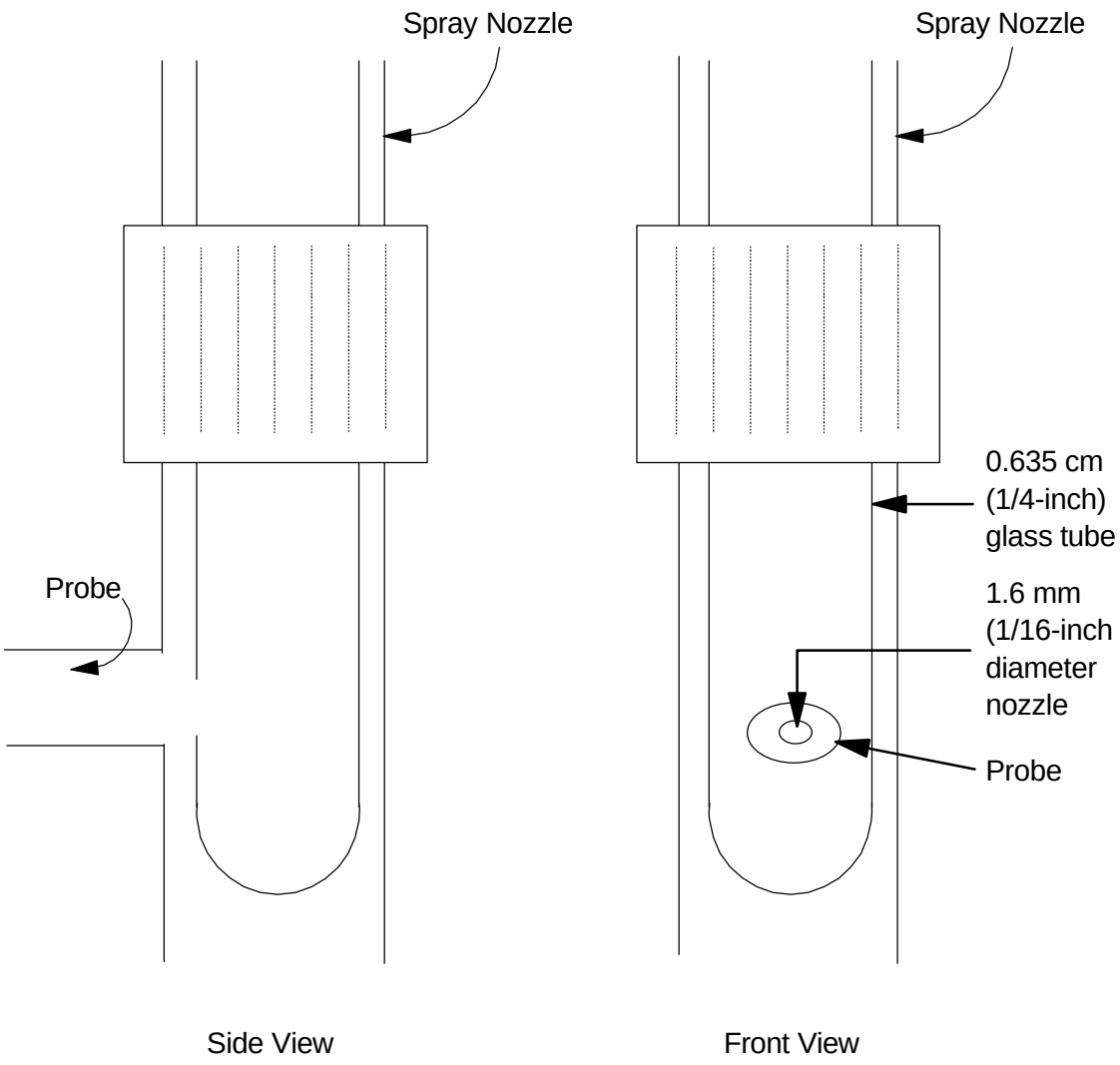

Figure XPHS-4. Reagent Spray Nozzle

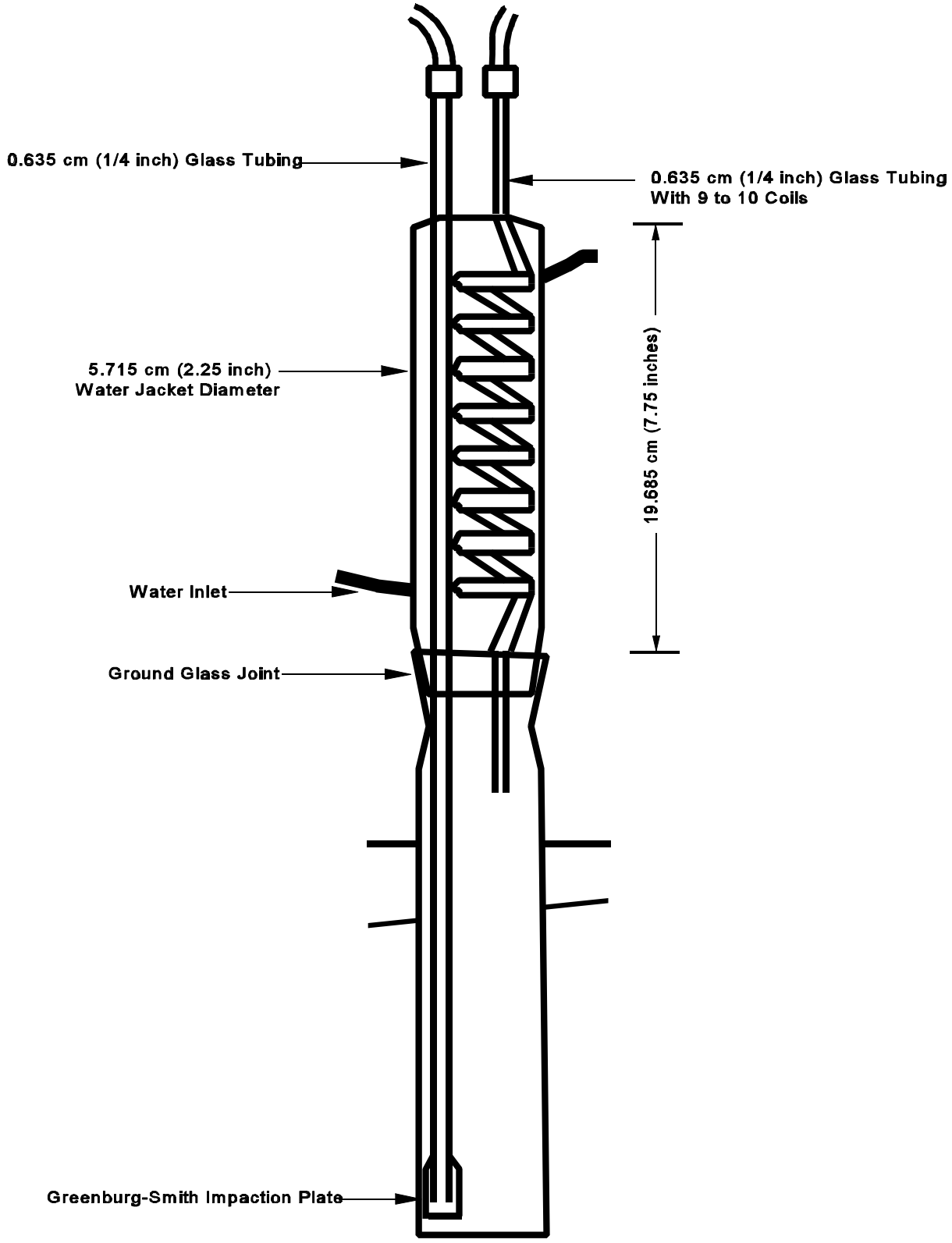

Figure XPHS-5. Second Impinger Condenser

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		Assumed Moisture (%)		
Sample Type		Meter ΔH@		O2 (%)		
Run Number		Yd		CO2 (%)		
Operator		K Factor		O2/CO2 (%)		
Ambient Temperature (°F)		Probe Heater Setting (°F)		Moisture Collected (g)		
Barometric Pressure (in)		Heater Box Setting (°F)		Final Leak Check		
Static Pressure (in H2O)		Initial 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 Temp. (°F)	Probe Temp. (°F)	Condenser Temp. (°F)	Dry Gas Meter Temperature		Impinger Exit (°F)	Pump Vacuum (in. Hg)
									Inlet (°F)	Outlet (°F)		

Comments:

Figure XPHS-6. Field Sampling Data Sheet

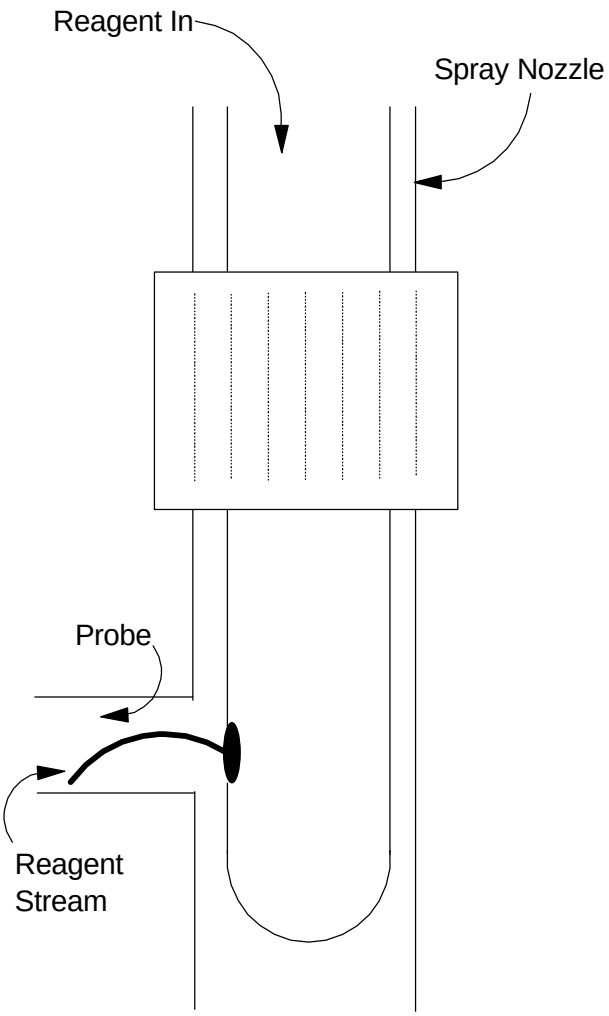

Figure XPHS-7. Adjustment of Reagent Spray