**DRAFT METHOD OTM-29**
**REVISED MARCH, 2011**

# OTHER TEST METHOD 29 - SAMPLING AND ANALYSIS FOR HYDROGEN CYANIDE EMISSIONS FROM STATIONARY SOURCES

**NOTE:** This other test method (OTM) provides a few changes from conditional test method (CTM) 33. The method was updated to address issues related to maintaining a pH of $\geq 12$ in the sodium hydroxide (NaOH) impingers during the test. EPA is proposing modifications to address this issue and is taking this opportunity to improve some of the recovery, analytical, and quality assurance procedures as well. EPA would like to acknowledge Sunoco Inc. for their contributions to this effort. EPA would also like to recognize Enthalpy Analytical Inc. for their assistance in modifying the analytical techniques.

## 1.0 *Scope And Application.*

**1.1** OTM-29 is applicable to the collection and analysis of gaseous cyanide (as HCN) in the gas phase and in suspended water droplets. Total gaseous cyanide includes hydrogen cyanide (HCN) and cyanogen $(CN)_2$. 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 does not quantify total cyanide compounds emissions, which include particulate bound cyanide where formal dissociation of $CN^-$ may occur. 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-1, A-2 and A-3, Method 1, Method 2, Method 3, Method 4, and Method 5.

**1.2** If desired, particulate matter may be recovered from the filter and analyzed following the procedures of Method 5 of Appendix A–3 to 40 CFR Part 60.

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

**1.4** 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 ion 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, three impingers containing sodium hydroxide (NaOH) solution, 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 ion chromatography (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 of Appendix A–3 to 40 CFR Part 60. Analysis is performed by liquid chromatography using an ion chromatograph equipped with an appropriate electrochemical detector.

**2.2** For increased accuracy or if your regulatory agency chooses, you may be required to run parallel sample trains. Follow the guidance in Section 8.5.4.

## 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 ($CO_2$), 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 the last NaOH impinger must be ≥ 12 at the end of the test run. The pH in all three NaOH impingers must be determined in the field at the end of the test using either a pH sensor or pH paper. The test is only valid if the pH of the NaOH solution in the final NaOH impinger is at or above 12 at the end of the test. If the pH of the solution in the first two impingers falls below 12 during the test, adjust the pH (Section 8.7.1.5) at the end of the test until it reaches 12 or higher. After the test, the pH of all three NaOH solutions must remain ≥ 12 until analysis. No test run should exceed 1 dry standard cubic meter (dscm). If you would like to test a larger volume, you must request permission from the regulating agency.

**4.2** Sulfide interferes with the determination of hydrogen cyanide in two ways. First, concentrations of sulfide greater than 25 mg of $H_2S$ per test 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 reacts to form SCN over time in the presence of sulfide at any concentration. If high levels of sulfides are expected, an initial impinger containing lead acetate should be employed.

**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 *check* for 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 (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, replacement or cleanup of the reagents may be necessary.

**4.6** Precipitation of sodium carbonate can occur if the sample is transported in ice or stored in a refrigerator at or below 0ºC. The precipitate will cause the liquid volume to decrease, therefore increasing the liquid-phase cyanide concentration. The precipitate must be dissolved back into the liquid phase before IC analysis. Otherwise, the results may be biased high.

**4.7** IC results may be biased high or low if the sample solution is not homogeneous. Because of the high viscosity of 6.0N NaOH solution, good mixing may require several short bursts of a vortex mixer rather than a continuous mixing process over time. Larger vials are recommended to allow more volume for solutions to mix.

**4.8** Correction for $CO_2$ absorption in the NaOH solution. The NaOH solution used to absorb the HCN will also absorb some of the $CO_2$ from the flue gas. Before starting the test, measure the percent $CO_2$ in the stack. If the percent $CO_2$ is $\geq 5\%$, the $CO_2$ concentration in the stack and at the outlet of the dry gas meter must be measured continuously throughout the test. The amount of $CO_2$ removed from the stack gas needs to be added back into the sample volume measured by the dry gas flow meter. Otherwise, the measured cyanide result will be higher than the true cyanide emissions. The isokinetic sample rate must be adjusted for $CO_2$ absorption if the $CO_2$% in the stack gas is $\geq 5\%$.

**4.9** 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. Only cyanogen is known to do so.

## 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.

**5.3** Solid sodium hydroxide or solutions of sodium hydroxide will cause chemical

burns, permanent injury or scarring upon contact with unprotected human tissue. Contact with eyes may cause blindness. Protective equipment such as rubber gloves, safety clothing and eye protection should be used when handling the material or related solutions.

**5.4** For safety purposes, use of certified cyanide standards is recommended over the use of potassium cyanide salt to prepare spiking solutions and calibration solutions.

## 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 1. This sampling train configuration is adapted from the Method 26A procedures. The majority of the required equipment is identical to that used in the Method 5 train, with the only change being the use of caustic solution in the impingers.

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. 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 quartz or fluoropolymer coated fiber filter, similar to that used with Method 5 of appendix A–3 to 40 CFR part 60, is used to collect filterable 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 6.1 of Method 2 of appendix A–1 to 40 CFR part 60 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 of appendix A–1 to 40 CFR part 60, Figure 2-7) during sampling. The Type S Pitot tube assembly shall have a known coefficient, determined as outlined in Section 10.1 of Method 2 of appendix A–1 to 40 CFR part 60

**6.1.5** Differential Pressure Gauge. Two inclined manometers or equivalent device as described in Section 6.2 of Method 2 of appendix A–1 to 40 CFR part 60. 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 four 500-mL impingers, connected in series immediately following the heated filter (as shown in Figure 1), with ground glass (or equivalent) vacuum-tight fittings.

**6.1.7.1** NaOH Train Configuration. The first three impingers shall be of the modified Greenburg-Smith design with the standard tip. The remaining impinger 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 three impingers with 100 mL of 6.0N NaOH solution per impinger. Fill the fourth impinger with a known mass (2/3 full) of desiccant. You may choose to add an additional NaOH impinger or increase the solution volumes to achieve the breakthrough requirement (*if the concentration in the final NaOH impinger is ≥ 5% of the total mass of cyanide captured, the test is invalid*).

**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 2%, and related equipment as shown in Figure 1. 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.

**6.1.9.** Volume Correction for $CO_2$ Adsorption. The $CO_2$ concentration in the stack and the $CO_2$ concentration at the exhaust of the dry gas meter must be measured continuously if the percent $CO_2$ in the stack gas is ≥ 5%.(e.g. integrated bag analyzed with Method 3A or 3B). Calculate the actual dry gas volume using the equation in Section 12.3.

**6.1.10** Barometer. 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.

**6.1.11** Gas Density Determination Equipment. Use a temperature sensor and pressure gauge as described in Section 6.3 and 6.4 of Method 2 of appendix A–1 to 40 CFR part 60 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 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).

**6.1.12** 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.

**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 for impinger weighing.

**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 6.0N NaOH solution.

**6.3.2** Large Glass Container. At least one large glass container (8 to 16 L) is required for preparing the aqueous NaOH 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 6.0N NaOH solution. A stir bar retriever is needed for removing the stir bar from the NaOH solution container.

**6.3.4** Beakers. Beakers are useful for holding/measuring liquids when preparing the aqueous NaOH solution and for weighing NaOH pellets.

**6.3.5** Funnels. At least one large funnel is needed for pouring the aqueous NaOH solution 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 solution.

**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 NaOH solution.

**6.3.8** Spatulas. Spatulas are needed for handling NaOH pellets when preparing the aqueous NaOH 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

**NOTE**: Section 6.4 outlines suggested chromatographic equipment. Any system capable of achieving quality control criteria outlined in Table 2 is acceptable.

**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** A data acquisition system for displaying chromatograms and measuring peak areas and retention times.

## 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, water that

conforms to American Society of Testing and Materials (ASTM) Specification D 1193-06, Type 3 or better (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 6.0N NaOH Reagent: Each batch of NaOH reagent may be purchased or prepared to meet the following requirements.

**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 (1920 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 6.0N 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** Shipment to the Field: Tightly cap the bottle containing NaOH 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 has passed the Quality Control criteria in Section 9, 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.

**7.4** Field Spike Standard Preparation. A 1000 mg/L certified potassium cyanide or certified cyanide calibration standard must be used. The spike standard may be purchased from a commercial vendor. Add 1-5mL of the spike standard to the NaOH impinger solution.

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

**7.6** Sodium Hydroxide. ACS Certified reagent grade or better NaOH pellets are required for preparation of the impinger reagent solution, the mobile phase buffer, and the 6.0N NaOH used to adjust the pH of recovered samples.

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

**7.8** Sodium Acetate and Ethylene Diamine. Required for the Mobile Phase Buffer.

**7.9** Potassium Cyanide or certified cyanide calibration standard. 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** Preparation of Aqueous 0.1N NaOH. Place a 1-L (or other appropriately sized)

container under a fume hood on a magnetic stirrer. Add a 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 (4g/L) and add to the stirring water. Fill the 1L container to the 1L mark with water and stir until dissolved. Alternatively you my purchase a certified reagent grade sodium hydroxide solutions for this purpose.

**7.11.2** 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 solution, and diluting to the line with 0.1N NaOH solution. Transfer the stock solutions to bottles with a polyfluoroethylene-lined screw caps and store at 4°C (39°F). Alternatively, you may purchase a certified reagent grade cyanide standard at 100 ng/µL.

**7.11.3** 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. You must use the same calibration standard for all analyses for a test. Using different calibration standards or standards from different vendors might result in an offset in the results.

**7.11.4** Check Standard. Prepare a calibration 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 solution. The check standard should be prepared prior to each analysis sequence and be used within 24 hours of preparation. Use the check standard to check the instrument response and the calibration accuracy in each analysis sequence. Replace stock, secondary and working calibration 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, fluoropolymer o-rings, 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 6.0N NaOH solution is prepared (Section 7.2.2) by dissolving 1920 grams of sodium hydroxide in deionized, distilled water and diluting to 8 L 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.

## 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 field 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 pre-weighing 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 of Appendix A-1 to 40 CFR Part 60. Check the Pitot lines for leaks according to 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 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 8.3 of Method 2).

**NOTE**: It is important to choose your sample nozzle and sample rates so that your total volume does not exceed 1 dscm as required in Section 8.3.4.

**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** The maximum sample volume to be collected is 1 dry standard cubic meter (dscm) (35.31 dry standard cubic feet [dscf]). Less than the maximum sample volume may be collected if prior testing indicates sufficient cyanide concentration is present in the sampled gas to meet the minimum detection limit required for the testing data quality objective or the regulatory compliance limit requirement.

**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 and Method 5 Section 8.2.5. 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 6.0N NaOH absorbing solution in each of the first three impingers (four impingers, if you choose). The last 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.

**8.4.3** 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 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 not 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. If a higher leakage rate is obtained, the tester must void the sampling run.

**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 a higher leakage rate is obtained, the tester must void the sampling run.

**8.5.4** Optional Parallel Train Procedures. Set up two identical sampling trains. One of the sampling trains shall be designated the spiked train and the other the unspiked train. Spike a known quantity of NaCN into the first impinger at a concentration 50 to 150 percent of the mass expected to be collected with the unspiked train or at the emission standard which ever is greater. Sample the stack gas with the two trains simultaneously following the same procedures used for the field samples. The total sample volume must be within ± 20 percent of the target sample

volume for the field sample test runs. Analyze the impinger solutions from the two trains utilizing the same analytical procedures and instrumentation as for the field samples. Determine the fraction of spiked HCN recovered (R) using the equations in Section 12.6. Repeat this procedure for a total of three runs. Report the individual R values in the test report; the average of the three R values must be between 75 and 125 percent.

**NOTE***:* It is acceptable to perform the field recovery test concurrent with actual test runs. It is also acceptable to use the unspiked field recovery test runs as test runs for emissions testing.

**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 2. Be sure to record the initial dry gas meter reading. Record the dry-gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak-check, and when sampling is halted. Take other readings indicated by Figure 2 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.

**NOTE**: Due to the $CO_2$ absorption in the NaOH solution, you will have to adjust your “k” factor.

**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.

**8.6.8** In-field co-located spikes and sample trains are recommended for greater accuracy. When co-located trains are used, components from each train shall be analyzed separately.

**8.6.9** Additional train(s) or impinger(s) may be used for sampling when the capacity of a single train is expected to be exceeded. You may analyze equivalent sets of impingers together (the first two impingers from each train, the second impinger from each train, and the third impinger from each train). You must document on the data sheet the time(s) when changes in trains/impingers occur and the reason for the change.

**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 Section 8.1 of 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 12, to determine whether the run was valid or another test should be performed.

**8.6.12** No test run should exceed 1 dry standard cubic meter (dscm). If you would like to test a larger volume, you must request permission from the regulating agency.

**8.7** Sample Recovery. Recover the sampling train in four fractions:

- 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 fraction;
- the first two impinger solutions (or first three impingers if optional impinger used) and rinses from impingers and connecting back half glassware comprise the third portion;
- the final impinger solution and rinse comprise the fourth fraction.

**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 from 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** Moisture Determination. Weigh the liquid collected in the water collection impingers and silica trap. Measure the liquid in the first impingers to within 0.5 g using a balance in the field. Record the weight of the liquid present to be used to calculate the moisture content of the effluent gas. Using a balance in the field, weigh the silica impinger to within 0.5 g. Note the color of the indicating silica gel in the last impinger to determine whether it has been completely spent and make a notation of its condition.

**8.7.1.5** Inspect the train before and during disassembly, and document on the data sheet any abnormal conditions. Measure the pH of each of the NaOH impinger solutions with pH paper or a pH meter and record the separate pH measurements on the data sheet. If the pH of the first impinger is below 12, add 10 ml of 6N NaOH and recheck the pH. Repeat this procedure until the pH is greater than 12. If the pH of the second impinger is less than 12, repeat the procedure used for impinger #1. Record the amounts of NaOH that were added. If the pH of the final NaOH impinger is less than 12 discard the samples and repeat the sample run making the appropriate adjustments to maintain a pH of >12 in the last NaOH impinger.

**8.7.1.6** Save a portion of all washing solutions (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 pre-labeled 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 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 (first two NaOH impinger solutions and rinses from first two impingers and connecting glassware). After recording the pH and weighing, pour the contents of impingers No. 1 and 2 (and 3 if optional impinger is used) into Container No. 3 along with the NaOH rinses of the impingers and connecting glassware. Rinse the impingers a minimum of three times with 0.1 N NaOH. 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.

**8.7.2.4** Container No. 4 (final NaOH impinger solution and rinse from impinger and connecting glassware). After recording the pH and weighing, pour contents of the final impinger into Container No. 4 along with the NaOH rinses of the impinger and connecting glassware. Rinse the impinger a minimum of three times. Mark the liquid level, seal the container, and add the proper sample label with appropriate descriptive information.

**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 are present in the solution. If 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 a possibility.

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

## 9.0 *Quality Control.*

**9.1** Sampling. Sampling quality control procedures are listed in Table 1. See References 8 and 9 for additional 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 1 lists laboratory quality control procedures.

**9.2.1** Check for Breakthrough. Recover and determine the cyanide concentration of the last NaOH impinger separately from the first two impingers. If the concentration in the final NaOH impinger is ≥ 5% of the total mass of cyanide captured, the test is invalid.

**9.2.2** 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. 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 is leak checked). 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.

**9.2.3** Field Reagent Blanks. Collect a 100 mL aliquot of 6N NaOH solution 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 particulate matter is being measured, it is also necessary to collect a 100 mL aliquot of the acetone. See table 2 for acceptance criteria.

**9.2.4** 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. See table 2 for acceptance criteria.

**9.2.5** 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. Recovery must be +/- 20%. Retain an aliquot of the Field Spike Standard in the laboratory for comparative analysis.

**9.2.6** Optional Parallel Sampling Train. The total sample volume must be within ± 20 percent of the target sample volume for the field sample test runs. Analyze the impinger solutions from the two trains utilizing the same analytical procedures and instrumentation as for the field samples. Determine the fraction of spiked HCN recovered (R) using the equations in Section 12.6. Repeat this procedure for a total of three runs. Report the individual R values in the test report; the average of the three R values must be between 75 and 125 percent.

## 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 10.1 of 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 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. 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, NIST traceable 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. Check the calibration of 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** Prepare calibration standards according to the procedure in Section 7.11.3. Calibrate the chromatographic system using the external standard technique (Section 10.8.2).

**10.8.2** External Standard Calibration Procedure.

**10.8.2.1** Suggested chromatographic conditions are provided in Section 11.2. Analyze each calibration standard 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 for each analysis sequence by the measurement of the check standard prepared in Section 7.11.4. If the response for hydrogen cyanide varies from the previously established response by more than 10% (see Table 2), the test must be repeated using a fresh calibration standard, but only after it has been verified that the analytical system is in control. If the fresh calibration standard response varies from the previous calibration response by more than 10% a new calibration curve may be prepared for hydrogen cyanide. If an auto-sampler is available, it is convenient to prepare a calibration curve daily by analyzing standards along with test samples.

**10.8.2.3** Analytical Calibration must be repeated after major instrument maintenance, IC column replacement, or detector electrode replacement. When using a new electrode, the

sensitivity may decrease during the first few hours and should be allowed to stabilize before conducting calibration or analysis.

**11.0** ***Analytical Procedures.***

**11.1** Analysis of Stack Gas Samples: Impinger Contents (Containers No. 3 and 4, Sections 8.7.2.3 and 8.7.2.4).

**11.1.1** Measure the sample volume. Sample dilution with 0.1N or 0.6N NaOH is recommended. The pH should not drop below 12 as a result of dilution. The pH must be recorded and reported with the analysis results. Perform analysis. If the response from the cyanide in any sample is greater than that of the highest calibration standard, dilute the sample with 0.1N or 0.6N NaOH and repeat the analysis until the response from the sample falls within the calibration curve.

**11.1.2** Store the samples at 4±2°C (39±4°F). The samples must 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. New detectors must be allowed to stabilize before use. |
| Injector Volume: | 50 µL |

**11.3** IC Analysis.

**11.3.1** Each sample injected for analysis must be accompanied by a duplicate injection.

**11.3.2** Perform a matrix spike at least once per set of samples or once per ten samples. The amount of HCN recovered must be 20% of the spiked value.

**11.3.3** Analyze all samples (including field and lab blanks) by IC, using conditions established in Section 11.2. These conditions are flexible and other IC columns, chromatographic conditions, or detectors may be used if the requirements in Table 2 are met.

**11.3.4** The width of the retention time window used to make identifications should be based upon measurements of actual retentionf 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.

**11.3.5** If the peak area exceeds the linear range of the calibration curve, dilute the final solution with 0.1 N NaOH and reanalyze it. Alternatively, a smaller sample volume may be used.

**11.3.6** 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 of appendix A–3 to 40 CFR part 60. 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.

**NOTE**: The procedures outlined in this method do not address particulate cyanide material. Additional recovery steps and fractions are necessary to quantify the particulate bound cyanide.

## 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:

| | | |
|---|---|---|
| $A_n$ | = | Cross-sectional area of nozzle, $m^2$ ($ft^2$). |
| $B_{ws}$ | = | Water vapor in the gas stream, proportion by volume. |
| $C_f$ | = | Concentration of hydrogen cyanide in stack gas (µg/dscm). |
| $C_{rec}$ | = | Concentration recovered from spiked train. |
| I | = | Percent of isokinetic sampling. |
| K | = | 35.31 $ft^3/m^3$ if $V_{actual}$ is expressed in English units. |
| K | = | 1.00 $m^3/m^3$ if $V_{actual}$ 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. |
| $M_d$ | = | 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). |
| $m_s$ | = | Mass determined from the spiked field recovery train (µg). |

$m_{spiked}$ = Mass of HCN spiked in Field Recovery Test (µg).
$m_u$ = Mass determined from the unspiked field recovery train (µg).
$P_{bar}$ = 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).
$R_{ec}$ = Spiked HCN recovery (%).
$T_m$ = 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).
$V_{actual}$ = Volume of gas sample, corrected for $CO_2$ absorption, dscm (dscf).
$V_{adj}$ = 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, dcm (dcf).
$V_{m(std)}$ = 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).
$V_{QC}$ = Volume of dry gas (dscm) collected in the spiked Field Recovery Test Train calculated in the same manner as $V_{actual}$.
$V_s$ = Stack gas velocity, calculated by Method 2 of appendix A–1 to 40 CFR part 60, Equation 2-7, using data obtained from Method 5 of appendix A–3 to 40 CFR part 60, m/sec (ft/sec).
$\gamma$ = Dry gas meter calibration factor, dimensionless.
$\Delta H$ = Average pressure differential across the orifice meter, mm $H_2O$ (in. $H_2O$).
$\rho_w$ = Density of water, 0.9982 g/mL (0.002201 lb/mL).
$\Theta$ = Total sampling time, min.
13.6 = Specific gravity of mercury.
60 = sec/min.
100 = Conversion to percent.
$\%CO_{2(dry)in}$ = $CO_2$ in the stack, % dry basis.
$\%CO_{2(dry)out}$ = $CO_2$ at the outlet of sampling train, % dry basis.

**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 1:

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

Then correct the sample measured by the dry gas meter for $CO_2$ absorption using the following equation (only if the percent $CO_2$ in the stack is ≥5%. Otherwise replace "$V_{actual}$" with "$V_{m(std)}$" in the equations below):

$$V_{actual} = \frac{V_{m(std)}\left(1 - \%CO_{2(dry)out}\right)}{\left(1 - \%CO_{2(dry)in}\right)} \qquad \text{Eq. 2}$$

**12.4** Volume of Water Vapor Condensed.

$$V_{w(std)} = V_{lc} \frac{\rho_w R T_{std}}{M_w P_{std}} \qquad \text{Eq. 3}$$

$$= K_2 V_{lc}$$

**12.5** Moisture Content.

$$B_{ws} = \frac{V_{w(std)}}{V_{actual} + V_{w(std)}} \qquad \text{Eq. 4}$$

**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 4) 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 the assumption of saturated conditions is given in Section 4.0 of 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** Spiked Train Field Recovery

Calculate the measured spike concentration using Equation 5.

$$C_{rec} = \frac{m_s}{V_{QC}} - \frac{m_s}{V_{Actual}} \qquad \text{Eq. 5}$$

Then calculate the spiked HCN recovery, $R_{ec}$, using Equation 6.

$$R_{ec} = \left[\frac{C_{rec} V_{QC}}{m_{spiked}}\right] x\,100 \qquad \text{Eq. 6}$$

**12.7** Conversion Factors.

| From | To | Multiply by |
|---|---|---|
| scf | $m^3$ | 0.02832 |
| $g/ft^3$ | $lb/ft^3$ | $2.205 \times 10^{-3}$ |
| $g/ft^3$ | $g/m^3$ | 35.31 |

**12.7.1** Nomenclature.

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

**12.8** Isokinetic Variation.

**12.8.1** Calculation from Raw Data.

$$I = \frac{100 T_s [K_3 V_{1c} + (V_{actual}\gamma / T_m)(P + \Delta H/13.6)]}{60\theta V_s P_s A_n} \qquad \text{Eq. 8}$$

**12.8.2** Calculation for Intermediate Values.

$$I = \frac{T_s V_{actual} P_{std} 100}{T_{std} V_s \theta A_n P_s 60(1-B_{ws})} \qquad \text{Eq. 9(a)}$$

$$= K_4 \frac{T_s V_{actual}}{P_s V_s A_n \theta (1-B_{ws})} \qquad \text{Eq. 9(b)}$$

**12.9** 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.

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

$$P_T = P_c M_{vol} \frac{V_{adj}}{V_{aliq}} \qquad \text{Eq. 10}$$

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

$$C_F = \frac{K P_T}{V_{actual}} \qquad \text{Eq. 11}$$

**13.0** ***Method Performance.*** Reserved.

**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.

**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.

**13**. Quanci, J., Hutchinson, M., Huag, C., Domingue, R., Smith, V, "Method to Measure Cyanide in Carbon Dioxide Rick FCCU Flue Gas," AM-10-111, Proceedings of the Natural Petrochemical & Refiners Association Annual Meeting, March, 2010.

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

**17.1** See Section 13.1 and References 10,11, and 13 for method performance and evaluation data.

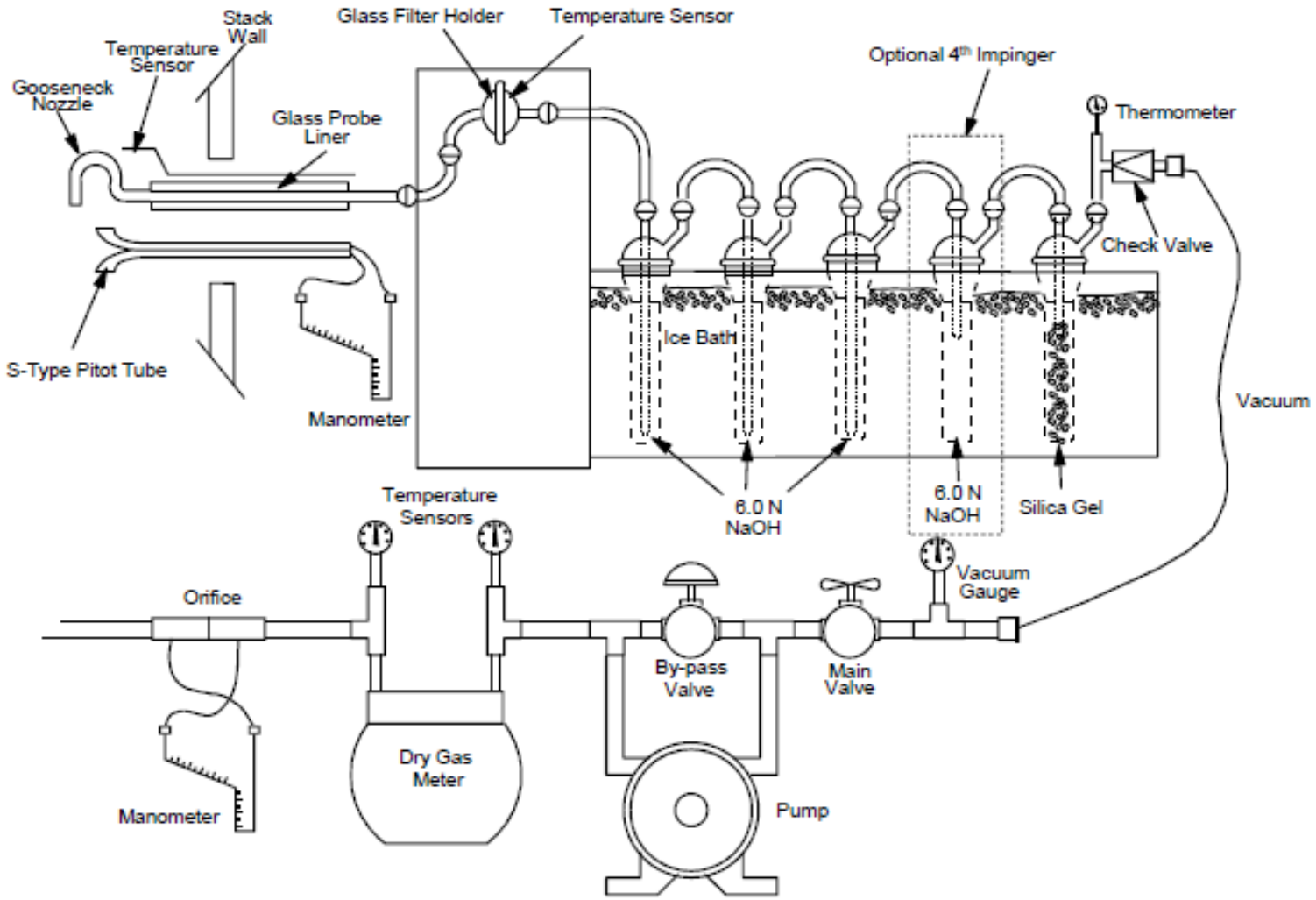


Figure 1. HCN Sampling Train, NaOH Configuration

**FIELD DATA SHEET**

Run Number _____
Page ____ of ____

| | | | |
|---|---|---|---|
| Plant | Nozzle Type & ID (in) | Meter Box Number | Diagram of Duct |
| Date | Filter Holder Setting (℉) | Meter delta H @ | |
| Operator | Probe Heater Setting (℉) | DGM Factor (gamma) | |
| Sampling Location | Heater Box Setting (℉) | K Factor | |
| Sample Type | Minimum Sample Volume ($ft^3$) | Moisture Collected (g) | |
| Ambient Temperature (℉) | Initial Leak Check | Assumed Moisture (% H2O) | |
| Static Pressure (±) (in H2O) | Final Leak Check | Fltr # | |
| Barometric Pressure (in H2O) | Height of Location (ft) | $CO_2$ % | |
| Probe Length & Type | Duct Dimensions (in) | $O_2/CO_2$ Method | |
| Read and record all data every _____ minutes | | $O_2$ % | |

| Traverse Point Number | Sampling Time (min) | Clock Time (24 hr) | Gas Meter Reading ((VM)($ft^3$)) | Velocity Head ((delta Pa) in $H_2O$) | Flue Gas Temp (℉) | Orfice Pressure Differential (Delta H . In $H_2O$) | | Probe Temp (℉) | Filter#1 Temp (℉) | Dry Gas Meter Temperature | | Impinger Exit Temp (℉) | Pump Vacuum (in Hg) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Desired | Actual | | | Inlet (Tm In) | Outlet (Tm out) | | |
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Figure 2: Example Sampling Field Data Form

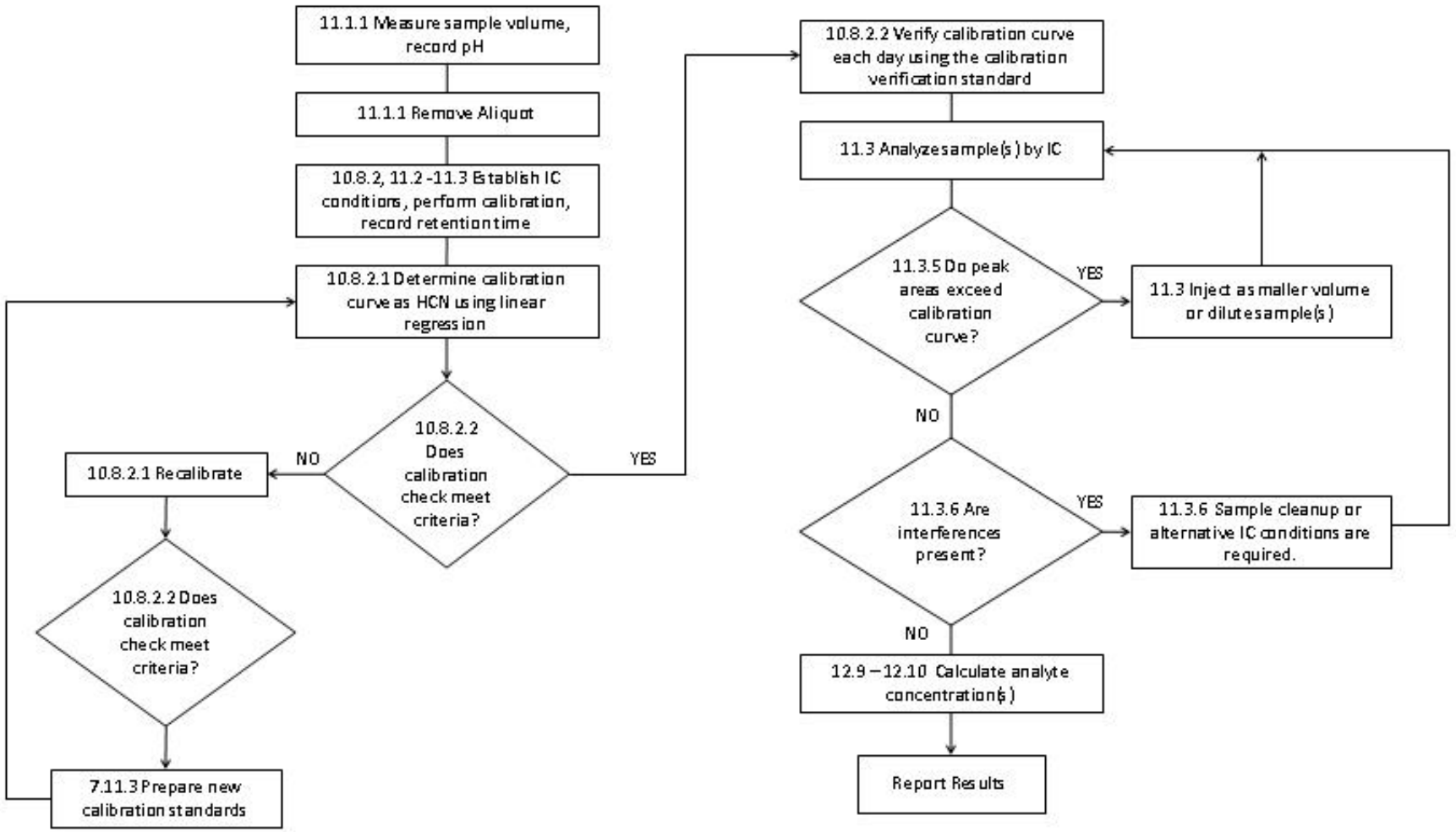


Figure 3. Hydrogen Cyanide by Ion Chromatography (IC)

## TABLE 1. 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 ($\gamma$) | 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 or NIST Traceable barometer. | Recalibrate. |

## TABLE 2. 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 ≥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. |
| Field Reagent/Method Blank | Analyze 6.0 N 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 | ±20% of spiked amount | Check integration, check instrument function, reanalyze , reprepare if possible |
| Replicate Samples | Analyze duplicate sample aliquot | 1/set or 1/10 samples | ±20% of first aliquot | Check integration, check instrument function, reanalyze, reprepare if possible |
| Field Spike | Analyze spiked sample | 1/set or 1/10 samples | ±20% of spiked amount | Check integration, check instrument function, reanalyze, reprepare if possible |