DRAFT METHOD XHCN

METHOD XHCN - SAMPLING AND ANALYSIS FOR HYDROGEN CYANIDE EMISSIONS FROM STATIONARY SOURCES

1.0 *Scope And Application.*

1.1 Method XHCN is applicable to the collection and analysis of hydrogen cyanide (HCN) in the gas phase and in suspended water droplets. Table XHCN-1 provides the Chemical Abstract Service (CAS) number, retention time, and detection limit for hydrogen cyanide. This method has been evaluated for collection of hydrogen cyanide in the laboratory and is believed to be applicable to processes where hydrogen cyanide might be emitted. 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 procedure. Therefore, to obtain reliable results, persons using this method should have a thorough knowledge of at least the following test methods: 40 CFR Part 60 Appendix A, Method 1, Method 2, Method 3, Method 4, and Method 5 (Reference 1).

1.2 If desired, particulate matter may be recovered from the filter and analyzed following the procedures of Method 5 (Reference 1).

1.3 When this method is used to analyze unfamiliar sample matrices, compound identification should be supported by a least one additional qualitative technique. An ion-selective electrode (ISE) may be used for the qualitative confirmation of results for the target analytes.

1.4 The method detection limit (MDL) is shown below, and in Table XHCN-1. The MDL for a specific sample may differ from the MDL listed in Table XHCN-1 depending on the nature of interferences in the sample matrix, the volume of sample collected, the amount of sample used in the procedure, and the use of sample concentration procedures.

Compound Name	CAS No.[a]	Retention Time (minutes)	Method Detection Limits (MDL) ($\mu g/m^3$)
Hydrogen Cyanide	74-90-8	6.7	12

[a] Chemical Abstract Services Registry Number

1.5 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 Method.*

2.1 Gaseous and particulate pollutants are withdrawn from an emission source at an isokinetic sampling rate and are collected in a multi component sampling train. The primary components of the sampling train include a heated probe, a heated filter, two impingers containing 0.1N sodium hydroxide (NaOH), an empty impinger, and an impinger containing silica gel. Hydrogen cyanide present in the stack gas stream reacts with the NaOH to form a cyanide ion, which is retained in the alkaline solution until analyzed by IC. Particulate cyanide salts are retained on the filter, and are not analyzed during routine execution of the method. Sampling is conducted isokinetically because of the significant solubility of HCN in water droplets which may be present in combustion stacks, especially those equipped with wet scrubber systems. If desired, particulate matter may be recovered from the filter and analyzed following the procedures of Method 5 (Reference 1).

3.0 *Definitions.*

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

Field Reagent Blank - Aliquots of each reagent used in the impinger train and each solution 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 and that is recovered using the same procedures as for a sample.

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

Isokinetic Variation - Measure (percentage) of how proportional the sampling velocity is to the source gas velocity.

Laboratory Method Blank - Blank reagent that is processed through the sample preparation procedures with the samples and that is used to evaluate whether or not any contamination has 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 Sample - A second aliquot of sample that is processed through the sample preparation procedures with the field samples.

4.0 *Interferences.*

4.1 High concentrations of acidic gases, including carbon dioxide, may lower the pH of the sodium hydroxide impinger solution. As the pH of the impinger solution decreases, the ability of the impinger to retain hydrogen cyanide also decreases. The performance of the method

depends on maintaining a high pH (≥ 12) in the impingers. As a result, the pH in both impingers must be routinely monitored throughout the duration of sampling. The pH in the impinger may be monitored by adding a pH indicator to the impinger solution, by inserting a pH sensor into the impinger, or by routinely stopping the run and manually checking the pH with pH paper. The pH in the impinger should be monitored at 15 minute intervals and the results noted on the sampling data sheet. When sampling sources that are known or suspected to be highly acidic, modify the sampling procedure using one or more of the following precautions: use a higher concentration (up to 1N) of sodium hydroxide solution in the impingers, add additional impingers to the train, add additional impinger solution to each impinger, or add a lead acetate impinger at the front of the train to absorb some of the acidity. Although the lead acetate solution is used primarily to remove sulfide interferences as discussed in Section 4.2, the impinger with lead acetate will also reduce the amount of acid gases reaching the sodium hydroxide impingers by collecting condensed moisture and by scrubbing some of the acid out of the sampled gas. Prior knowledge of the qualitative composition of the gas stream will aid in minimizing this type of interference. The reagent must be stored in an uncontaminated environment both before and after sampling to minimize blank problems.

4.2 Sulfide interferes with the determination of hydrogen cyanide in two ways. First, concentrations of sulfide greater than 50 ppm in solution (25 mg of H_2S per cubic meter of air for an 849 L sample) interfere with the analysis of cyanide because sulfide elutes before cyanide. Thus, the large sulfide peak will cover up a small cyanide peak. Second, cyanide is degraded over time in the presence of sulfide at any concentration. Thus, when sampling sources known to contain sulfide, an impinger containing lead acetate should be added to the train to precipitate sulfide as lead sulfide before it reaches the sodium hydroxide solution. Although very little cyanide is expected to collect in the lead acetate impinger, it should be recovered as a separate sample and analyzed for cyanide ion.

4.3 Oxidizing agents may decompose most of the cyanides. Oxidizing agents may be removed during sample recovery by adding ascorbic acid. However, the affect of ascorbic acid on the IC analysis has not been determined. Thus, before removing oxidizing agents using ascorbic acid the tester must demonstrate that the ascorbic acid will not interfere with the analysis. To remove oxidizing agents, test a drop of the sample with potassium iodide-starch test paper. A blue color indicates the presence of oxidizing agents. To remove the oxidizing agents, add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the potassium iodide-starch indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume (Reference 2).

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

4.4.1 Glassware must be scrupulously cleaned. Clean all glassware as soon as possible after use by rinsing with the last solvent used. Follow this rinse by washing the glassware with

hot water and detergent, and rinsing with tap water and deionized water. Drain the glassware and then rinse it using reagent grade acetone. Store the glassware in a clean environment to prevent any accumulation of dust or other contaminants.

4.4.2 Use high purity reagents and solvents to minimize interference problems. Purify solvents by distillation in an all-glass system if required.

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

4.6 The extent of interferences that may be encountered using ion chromatographic techniques has not been fully assessed. Although the IC conditions described allow for a resolution of the hydrogen cyanide from sulfide, other matrix components may interfere. Since the IC provides good separation capability and the electrolytic detection system can be made selective for cyanide ion, the two working together should offer very good resolution. In cases of extreme interference, a different analytical finish can be substituted.

4.7 Any gaseous material which can pass through the filter and form cyanide ion in the collection medium will cause a positive bias in this method. Fortunately, only cyanogen is known to do so. Further investigation of the existence of other compounds with the ability to interfere in this manner would be worthwhile.

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. Field sample collection and recovery should be conducted using approved personal safety apparatus as well as an exhaust hood for collection of hazardous fumes. 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 Hydrogen cyanide smells like almonds. It is flammable in the range of 5.6-40% in air. It is extremely toxic when inhaled.

6.0 *Equipment And Supplies.*

6.1 The following items are required for sample collection. A schematic diagram of the sampling train used in this method is shown in Figure XHCN-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 the EPA Method 5 train, with the only change being the use of caustic solution in the impingers. When sampling sources containing sulfides, use the sampling train shown in Figure XHCN-2 to eliminate any sulfide interference with the analysis and with the stability of cyanide in solution. This train uses an initial impinger containing lead acetate to precipitate sulfide as lead sulfide and prevent any sulfide from being collected with the cyanide in the NaOH solution.

Construction details for the basic train components are given in APTD-0581 (Reference 3). Commercial models of this equipment are also available. The following subsections list changes to APTD-0581 and identify allowable train configuration modifications. Basic operating and maintenance procedures for the sampling train are described in APTD-0576 (Reference 4). 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.

6.1.1 Probe Nozzle. Quartz or borosilicate glass with sharp, leading edge, 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.

6.1.2 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. 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 Heated Filter. A glass or quartz filter, similar to that used with Method 5, is used to collect particulate material for subsequent extraction and analysis. The filter is supported by a Teflon filter support which is housed in an all-glass filter holder. The filter is maintained at 120 ± 14 °C (248 ± 25 °F) during sampling.

6.1.4 Pitot tube. Type S, as described in Section 2.1 of promulgated Method 2 (Section 6.1 of Reformatted Draft Method 2), or other appropriate devices (see Vollaro, 1976 in Section 17.0, Reference 5). 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 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 Method 2).

6.1.5 Differential Pressure Gauge. Two inclined manometers or equivalent device as

described in Section 2.2 of promulgated Method 2 (Section 10.0 of Reformatted Draft Method 2). One manometer shall be used for velocity-head readings (ΔP) and the other for orifice differential pressure (ΔH) readings.

6.1.6 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.

6.1.7 Impinger Train. The sampling train requires a minimum of four 500-mL impingers, connected in series immediately following the heated filter (as shown in Figures XHCN-1 and XHCN-2), with ground glass (or equivalent) vacuum-tight fittings.

6.1.7.1 NaOH Train Configuration. The first and second impingers shall be of the Greenburg-Smith design with the standard tip. The remaining two impingers shall be of the modified Greenburg-Smith design, modified by replacing the tip with a 1.3 cm (½ in.) inside diameter glass tube extending to 1.3 cm (½ in.) from the bottom of the outer cylinder. Fill the first and second impingers with 100 mL of 0.1N NaOH per impinger. Leave the third impinger empty and fill the fourth impinger with a known mass (2/3 full) of desiccant.

6.1.7.2 Lead Acetate/NaOH Train Configuration. The first, third, and fourth impingers shall be of the Greenburg-Smith design with the standard tip. The remaining two impingers shall be of the modified Greenburg-Smith design, modified by replacing the tip with a 1.3 cm (½ in.) inside diameter glass tube extending to 1.3 cm (½ in.) from the bottom of the outer cylinder. Fill the first impinger with 10% by weight acidified lead acetate solution. Leave the second impinger empty to prevent carryover of the lead acetate solution into the NaOH solution. Fill the third and fourth impingers with 100 mL of 0.1N NaOH per impinger. Fill the fifth impinger (2/3 full) with a known mass of desiccant. Although the Pb acetate/NaOH sampling train performed well in the laboratory, with no sign of excessive pressure drop across the system, experienced samplers have expressed concern that the presence of three GS impingers with tips might lead to problems in field situations. If particulate collection on the filter becomes heavy, the combined pressure drop across the train might become unacceptable. If that situation occurs, a tube with a more open tip should be substituted for the standard GS tube in the second NaOH impinger (the 4th impinger overall). Since it is desirable to keep the bubble size as small as possible in order to maximize gas-liquid contact, a tube with a tapered tip (maybe ¼" opening) would be preferable to the usual ½" modified GS tip.

6.1.8 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 XHCN-1. At a minimum, the pump should be capable of 4 cubic feet per minute (cfm) free flow, and the dry gas meter should have a volume measuring capacity of 0-999.9 cubic feet with a resolution of 0.005 cubic feet. Other metering systems capable of maintaining sample rates within 10% of isokinetic variation 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.

6.1.9 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, request the station value (which is the absolute barometric pressure) and adjust the value for elevation differences between the weather station and sampling point 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.

6.1.10 Gas Density Determination Equipment. Temperature sensor and pressure gauge (as described in Sections 2.3 and 2.4 of Promulgated Method 2 as well as Sections 6.3 and 6.4 of Reformatted Method 2), and gas analyzer, if necessary, as described in 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 ½ in. 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 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).

6.1.11 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.

6.1.12 Viton A O-ring.

6.1.13 Heat Resistant Tape.

6.1.14 Teflon Tape.

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. Teflon or glass wash bottles are recommended; polyethylene wash bottles should not be used for acetone because organic contaminants may be extracted by exposure to acetone.

6.2.3 Sample Storage Containers. Alkali resistant polyethylene (not for acetone) bottles, 500 mL or 1000 mL. Screw-cap liners shall be either Teflon or constructed to be leak-free and resistant to chemical attack by caustic solution. Narrow-mouth bottles have been found to exhibit less tendency toward leakage. Fold the filter into quarters before transferring it to the bottle.

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 material into and out of containers in the field.

6.2.7 Coolers. To store and ship sample containers.

6.3 Reagent Preparation Apparatus.

6.3.1 Bottles/Caps. High density polyethylene 1 or 4 L bottles with Teflon-lined caps are required for storing 0.1N NaOH solution and lead acetate solution.

6.3.2 Large Glass Container. At least one large glass container (8 to 16 L) is required for preparing the aqueous 0.1N NaOH solution and the lead acetate solution.

6.3.3 Stir Plate/Large Stir Bars/Stir Bar Retriever. A magnetic stir plate and large stir bar are required to mix the aqueous 0.1N NaOH solution and the lead acetate solution. A stir bar retriever is needed for removing the stir bar from the NaOH solution container.

6.3.4 Beakers. Beakers (150 mL, 250 mL, and 400 mL) are useful for holding/measuring liquids when preparing the aqueous 0.1N NaOH and the lead acetate solutions and for weighing NaOH pellets and lead acetate.

6.3.5 Funnels. At least one large funnel is needed for pouring the aqueous 0.1N NaOH and the lead acetate solutions into bottles.

6.3.6 Graduated Cylinders. At least one large graduated cylinder (1 to 2 L) is required for measuring water when preparing the NaOH and lead acetate solutions.

6.3.7 Top-Loading Balance. A top loading balance readable to the nearest 0.1 g is needed for weighing the NaOH pellets used to prepare the aqueous 0.1N NaOH solution and the lead acetate used to prepare the 10% lead acetate solution.

6.3.8 Spatulas. Spatulas are needed for handling NaOH pellets when preparing the aqueous NaOH solution and the lead acetate when preparing the 10% lead acetate solution.

6.4 Analysis

6.4.1 Vials. 10 and 25 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 Volumetric Flasks.

6.4.4 Ion Chromatograph (Modular).

6.4.4.1 Pumping system. Isocratic with constant flow control capable of 1.0 mL/min.

6.4.4.2 High Pressure Injection Valve with 50 µL loop.

6.4.4.3 Column. 250 mm x 4 mm ID, IonPac AS7A (or equivalent) with an AG7A (or equivalent) guard column.

6.4.4.4 Electrochemical Detector with Silver Working Electrode and Silver/Silver Chloride Reference Electrode.

6.4.4.5 Strip Chart Recorder Compatible With Detector. Use of a data acquisition

system for measuring peak areas and retention times is recommended.

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 Water. All references to water in this method refer to deionized, distilled water that conforms to American Society of Testing and Materials (ASTM) Specification D 1193-91, Type 3 (Reference 6). If high concentrations of organic matter are not expected to be present, the analyst may omit the potassium permanganate test for oxidizable organic matter.

7.2.1 All laboratory glassware must be washed with laboratory detergent and rinsed with water and acetone before use.

7.2.2 Preparation of Aqueous 0.1N NaOH Reagent: Each batch of NaOH reagent should be prepared according to the procedure described below.

NOTE: NaOH pellets or solution should be handled with plastic gloves at all times with prompt and extensive use of running water in case of skin exposure.

7.2.2.1 Place an 8-L (or other appropriately sized) container under a fume hood on a magnetic stirrer. Add a large stir bar and fill the container half-full with water. Start the stirring bar and adjust it to stir as fast as possible. Weigh the NaOH pellets on a one-place balance (32 g/8 L) and add to the stirring water. Fumes may be generated and the water may become warm. Fill the 8 L container to the 8 L mark with water and stir until dissolved.

7.2.2.2 Transfer the 0.1N NaOH reagent solution into a high density polyethylene bottle. Label the bottle with the reagent identification and concentration, the date prepared, and who prepared it.

7.2.3 Preparation of 10% Lead Acetate Solution: Each batch of lead acetate reagent should be prepared according to the procedure described below.

7.2.3.1 Place an 8-L (or other appropriately sized) container under a fume hood on a magnetic stirrer. Add a large stir bar and fill the container half-full with water. Start the stirring bar and adjust it to stir as fast as possible. Weigh the lead (II) acetate trihydrate on a one-place balance (933 g/8 L) and add to the stirring water. Adjust the pH to less than 4.5 by adding glacial acetic acid. Fill the 8-L container to the 8-L mark with deionized, distilled water and stir until well mixed. Check the pH. If greater than 4.5, add additional glacial acetic acid to adjust the pH below 4.5.

7.2.3.2 Transfer the lead acetate solution into a high density polyethylene bottle.

7.2.4 Shipment to the Field: Tightly cap the bottles containing 0.1N NaOH reagent and lead acetate reagent using Teflon-lined caps. Seal the bottles with Teflon tape. If numerous bottles are shipped, cushion the bottles to ensure that breakage does not occur. If the NaOH reagent and the lead acetate reagent have passed the Quality Control criteria in Section 9.2.5, the reagents may be packaged to meet necessary shipping requirements and sent to the sampling area.

If the Quality Control criteria are not met, the reagent solutions must be re-prepared.

7.3 Field Spike Standard Preparation. To prepare a cyanide field spiking standard at 4.0 mg/mL, weigh 500 mg of potassium cyanide in a 50 mL volumetric flask. Fill the flask half full with 0.1N NaOH and shake vigorously. After all of the potassium cyanide dissolves, dilute to 50 mL with 0.1N NaOH.

7.4 Ascorbic Acid. Ascorbic Acid may be required to remove oxidizing agents during sample recovery.

7.5 Sodium Hydroxide. NaOH pellets are required for preparation of the impinger reagent solution, the mobile phase buffer, and the 10N NaOH used to adjust the pH of recovered samples.

7.6 Alizarin-Yellow R Indicator Solution. Dissolve 0.10 g of Alizarin-Yellow R in 100 mL of deionized, distilled water. Agitate on a stir plate for 30 minutes to completely dissolve the Alizarin-Yellow R.

7.7 Acetone. HPLC grade or equivalent is required for rinsing glassware.

7.8 Sodium Acetate and Ethylene Diamine. Re required for the Mobile Phase Buffer.

7.9 Potassium Cyanide. Required for preparation of analytical standards.

7.10 Sodium Acetate Buffer Solution. Needed for mobile phase. Prepare the sodium acetate buffer solution each day by dissolving 4 g of NaOH and 41 g of sodium acetate in water. Add 5 mL of ethylene diamine and dilute to 1 L with water.

7.11 Preparation of Standards for Chromatographic Analyses.

7.11.1 Stock Standards. Prepare potassium cyanide stock standards at concentrations of 100 ng/μL by weighing 25 mg (± 0.01 mg) of potassium cyanide into 100-mL volumetric flasks, dissolving the crystals in 0.1N NaOH, and diluting to the line with 0.1N NaOH. Transfer the stock solutions to bottles with a polyfluoroethylene-lined screw caps and store at 4°C (39°F).

7.11.2 Calibration Standards. Prepare calibration standards by diluting 100, 500, 1,000, 1,500, and 2,000 μL of one of the potassium cyanide stock solutions to 100 mL with 0.1N NaOH to provide a standard curve with CN^- calibration points at 0.1, 0.5, 1.0, 1.5, and 2.0 ng/μL of 0.1N NaOH.

7.11.3 Check Standard. Prepare a check standard, using potassium cyanide from a second vendor, at a concentration of 1.0 ng/μL of CN^- by taking 1000 μL of a 100 ng/μL potassium cyanide stock standard and diluting to 100 mL with 0.1N NaOH. Use the check standard to check the instrument response and the calibration accuracy. Replace standard solutions after six months, or sooner, if comparison with check standards indicates a problem.

7.12 Crushed Ice. Quantities ranging from 10-50 pounds may be necessary during a sampling run, depending upon the temperature of ambient air and the moisture content of the gas stream. Although normal ambient temperatures will not harm the samples, they may need to be packed in ice to avoid excessive heat during shipping in hot weather; sufficient ice for this purpose must be allowed.

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

7.14 Silica Gel. Indicating type, 6-16 mesh. If previously used, dry at 180 °C (350 °F)

for 2 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.

7.15 Impinger Solutions. The impinger solutions can be prepared in the laboratory or in the field. Place labels on the containers specifying the reagent identification and concentration, the date prepared, and who prepared it.

7.15.1 The 0.1N NaOH solution is prepared (Section 7.2.2) by dissolving 4 grams of sodium hydroxide in deionized, distilled water and diluting to 1 liter with water . This solution should be stored in high density polyethylene containers and used within ten days of preparation. Alternatively, commercially-prepared NaOH solution may be used.

7.15.2 The 10% by weight acidified lead acetate solution is prepared (Section 7.2.3) by dissolving 117 grams of lead (II) acetate trihydrate in water, diluting to 1 liter with water (10% lead acetate), and acidifying the solution to a pH of 4.5 or below with glacial acetic acid. This solution should be stored in high density polyethylene containers and used within ten days of preparation.

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 4), 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 containers. As an alternative to preweighing the silica gel, the silica gel may be weighed directly in the impinger or sampling holder 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 Method 1 or other relevant criteria. Determine the stack pressure, temperature, and range of velocity heads using Method 2 (Reference 1). Check the Pitot lines for leaks according to Promulgated Method 2, Section 3.1 (Reformatted Method 2, Section 8.1). Determine the stack gas moisture content using 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 Method 2, Section 3.6 (Reformatted Method 2, Section 8.6). If integrated 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 Method 2, as well as

Section 8.2 of Reformatted 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. A minimum sample volume should also be determined that will provide sufficient collection of the analyte so that the in-stack detection limit is consistent with the data quality objective for the project.

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 Method 1 (Reference 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 This section describes the basic NaOH train configuration which may be modified as outlined to reduce potential interferences.

8.4.2.1 For the basic NaOH train configuration, place 100 mL of 0.1N NaOH absorbing solution in each of the first two impingers. Add 10 drops of Alizarin-Yellow indicator solution to each impinger (if not using a pH probe or pH paper to monitor impinger pH). The third impinger shall remain empty. The fourth impinger shall have 200 to 300 g of pre-weighed silica gel. Be careful to ensure that the silica gel is not entrained and carried out from the impinger during sampling. Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded. For moisture determination, weigh all of the impingers after filling them with reagent.

8.4.2.2 When high concentrations of acidic gases are expected to be present in the source, modify the basic NaOH train configuration by one or more of the following procedures: 1) increase the volume of 0.1N NaOH absorbing solution in each of the first two impingers to 200 mL; 2) add one or more additional impingers containing NaOH solution to the train; 3) increase the concentration of the NaOH solution in the impingers to 0.2N, 0.5N, 1N or 2N; or 4) use the lead acetate/NaOH train configuration.

8.4.2.3 For the lead acetate/NaOH train configuration, place 100 mL of 10%

acidified lead acetate solution in the first impinger. Leave the second impinger empty. Fill the third and fourth impingers with 100 mL of 0.1N NaOH absorbing solution. Add 10 drops of Alizarin-Yellow indicator solution to each impinger (if not using a pH probe or pH paper to monitor impinger pH). Place 200 to 300 g of pre-weighed silica gel in the fifth impinger.

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 (Reference 4) for details. Other connecting systems using either 316 stainless steel or 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 traverse sampling point.

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

8.4.5 Place crushed ice around the impingers.

8.4.6 Switch on and set the probe and filter heating systems at the desired temperature. Allow time for the temperature to stabilize for 30 min.

8.5 Leak-Check Procedures.

8.5.1 Pretest Leak-check.

8.5.1.1 A pretest leak-check of the sampling system is not required but is highly recommended. A pre-test leak-check of the pitot lines is also not required but is highly recommended (see Method 2).

8.5.1.2 After the sampling train has been assembled, switch 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-0581 and APTD-0576 (References 3 and 4) 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, a leak-check shall be conducted immediately after the interruption of sampling and before the change is made. The leak-check shall be performed according to the procedure described in Section 8.5.1, except that it shall be performed 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, the tester must 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, a leak-check similar to a pretest leak-check should also be conducted.

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. The leak-check shall be performed in accordance with the same procedures as the pre-test leak-check, except that the post-test leak-check shall be conducted 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, the tester shall record the leakage rate, correct the sample volume (as shown in Section 12.3 of this method) and clearly mark the data obtained of questionable reliability, or void the sampling run.

8.6 Sampling Train Operation.

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

8.6.2 For each run, record the data on a data sheet such as the one shown in Figure XHCN-3. 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 XHCN-3 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. Also, record the results of any pH checks that were made and the time that they were made.

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 4) 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 (Reference 7) 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 switched 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.

8.6.6 Traverse the stack cross-section, as required by Method 1 (Reference 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 the heated filter 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 and the pH of the impingers containing 0.1N NaOH solution. If the pH of the NaOH solution is < 12, replace that impinger with another impinger containing fresh NaOH solution. Document the change on the data sheet.

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 (e.g., when the pH drops below 12). Document on the data sheet the times when changes in trains occur, especially if meter boxes are changed.

8.6.9 When two or more trains are used, components from each train shall be analyzed separately. 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, remove the probe and nozzle from the stack, switch 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 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 in Section 12.11 of Reformatted Method 5) to determine whether the run was valid or another test should be performed.

8.7 Sample Recovery. The sampling train is recovered in three fractions (four, if the Pb acetate impinger is needed): the front half rinse of the nozzle, probe, and connecting glassware ahead of the filter constitute the first fraction; the filter makes up the second subsample; the three impinger solutions and rinses from impingers and connecting back half glassware comprise the third portion. A fourth fraction is necessary if the Pb Acetate/ NaOH train configuration is employed.

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 or particulate 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 or tape of other inert materials may be used to seal all openings.

8.7.1.3 Transfer the probe and impinger assembly to an area that is clean 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 document on the data sheet any abnormal conditions. If indicator was added to the impingers, document on the data sheet the color of the indicator; otherwise, measure the pH of each of the 0.1N NaOH impinger solutions with pH paper or a pH meter and record the separate pH measurements on the data sheet.

8.7.1.5 Save a portion of all washing solutions (0.1N NaOH and acetone) used for cleanup as a blank. Transfer 100 mL of each solution directly from the wash bottle and place each in a separate prelabeled sample reagent “blank” container (see Section 9.2.2).

8.7.2 Sample Containers.

8.7.2.1 Container No. 1 (front-half rinse for particulate determination). Using two people, rinse the probe/nozzle with acetone 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 sample container. If particulate is visible, use a Teflon brush to loosen/remove the particulate material and follow with a second rinse and brushing, which is followed by a final rinse. Add the rinse of the front half of the filter housing (see 8.7.2.2) to this container. Add the proper label describing the facility tested, test location, run number, date, time, contents, sample volume or weight, and any applicable notes. If a determination of particulate matter is not needed, the filter catch and front half rinses may be discarded following procedures for proper disposal of potentially hazardous materials.

8.7.2.2 Container No. 2 (filter catch for particulate determination). Disassemble the filter holder and carefully remove the filter with Teflon tweezers, fold into quarters and place in a precleaned glass bottle. Cap the bottle, add the proper label, and seal with Teflon tape. Rinse the front half of the filter holder, the filter support, and any other front half connecting glass pieces with acetone and add the rinses to Container No. 1. Mark the liquid level in Container No. 1 and seal for shipment. If a determination of particulate matter is not needed, the filter catch and front half rinses may be discarded following procedures for proper disposal of potentially hazardous materials.

8.7.2.3 Container No. 3. After recording the pH and weighing, pour the contents of Impingers No. 1, 2 and 3 into Container No. 3 along with the 0.1N NaOH rinses of the impingers and connecting glassware. Rinse the impingers a minimum of three times. Do not rinse the back half of the filter holder. Rinsing the back of the filter holder may, under certain circumstances, increase transfer of water soluble cyanide salts from the front half and thereby cause a positive bias in the HCN results. Mark the liquid level, seal the container, and add the proper sample label with appropriate descriptive information. If the Pb Acetate/ NaOH train configuration is employed, a fourth container is necessary. The contents of the Pb Acetate impinger, the following empty impinger, and rinses of the two (Pb Acetate related impingers) and connecting glassware between the two are recovered, shipped, and analyzed separately from the NaOH solution.

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

8.7.2.5 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, packed in ice (if necessary to avoid excessive heating during shipping in hot weather), using the proper shipping materials as prescribed for hazardous materials.

8.7.2.6 Samples are stable in basic solution for approximately four months when no interferents, such as sulfide, are present in the solution. When sulfide is present in solution, the cyanide is stable for less than one month. All samples should be analyzed within 30 days of acquisition, since the presence of impurities from the emission matrix is always in question.

9.0 *Quality Control.*

9.1 Sampling. Sampling quality control procedures are listed in Table XHCN-2. See References 8 and 9 for additional Method 5 quality control.

9.2 Analysis. The quality assurance program required for this method includes the analysis of the field, reagent and method blanks, procedure validations, and analysis of field spikes. The assessment of combustion data and positive identification and quantitation of hydrogen cyanide is dependent 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

information necessary for undertaking corrective action if problems are observed in laboratory operations or in field sampling activities. Table XHCN-3 lists laboratory quality control procedures.

9.2.1 Field Train Blanks. Submit field blanks with the samples collected at each sampling site. The field blanks include the sample bottles containing aliquots of unused NaOH reagent (and lead acetate reagent, if used). At a minimum, assemble one complete sampling train in the field staging area, transport the train to the sampling area, and leak-check the train 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 blank train during the sample test. Recover the train as if it were an actual test sample. Do not pass any stack gas through the blank sampling train.

9.2.2 Reagent Blanks. Collect a 100 mL aliquot of 0.1N NaOH in the field as a separate sample and return to the laboratory for analysis to evaluate artifacts that may be observed in the actual samples. When the lead acetate/NaOH train configuration is used, collect a 100 mL aliquot of 10% lead acetate solution. When particulate matter is being measured, it is also necessary to collect a 100 mL aliquot of the acetone.

9.2.3 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.

9.2.4 Field Spike. Perform a field spike by introducing 2 mL of the Field Spike Standard into a single impinger (taken to the field expressly for this purpose, and not part of the actual stack sample) containing 100 mL of NaOH 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.

9.2.5 Preparation of Reagent. Take two aliquots of the NaOH reagent and two aliquots of the lead acetate reagent. The size of the aliquots depends on the exact sampling procedure used, but 100 mL is reasonably representative. To ensure that the background in the reagent is acceptable for field use, analyze one aliquot of each reagent according to the procedure in Section 11. Save the remaining portion of each reagent for use as a laboratory method blank when the analysis is performed.

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 the glass nozzles become cracked, chipped, or broken they must be replaced. Each nozzle must be permanently and uniquely identified.

10.2 Pitot Tube Assembly. The Type S Pitot tube assembly must be calibrated according to the procedure outlined in Section 4 of Promulgated Method 2 (Section 10.1 of

Reformatted Draft Method 2), or assigned 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, the metering system shall be calibrated according to the procedure outlined in APTD-0576 (Reference 4). 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, a leak-check procedure may not detect leakages within the pump. For these cases, the following leak-check procedure will apply. Make a ten-minute calibration run at 0.00057 m^3/min (0.020 cfm). At the end of the run, record 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 4).

10.3.3 Leak-Check of Metering System. The portion of the sampling train from the pump to the orifice meter (see Figure XHCN-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. 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. The probe heating system must be calibrated before its initial use in the field according to the procedure outlined in APTD-0576 (Reference 4). Probes constructed according to APTD-0581 (Reference 3) need not be calibrated if the calibration curves in APTD-0576 (Reference 4) 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. The initial temperature acquired from the sensor must be corrected to obtain the final temperature 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, a three-point calibration at ice water, boiling water, and room air temperatures must be performed. The reference thermometer and thermocouple must agree to within 1.5% at each of the calibration points. A calibration curve may be constructed 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 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 ion chromatographic operating parameters to produce a retention time equivalent to that indicated in Table XHCN-1. Suggested chromatographic conditions are provided in Section 11.2. Prepare calibration standards according to the procedure in Section 7.11.2. Calibrate the chromatographic system using the external standard technique (Section 10.8.2).

10.8.2 External Standard Calibration Procedure.

10.8.2.1 Analyze each calibration standard using the chromatographic conditions listed in Section 11.2, and tabulate peak area against the concentration injected. Use the results to prepare a calibration curve for hydrogen cyanide.

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 hydrogen cyanide varies from the previously established response by more than 10% (see Table XHCN-3), the test must be repeated using a fresh calibration standard, but only after it has been verified that the analytical system is in control. Alternatively, a new calibration curve may be prepared for hydrogen cyanide. 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 Periodically use the check standard prepared in Section 7.11.3 to check the instrument response and calibration curve.

11.0 ***Analytical Procedures.***

11.1 Analysis of Stack Gas Samples: Impinger Contents (Container No. 3, Section 8.7.2.3). If the Pb Acetate/ NaOH train configuration is employed, the contents of the Pb Acetate impinger is analyzed separately from the NaOH solution, but the same analysis procedure is followed.

11.1.1 Measure the sample volume. Decide whether the samples need to be diluted. Perform analysis. If analytes saturate, dilute the solution.

11.1.2 Store the samples at 4±2°C (39±4°F). The samples should be analyzed within 30 days of collection.

11.2 Chromatographic Conditions.

Column:	IonPac AS7 Analytical, 4 x 250 mm with AG7A Guard column
Mobile Phase:	0.1N NaOH and 0.5 M sodium acetate in 0.5% ethylene diamine
Flow Rate:	1.0 mL/min.
Detector:	Electrochemical detector with silver working electrode and silver/silver chloride reference electrode
Injector Volume:	50 μL

11.3 IC Analysis.

11.3.1 Analyze samples by IC, using conditions established in Section 11.2. Table XHCN-1 lists the retention time and MDL that were obtained under these conditions. Other IC 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 XHCN-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 mobile phase and reanalyzed.

11.3.4 If the peak area measurement is prevented by the presence of observed interferences, different chromatographic procedures or sample cleanup may be required. However, no method has been evaluated for this procedure. If absolutely necessary to avoid specific interferences, alternate methods for analysis of cyanide ion can be substituted.

11.4 Analysis of Filter Catch and Front Half Rinses (Containers 1 and 2, Sections 8.7.2.1 and 8.7.2.2).

11.4.1 The filter catch and front half rinses may be analyzed for particulate matter following the procedures of Method 5 (Reference 1). If a determination of particulate matter is

not needed, the filter catch and front half rinses may be discarded following proper procedures for disposal of potentially hazardous materials. The filter and front half rinses are not analyzed for cyanide ion, since they will contain only particulate cyanide material and should not be added to the HCN results.

12.0 *Calculations and Data Analysis.*

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:

AIC	=	Acceptable Impurity Concentration (μg/mL)
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 hydrogen cyanide in stack gas (μg/dscm)
EAC	=	Expected Analyte Concentration (ppbv)
FW	=	Formula weight of analyte (g/mole)
I	=	Percent of isokinetic sampling.
K	=	35.31 ft^3/m^3 if $V_{m(std)}$ is expressed in English units
K	=	1.00 m^3/m^3 if $V_{m(std)}$ is expressed in metric units
K_1	=	0.3853 K/mm Hg for metric units, or
K_1	=	17.64 °R/in. Hg for English units.
K_2	=	0.001333 m^3/mL for metric units, or
K_2	=	0.04707 ft^3/mL for English units.
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.
K_4	=	4.320 for metric units, or
K_4	=	0.09450 for English units.
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 pretest 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).
M_{vol}	=	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 hydrogen cyanide in sample (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 hydrogen cyanide 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).
R_{vol}	=	Volume of NaOH reagent used in the impingers (mL).
S_{vol}	=	Volume of air sampled at standard conditions (L).
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 dilution.
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 Method 2, Equation 2-9, using data obtained from 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.

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 XHCN-1:

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

It should be noted that Equation XHCN-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 XHCN-1 must be modified as follows:

a. Case I (no component changes made during sampling run): Replace V_m in Equation XHCN-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 XHCN-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.

12.5 Moisture Content.

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

NOTE: In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation XHCN-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 Method 4 (Section 4.0 of Reformatted Draft 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

12.6.1 Nomenclature.

scf standard cubic feet
g/ft^3 grams per cubic foot
gr/ft^3 grains per cubic foot

12.7 Isokinetic Variation.

12.7.1 Calculation From Raw Data.

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

12.7.2 Calculation For Intermediate Values.

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

12.8 Concentration of Hydrogen Cyanide in Sample. A least squares linear regression analysis of the calibration standards shall be used to calculate a correlation coefficient, slope, and intercept. Concentrations are the X-variable, and response is the Y-variable.

12.9 Calculation of Total Weight of Hydrogen Cyanide in the Sample. To determine the total hydrogen cyanide use the following equation:

$$P_T = P_C \times M_{vol} \times \frac{V_{adj}}{V_{aliq}} \qquad \textbf{Eq. XHCN-6}$$

NOTE: Add the μg of HCN found in the Pb Acetate impinger (whenever it is utilized) to the total before calculating the concentration in the stack gas.

12.10 Hydrogen Cyanide Concentration in Stack Gas. Determine the hydrogen cyanide concentration in the stack gas using the following equation:

$$C_f = \frac{KxP_T}{V_{m(std)}} \qquad \textbf{Eq. XHCN-7}$$

12.11 Calculate the Acceptable Concentrations of Impurities in NaOH Reagent as follows:

$$AIC = 0.1 \times \frac{E_{ac} \times S_{vol} \times \frac{FW}{22.4}}{R_{vol} \times 1{,}000} \qquad \textbf{Eq. XHCN-8}$$

where:

0.1 is the acceptable contaminant concentration,
22.4 is a factor relating ppbv to g/L,
1,000 is a unit conversion factor.

13.0 ***Method Performance.***

13.1 Method Performance Evaluation. The expected method performance parameters for precision and accuracy are provided in Table XHCN-4. This information was determined as part of the method development and evaluation project reported in References 10 and 11. A field test program was conducted in order to evaluate the method according to Method 301. The draft sampling method exhibited outstanding performance in the laboratory collection efficiency trials, but performed poorly during the Method 301 (Reference 12) field test at a hazardous waste incinerator. Subsequent laboratory experiments supported the hypothesis that the field failure was due to excessive levels of acidity in the incinerator emissions. This revised draft method, which is designed to be tolerant to higher acid levels is presented in this document and is recommended for use on hazardous waste incinerators, coal-fired power plants, and similar combustion sources. In spite of the failed field test, this is the best documented and verified method available for sampling HCN from stationary sources (References 10 and 11).

13.2 The MDL concentrations listed in Table XHCN-1 were obtained using instrument detection limits determined using the method reported in the Federal Register (Appendix B to Part 136 - Definition and Procedure for the Determination of the Method Detection Limit Revision 1.11, Federal Register, Vol. 49, No. 209, Friday, October 26, 1984.)

14.0 ***Pollution Prevention.*** Reserved.

15.0 ***Waste Management.***

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

15.2 Disposal of Excess Lead Acetate Reagent. Excess lead acetate reagent may be returned to the laboratory and recycled or treated as aqueous waste for disposal purposes.

16.0 ***References.***

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

2. California Environmental Protection Agency, Air Resources Board, CARB Method 426, "Determination of Cyanide Emissions from Stationary Sources", January 22, 1987.

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

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

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

6. American Society for Testing and Materials, D1193-91 Reagent Water, 1997.

7. 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.

8. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III. Stationary Source Specific Methods (Interim Edition)," EPA/600/R-94-038c, U.S. Environmental Protection Agency, Washington D.C., April 1994.

9. Schlickenrieder, L.M., Adams, J.W., and Thrun, K.E., "Modified Method 5 Train and Source Assessment Sampling System Operator's Manual," EPA/600/8-85-

003, PB85-169878, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, February 1985.

10. Steger, J.L., Merrill, R.G., Parrish, C.R., and Johnson, L.D., "Development and Evaluation of a Source Sampling and Analysis Method for Hydrogen Cyanide," EPA/600/R—, March 1998.

11. Steger, J.L., Merrill, R.G., Fuerst, R.G., Johnson, L.D., Jackson, M.D. and Parrish, C.R., "Development and Evaluation of a Source Sampling and Analysis Method for Hydrogen Cyanide," Proceedings of the EPA/A&WMA International Symposium: Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, April 1997, VIP-74, Air & Waste Management Association, Pittsburgh, PA, 1997, pp 114-122.

12. *Code of Federal Regulations, Title 40, Part 63, Appendix A*, U.S. Government Printing Office, Washington, DC, 1993, pp 324-331.

17.0 *Tables, Diagrams, Flowcharts, and Validation Data.*

17.1 See Section 13.1, Table XHCN1, Table XHCN4, and References 10 and 11 for method performance and evaluation data.

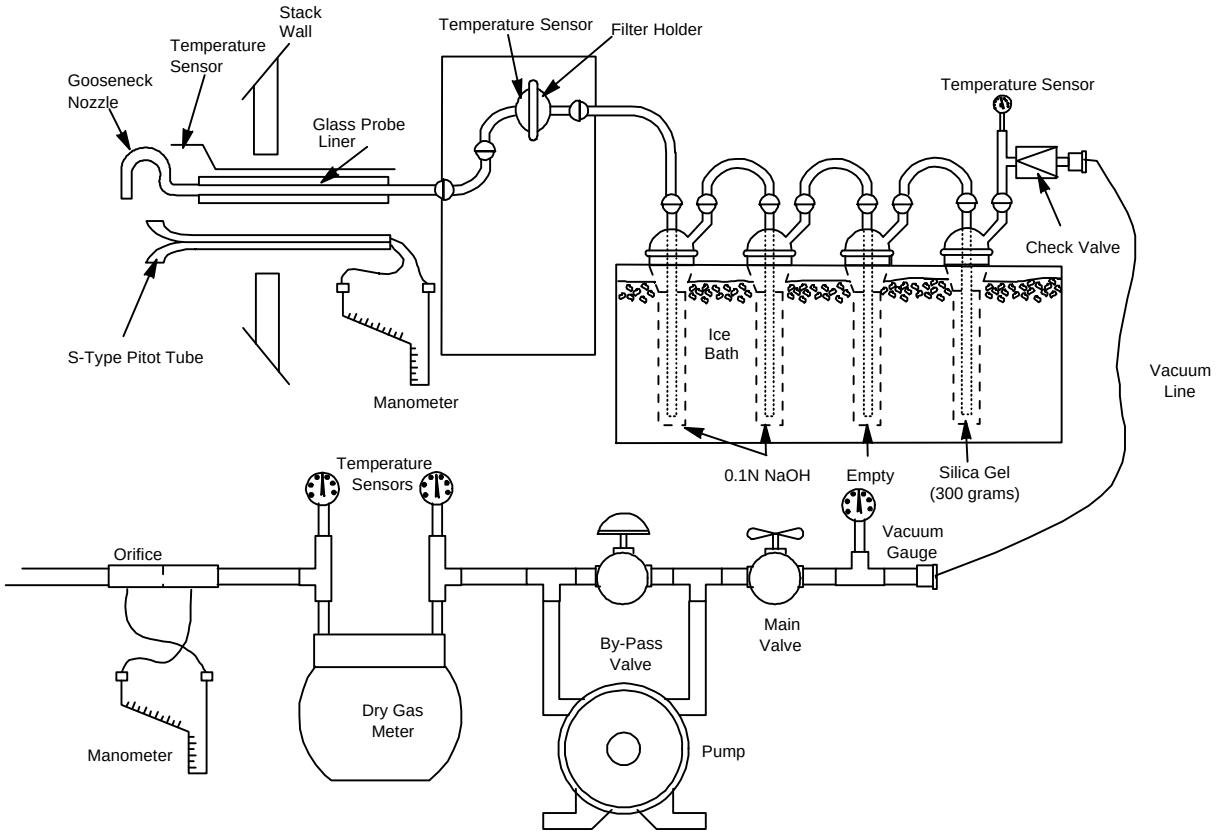

Figure XHCN-1. HCN Sampling Train, NaOH Configuration

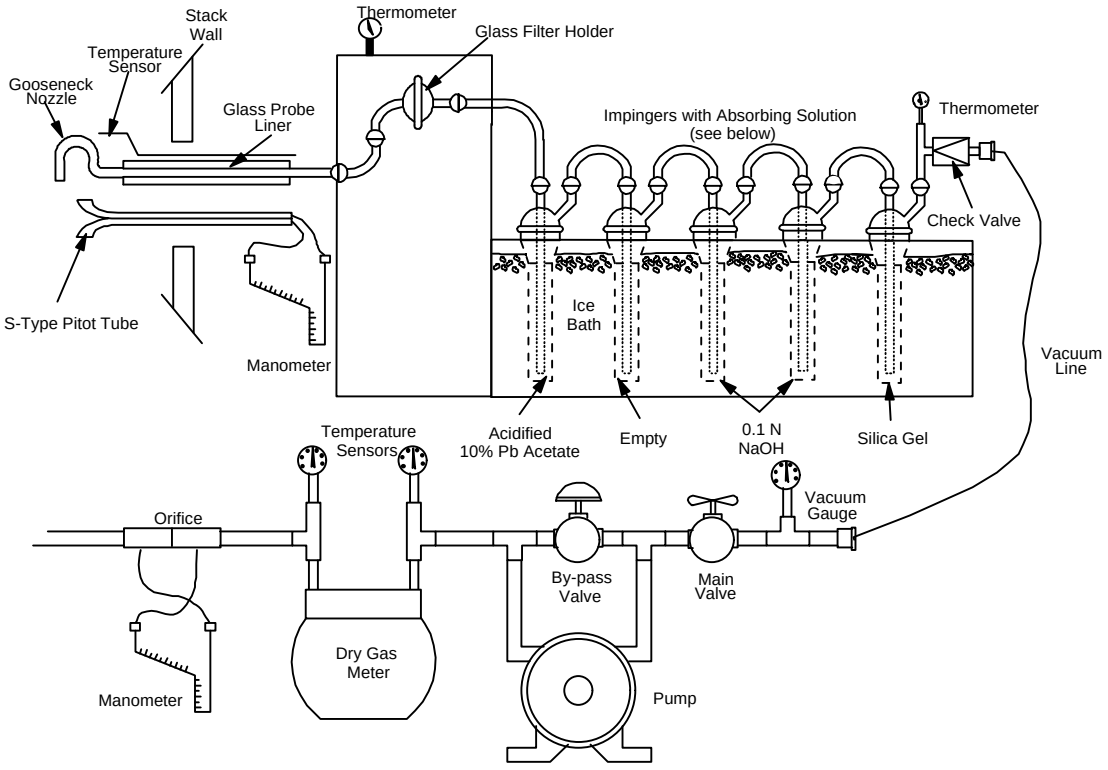

Figure XHCN-2. HCN Sampling Train, Lead Acetate/NaOH Configuration

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:

Figure XHCN-3. Example Data Sheet

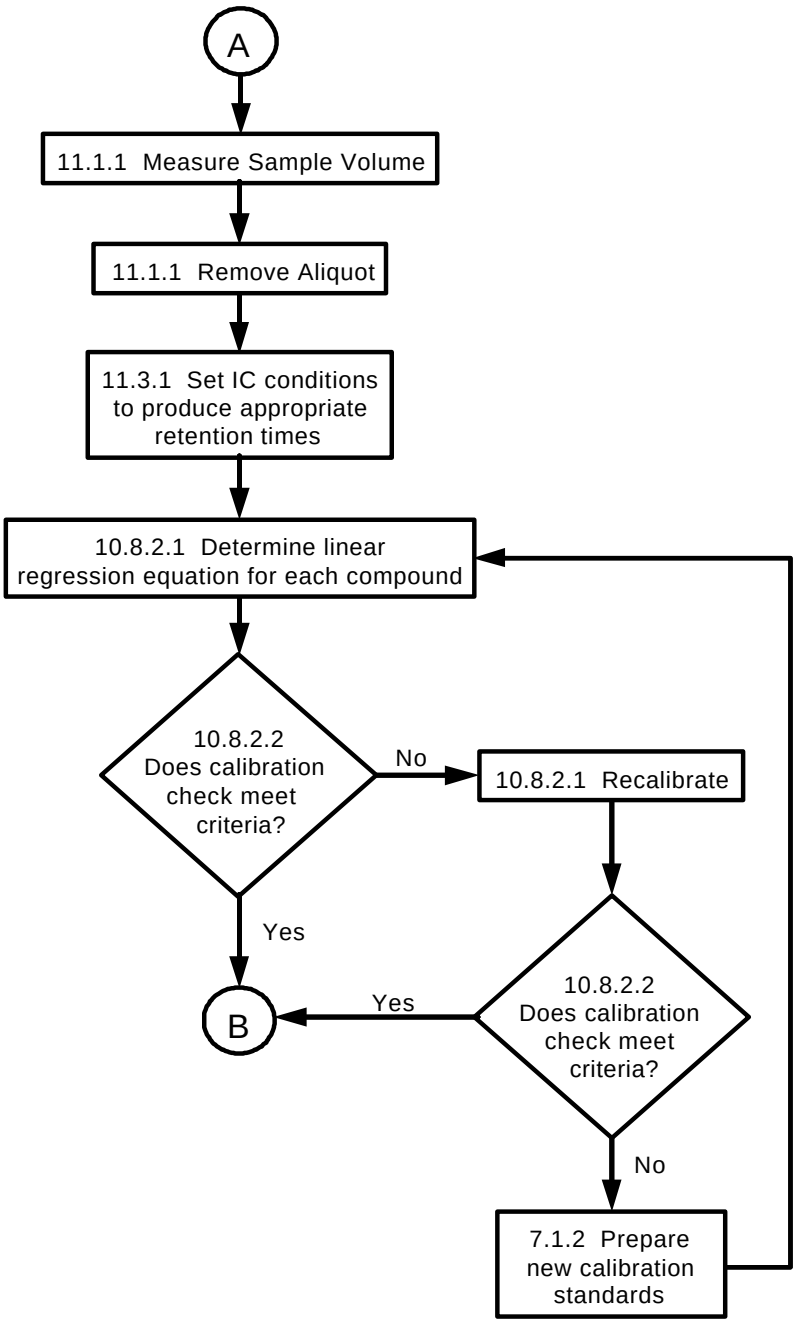

Figure XHCN-4. Hydrogen Cyanide by Ion Chromatography (IC)

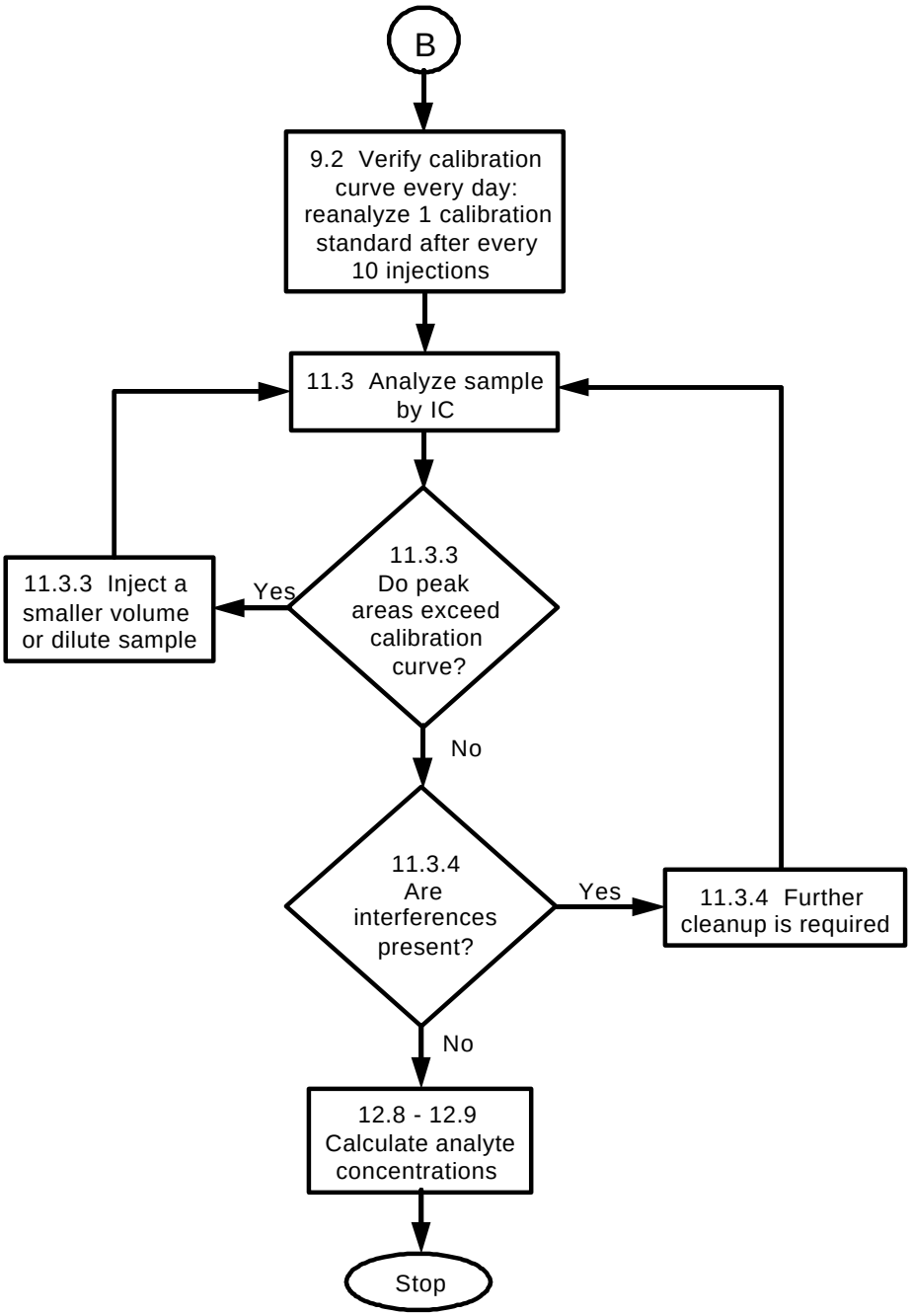

Figure XHCN-4 Hydrogen Cyanide by Ion Chromatography (IC) (Continued)

DRAFT METHOD XHCN

TABLE XHCN-1. LIST OF ANALYTES, CAS NUMBERS, RETENTION TIMES, AND DETECTION LIMITS

Compound Name	CAS No.[a]	Retention Time (minutes)[b]	Method Detection Limits (MDL) ($\mu g/m^3$)[c]
Hydrogen Cyanide	**74-90-8**	**6.7**	**12**

[a] Chemical Abstract Services Registry Number

[b] Analytical conditions (ion chromatography, IC): AS7A column, 4 x 250 mm, with AG7A guard column; isocratic elution using 0.5% ethylene diamine, 0.5M sodium acetate, and 0.1N sodium hydroxide; flow rate 1.0 mL/min.; electrochemical detector with silver working electrode and silver/silver chloride reference electrode; injection volume 50 µL.

[c] For an 849 Liter (30 cubic foot) sample, based on an instrument detection limit of 24.54 ppb as determined using Appendix B Part 136 - Definition and Procedure for the Determination of the Method Detection Limit Revision 1.11, Federal Register, Vol. 49, No. 209, Friday, October 26, 1984.

TABLE XHCN-2. SAMPLING QUALITY CONTROL PROCEDURES

Criteria	Control Limits[a]	Corrective Action
Final Leak Rate	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 test average dry gas-meter calibration factor agrees ±5% of pre-test dry gas meter calibration factor.	Adjust sample volumes using the factor that gives the smallest volume.
Individual Correction Factor (γ)	Agree with 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 NBS 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.

TABLE XHCN-3. LABORATORY QUALITY CONTROL PROCEDURES FOR IC 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	Correlation coefficient $\geq$0.995	Check integration, reintegrate. If necessary recalibrate.
Retention Time	Analyze check standard	1/10 samples	Within three standard deviations of average calibration relative retention time	Check instrument function for plug, etc. Heat column.
Calibration Check	Analyze check standard	1/10 injections, minimum 2/set	±10% of calibration curve	Check integration, remake standard. Or recalibrate.
Method Blank	Analyze 0.1N NaOH	1/day	<5% level of expected analyte	Locate source of contamination; reanalyze
Matrix Spike/Matrix Spike Duplicate	Analyze spiked sample	1/set or 1/10 samples	±15% of spiked amount	Check integration, check instrument function, reanalyze , reprepare if possible
Replicate Samples	Analyze duplicate sample aliquot	1/set or 1/10 samples	±25% of first aliquot	Check integration, check instrument function, reanalyze, reprepare if possible

TABLE XHCN-4. EXPECTED METHOD PERFORMANCE FOR HYDROGEN CYANIDE BASED ON LABORATORY EVALUATION

Train	Precision (% RSD)[a]	Accuracy (% Recovery)[b]	Matrix	Concentration Level (ppmv)
NaOH	4.08	97.0	Dry air	1.2
PbAc/NaOH	1.18	93.5	25% moisture	1.2
PbAc/NaOH	40.73	56.3	Dry air/10 ppmv H_2S	0.5
NaOH	26.17	69.3	27% moisture/10 ppmv H_2S	0.5

[a] Relative Standard Deviation (%) for three spiked trains.
[b] Average percent of spiked HCN recovered for three spiked trains