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METHOD 202—DRY IMPINGER METHOD FOR DETERMINING CONDENSABLE PARTICULATE EMISSIONS FROM STATIONARY SOURCES

1.0 Scope and Applicability

1.1 Scope. The U.S. Environmental Protection Agency (U.S. EPA or "we") developed this method to describe the procedures that the stack tester ("you") must follow to measure condensable particulate matter (CPM) emissions from stationary sources. This method includes procedures for measuring both organic and inorganic CPM.

1.2 Applicability. This method addresses the equipment, preparation, and analysis necessary to measure only CPM. You can use this method only for stationary source emission measurements. You can use this method to measure CPM from stationary source emissions after filterable particulate matter (PM) has been removed. CPM is measured in the emissions after removal from the stack and after passing through a filter.

(a) If the gas filtration temperature exceeds 30 °C (85 °F) and you must measure both the filterable and condensable (material that condenses after passing through a filter) components of total primary (direct) PM emissions to the atmosphere, then you must combine the procedures in this method with the procedures in Method 201A of appendix M to this part for measuring filterable PM. However, if the gas filtration temperature never exceeds 30 °C (85 °F), then use of this method is not required to measure total primary PM.

(b) If Method 17 of appendix A-6 to part 60 is used in conjunction with this method and constant weight requirements for the in-stack filter cannot be met, the Method 17 filter and sampling nozzle rinse must be treated as described in Sections 8.5.4.4 and 11.2.1 of this method. (*See* Section 3.0 for a definition of constant weight.) Extracts resulting from the use of this procedure must be filtered to remove filter fragments before the filter is processed and weighed.

1.3 Responsibility. You are responsible for obtaining the equipment and supplies you will need to use this method. You should also develop your own procedures for following this method and any additional procedures to ensure accurate sampling and analytical measurements.

1.4 Additional Methods. To obtain reliable results, you should have a thorough knowledge of the following test methods that are found in appendices A-1 through A-3 and A-6 to part 60, and in appendix M to this part:

(a) Method 1—Sample and velocity traverses for stationary sources.

(b) Method 2—Determination of stack gas velocity and volumetric flow rate (Type S pitot tube).

(c) Method 3—Gas analysis for the determination of dry molecular weight.

(d) Method 4—Determination of moisture content in stack gases.

(e) Method 5—Determination of particulate matter emissions from stationary sources.

(f) Method 17—Determination of particulate matter emissions from stationary sources (in-stack filtration method).

(g) Method 201A—Determination of PM_{10} and $PM_{2.5}$ emissions from stationary sources (Constant sampling rate procedure).

(h) You will need additional test methods to measure filterable PM. You may use Method 5 (including Method 5A, 5D and 5I but not 5B, 5E, 5F, 5G, or 5H) of appendix A-3 to part 60, or Method 17 of appendix A-6 to part 60, or Method 201A of appendix M to this part to collect filterable PM from stationary sources with temperatures above 30 °C (85 °F) in conjunction with this method. However, if the gas filtration temperature never exceeds 30 °C (85 °F), then use of this method is not required to measure total primary PM.

1.5 Limitations. You can use this method to measure emissions in stacks that have entrained droplets only when this method is combined with a filterable PM test method that operates at high enough temperatures to cause water droplets sampled through the probe to become vaporous.

1.6 Conditions. You must maintain isokinetic sampling conditions to meet the requirements of the filterable PM test method used in conjunction with this method. You must sample at the required number of sampling points specified in Method 5 of appendix A-3 to part 60, Method 17 of appendix A-6 to part 60, or Method 201A of appendix M to this part. Also, if you are using this method as an alternative to a required performance test method, you must receive approval from the regulatory authority that established the requirement to use this test method prior to conducting the test.

2.0 Summary of Method

2.1 Summary. The CPM is collected in dry impingers after filterable PM has been collected on a filter maintained as specified in either Method 5 of appendix A-3 to part 60, Method 17 of appendix A-6 to part 60, or Method 201A of appendix M to this part. The organic and aqueous fractions of the impingers and an out-of-stack CPM filter are then taken to dryness and weighed. The total of the impinger fractions and the CPM filter represents the CPM. Compared to the version of Method 202 that was promulgated on December 17, 1991, this method eliminates the use of water as the collection media in impingers and includes the addition of a condenser followed by a water dropout impinger immediately after the final in-stack or heated filter. This method also includes the addition of one modified Greenburg Smith impinger (backup impinger) and a CPM filter following the water dropout impinger. Figure 1 of Section 18 presents the schematic of the sampling train configured with these changes.

2.1.1 Condensable PM. CPM is collected in the water dropout impinger, the modified Greenburg Smith impinger, and the CPM filter of the sampling train as described in this method.

The impinger contents are purged with nitrogen immediately after sample collection to remove dissolved sulfur dioxide (SO_2) gases from the impinger. The CPM filter is extracted with water and hexane. The impinger solution is then extracted with hexane. The organic and aqueous fractions are dried and the residues are weighed. The total of the aqueous and organic fractions represents the CPM.

2.1.2 Dry Impinger and Additional Filter. The potential artifacts from SO_2 are reduced using a condenser and water dropout impinger to separate CPM from reactive gases. No water is added to the impingers prior to the start of sampling. To improve the collection efficiency of CPM, an additional filter (the "CPM filter") is placed between the second and third impingers.

3.0 Definitions

3.1 *Condensable PM (CPM)* means material that is vapor phase at stack conditions, but condenses and/or reacts upon cooling and dilution in the ambient air to form solid or liquid PM immediately after discharge from the stack. Note that all condensable PM is assumed to be in the $PM_{2.5}$ size fraction.

3.2 *Constant weight* means a difference of no more than 0.5 mg or one percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than six hours of desiccation time between weighings.

3.3 *Field Train Proof Blank.* A field train proof blank is recovered on site from a clean, fully-assembled sampling train prior to conducting the first emissions test.

3.4 *Filterable PM* means particles that are emitted directly by a source as a solid or liquid at stack or release conditions and captured on the filter of a stack test train.

3.5 *Primary PM* (also known as direct PM) means particles that enter the atmosphere as a direct emission from a stack or an open source. Primary PM comprises two components: filterable PM and condensable PM. These two PM components have no upper particle size limit.

3.6 *Primary* $PM_{2.5}$ (also known as direct $PM_{2.5}$, total $PM_{2.5}$, $PM_{2.5}$, or combined filterable $PM_{2.5}$ and condensable PM) means PM with an aerodynamic diameter less than or equal to 2.5 micrometers. These solid particles are emitted directly from an air emissions source or activity, or are the gaseous emissions or liquid droplets from an air emissions source or activity that condense to form PM at ambient temperatures. Direct $PM_{2.5}$ emissions include elemental carbon, directly emitted organic carbon, directly emitted sulfate, directly emitted nitrate, and other inorganic particles (including but not limited to crustal material, metals, and sea salt).

3.7 *Primary* PM_{10} (also known as direct PM_{10}, total PM_{10}, PM_{10}, or the combination of filterable PM_{10} and condensable PM) means PM with an aerodynamic diameter equal to or less than 10 micrometers.

4.0 Interferences

[Reserved]

5.0 Safety

Disclaimer. Because the performance of this method may require the use of hazardous materials, operations, and equipment, you should develop a health and safety plan to ensure the safety of your employees who are on site conducting the particulate emission test. Your plan should conform with all applicable Occupational Safety and Health Administration, Mine Safety and Health Administration, and Department of Transportation regulatory requirements. Because of the unique situations at some facilities and because some facilities may have more stringent requirements than is required by State or federal laws, you may have to develop procedures to conform to the plant health and safety requirements.

6.0 Equipment and Supplies

The equipment used in the filterable particulate portion of the sampling train is described in Methods 5 and 17 of appendix A-1 through A-3 and A-6 to part 60 and Method 201A of appendix M to this part. The equipment used in the CPM portion of the train is described in this section.

6.1 Condensable Particulate Sampling Train Components. The sampling train for this method is used in addition to filterable particulate collection using Method 5 of appendix A-3 to part 60, Method 17 of appendix A-6 to part 60, or Method 201A of appendix M to this part. This method includes the following exceptions or additions:

6.1.1 Probe Extension and Liner. The probe extension between the filterable particulate filter and the condenser must be glass- or fluoropolymer-lined. Follow the specifications for the probe liner specified in Section 6.1.1.2 of Method 5 of appendix A-3 to part 60.

6.1.2 Condenser and Impingers. You must add the following components to the filterable particulate sampling train: A Method 23 type condenser as described in Section 2.1.2 of Method 23 of appendix A-8 to part 60, followed by a water dropout impinger or flask, followed by a modified Greenburg-Smith impinger (backup impinger) with an open tube tip as described in Section 6.1.1.8 of Method 5 of appendix A-3 to part 60.

6.1.3 CPM Filter Holder. The modified Greenburg-Smith impinger is followed by a filter holder that is either glass, stainless steel (316 or equivalent), or fluoropolymer-coated stainless steel. Commercial size filter holders are available depending on project requirements. Use a commercial filter holder capable of supporting 47 mm or greater diameter filters. Commercial size filter holders contain a fluoropolymer O-ring, stainless steel, ceramic or fluoropolymer filter support and a final fluoropolymer O-ring. A filter that meets the requirements specified in Section 7.1.1 may be placed behind the CPM filter to reduce the pressure drop across the CPM filter. This support filter is not part of the PM sample and is not recovered with the CPM filter. At the exit of the CPM filter, install a fluoropolymer-coated or stainless steel encased thermocouple that is in contact with the gas stream.

6.1.4 Long Stem Impinger Insert. You will need a long stem modified Greenburg Smith impinger insert for the water dropout impinger to perform the nitrogen purge of the sampling train.

6.2 Sample Recovery Equipment.

6.2.1 Condensable PM Recovery. Use the following equipment to quantitatively determine the amount of CPM recovered from the sampling train.

(a) Nitrogen purge line. You must use inert tubing and fittings capable of delivering at least 14 liters/min of nitrogen gas to the impinger train from a standard gas cylinder (*see* Figures 2 and 3 of Section 18). You may use standard 0.6 centimeters (¼ inch) tubing and compression fittings in conjunction with an adjustable pressure regulator and needle valve.

(b) Rotameter. You must use a rotameter capable of measuring gas flow up to 20 L/min. The rotameter must be accurate to five percent of full scale.

(c) Nitrogen gas purging system. Compressed ultra-pure nitrogen, regulator, and filter must be capable of providing at least 14 L/min purge gas for one hour through the sampling train.

(d) Amber glass bottles (500 ml).

6.2.2 Analysis Equipment. The following equipment is necessary for CPM sample analysis:

(a) Separatory Funnel. Glass, 1 liter.

(b) Weighing Tins. 50 ml. Glass evaporation vials, fluoropolymer beaker liners, or aluminum weighing tins can be used.

(c) Glass Beakers. 300 to 500 ml.

(d) Drying Equipment. A desiccator containing anhydrous calcium sulfate that is maintained below 10 percent relative humidity, and a hot plate or oven equipped with temperature control.

(e) Glass Pipets. 5 ml.

(f) Burette. Glass, 0 to 100 ml in 0.1 ml graduations.

(g) Analytical Balance. Analytical balance capable of weighing at least 0.0001 g (0.1 mg).

(h) pH Meter or Colormetric pH Indicator. The pH meter or colormetric pH indicator (e.g., phenolphthalein) must be capable of determining the acidity of liquid within 0.1 pH units.

(i) Sonication Device. The device must have a minimum sonication frequency of 20 kHz and be approximately four to six inches deep to accommodate the sample extractor tube.

(j) Leak-Proof Sample Containers. Containers used for sample and blank recovery must not contribute more than 0.05 mg of residual mass to the CPM measurements.

(k) Wash bottles. Any container material is acceptable, but wash bottles used for sample and blank recovery must not contribute more than 0.1 mg of residual mass to the CPM measurements.

7.0 Reagents and Standards

7.1 Sample Collection. To collect a sample, you will need a CPM filter, crushed ice, and silica gel. You must also have water and nitrogen gas to purge the sampling train. You will find additional information on each of these items in the following summaries.

7.1.1 CPM Filter. You must use a nonreactive, nondisintegrating polymer filter that does not have an organic binder and does not contribute more than 0.5 mg of residual mass to the CPM measurements. The CPM filter must also have an efficiency of at least 99.95 percent (less than 0.05 percent penetration) on 0.3 micrometer dioctyl phthalate particles. You may use test data from the supplier's quality control program to document the CPM filter efficiency.

7.1.2 Silica Gel. Use an indicating-type silica gel of six to 16 mesh. You must obtain approval of the Administrator for other types of desiccants (equivalent or better) before you use them. Allow the silica gel to dry for two hours at 175 °C (350 °F) if it is being reused. You do not have to dry new silica gel if the indicator shows the silica gel is active for moisture collection.

7.1.3 Water. Use deionized, ultra-filtered water that contains 1.0 parts per million by weight (ppmw) (1 mg/L) residual mass or less to recover and extract samples.

7.1.4 Crushed Ice. Obtain from the best readily available source.

7.1.5 Nitrogen Gas. Use Ultra-High Purity compressed nitrogen or equivalent to purge the sampling train. The compressed nitrogen you use to purge the sampling train must contain no more than 1 parts per million by volume (ppmv) oxygen, 1 ppmv total hydrocarbons as carbon, and 2 ppmv moisture. The compressed nitrogen must not contribute more than 0.1 mg of residual mass per purge.

7.2 Sample Recovery and Analytical Reagents. You will need acetone, hexane, anhydrous calcium sulfate, ammonia hydroxide, and deionized water for the sample recovery and analysis. Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society. If such specifications are not available, then use the best available grade. Additional information on each of these items is in the following paragraphs:

7.2.1 Acetone. Use acetone that is stored in a glass bottle. Do not use acetone from a metal container because it normally produces a high residual mass in the laboratory and field reagent blanks. You must use acetone that has a blank value less than 1.0 ppmw (0.1 mg/100 g) residue.

7.2.2 Hexane, American Chemical Society grade. You must use hexane that has a blank residual mass value less than 1.0 ppmw (0.1 mg/100 g) residue.

7.2.3 Water. Use deionized, ultra-filtered water that contains 1 ppmw (1 mg/L) residual mass or less to recover material caught in the impinger.

7.2.4 Condensable Particulate Sample Desiccant. Use indicating-type anhydrous calcium sulfate to desiccate water and organic extract residue samples prior to weighing.

7.2.5 Ammonium Hydroxide. Use National Institute of Standards and Technology-traceable or equivalent (0.1 N) NH_4OH.

7.2.6 Standard Buffer Solutions. Use one buffer solution with a neutral pH and a second buffer solution with an acid pH of no less than 4.

8.0 Sample Collection, Preservation, Storage, and Transport

8.1 Qualifications. This is a complex test method. To obtain reliable results, you should be trained and experienced with in-stack filtration systems (such as, cyclones, impactors, and thimbles) and impinger and moisture train systems.

8.2 Preparations. You must clean all glassware used to collect and analyze samples prior to field tests as described in Section 8.4 prior to use. Cleaned glassware must be used at the start of each new source category tested at a single facility. Analyze laboratory reagent blanks (water, acetone, and hexane) before field tests to verify low blank concentrations. Follow the pretest preparation instructions in Section 8.1 of Method 5.

8.3 Site Setup. You must follow the procedures required in Methods 5, 17, or 201A, whichever is applicable to your test requirements including:

(a) Determining the sampling site location and traverse points.

(b) Calculating probe/cyclone blockage (as appropriate).

(c) Verifying the absence of cyclonic flow.

(d) Completing a preliminary velocity profile, and selecting a nozzle(s) and sampling rate.

8.3.1 Sampling Site Location. Follow the standard procedures in Method 1 of appendix A-1 to part 60 to select the appropriate sampling site. Choose a location that maximizes the distance from upstream and downstream flow disturbances.

8.3.2 Traverse points. Use the required number of traverse points at any location, as found in Methods 5, 17, or 201A, whichever is applicable to your test requirements. You must prevent the disturbance and capture of any solids accumulated on the inner wall surfaces by maintaining a 1-

inch distance from the stack wall (0.5 inch for sampling locations less than 24 inches in diameter).

8.4 Sampling Train Preparation. A schematic of the sampling train used in this method is shown in Figure 1 of Section 18. All glassware that is used to collect and analyze samples must be cleaned prior to the test with soap and water, and rinsed using tap water, deionized water, acetone, and finally, hexane. It is important to completely remove all silicone grease from areas that will be exposed to the hexane rinse during sample recovery. After cleaning, you must bake glassware at 300 °C for six hours prior to beginning tests at each source category sampled at a facility. As an alternative to baking glassware, a field train proof blank, as specified in Section 8.5.4.10, can be performed on the sampling train glassware that is used to collect CPM samples. Prior to each sampling run, the train glassware used to collect condensable PM must be rinsed thoroughly with deionized, ultra-filtered water that that contains 1 ppmw (1 mg/L) residual mass or less.

8.4.1 Condenser and Water Dropout Impinger. Add a Method 23 type condenser and a condensate dropout impinger without bubbler tube after the final probe extension that connects the in-stack or out-of-stack hot filter assembly with the CPM sampling train. The Method 23 type stack gas condenser is described in Section 2.1.2 of Method 23. The condenser must be capable of cooling the stack gas to less than or equal to 30 °C (85 °F).

8.4.2 Backup Impinger. The water dropout impinger is followed by a modified Greenburg Smith impinger (backup impinger) with no taper (see Figure 1 of Section 18). Place the water dropout and backup impingers in an insulated box with water at less than or equal to 30 °C (less than or equal to 85 °F). At the start of the tests, the water dropout and backup impingers must be clean, without any water or reagent added.

8.4.3 CPM Filter. Place a filter holder with a filter meeting the requirements in Section 7.1.1 after the backup impinger. The connection between the CPM filter and the moisture trap impinger must include a thermocouple fitting that provides a leak-free seal between the thermocouple and the stack gas. (NOTE: A thermocouple well is not sufficient for this purpose because the fluoropolymer- or steel-encased thermocouple must be in contact with the sample gas.)

8.4.4 Moisture Traps. You must use a modified Greenburg-Smith impinger containing 100 ml of water, or the alternative described in Method 5 of appendix A-3 to part 60, followed by an impinger containing silica gel to collect moisture that passes through the CPM filter. You must maintain the gas temperature below 20 °C (68 °F) at the exit of the moisture traps.

8.4.5 Silica Gel Trap. Place 200 to 300 g of silica gel in each of several air-tight containers. Weigh each container, including silica gel, to the nearest 0.5 g, and record this weight on the filterable particulate data sheet. As an alternative, the silica gel need not be preweighed, but may be weighed directly in its impinger or sampling holder just prior to train assembly.

8.4.6 Leak-Check (Pretest). Use the procedures outlined in Method 5 of appendix A-3 to part 60, Method 17 of appendix A-6 to part 60, or Method 201A of appendix M to this part as

appropriate to leak check the entire sampling system. Specifically, perform the following procedures:

8.4.6.1 Sampling train. You must pretest the entire sampling train for leaks. The pretest leak-check must have a leak rate of not more than 0.02 actual cubic feet per minute or 4 percent of the average sample flow during the test run, whichever is less. Additionally, you must conduct the leak-check at a vacuum equal to or greater than the vacuum anticipated during the test run. Enter the leak-check results on the field test data sheet for the filterable particulate method. (NOTE: Conduct leak-checks during port changes only as allowed by the filterable particulate method used with this method.)

8.4.6.2 Pitot tube assembly. After you leak-check the sample train, perform a leak-check of the pitot tube assembly. Follow the procedures outlined in Section 8.4.1 of Method 5.

8.5 Sampling Train Operation. Operate the sampling train as described in the filterable particulate sampling method (*i.e.,* Method 5 of appendix A-3 to part 60, Method 17 of appendix A-6 to part 60, or Method 201A of appendix M to this part) with the following additions or exceptions:

8.5.1 Impinger and CPM Filter Assembly.

8.5.1.1 Monitor the moisture condensation in the knockout and backup impingers. If the accumulated water from moisture condensation overwhelms the knockout impinger, i.e., the water level is more than approximately one-half the capacity of the knockout impinger, or if water accumulates in the backup impinger sufficient to cover the impinger insert tip, then you may interrupt the sampling run, recover and weigh the moisture accumulated in the knockout and backup impinger, reassemble and leak check the sampling train, and resume the sampling run. You must purge the water collected during the test interruption as soon as practical following the procedures in Section 8.5.3.

8.5.1.2 You must include the weight or volume of the moisture in your moisture calculation and you must combine the recovered water with the appropriate sample fraction for subsequent CPM analysis.

8.5.1.3 Use the field data sheet for the filterable particulate method to record the CPM filter temperature readings at the beginning of each sample time increment and when sampling is halted. Maintain the CPM filter greater than 20 °C (greater than 65 °F) but less than or equal to 30 °C (less than or equal to 85 °F) during sample collection. (Note: Maintain the temperature of the CPM filter assembly as close to 30 °C (85 °F) as feasible.)

8.5.2 Leak-Check Probe/Sample Train Assembly (Post-Test). Conduct the leak rate check according to the filterable particulate sampling method used during sampling. If required, conduct the leak-check at a vacuum equal to or greater than the maximum vacuum achieved during the test run. If the leak rate of the sampling train exceeds 0.02 actual cubic feet per minute or four percent of the average sampling rate during the test run (whichever is less), then the run is invalid and you must repeat it.

8.5.3 Post-Test Nitrogen Purge. As soon as possible after the post-test leak-check, detach the probe, any cyclones, and in-stack or hot filters from the condenser and impinger train. If no water was collected before the CPM filter, then you may skip the remaining purge steps and proceed with sample recovery (see Section 8.5.4). You may purge the CPM sampling train using the sampling system meter box and vacuum pump or by passing nitrogen through the train under pressure. For either type of purge, you must first attach the nitrogen supply line to a purged inline filter.

8.5.3.1 If you choose to conduct a pressurized nitrogen purge at the completion of CPM sample collection, you may purge the entire CPM sample collection train from the condenser inlet to the CPM filter holder outlet or you may quantitatively transfer the water collected in the condenser and the water dropout impinger to the backup impinger and purge only the backup impinger and the CPM filter. You must measure the water in the knockout and backup impingers and record the volume or weight as part of the moisture collected during sampling as specified in Section 8.5.3.4.

8.5.3.1.1 If you choose to conduct a purge of the entire CPM sampling train, you must replace the short stem impinger insert in the knock out impinger with a standard modified Greenburg Smith impinger insert.

8.5.3.1.2 If you choose to combine the knockout and backup impinger catch prior to purge, you must purge the backup impinger and CPM filter holder.

8.5.3.1.3 If the tip of the impinger insert does not extend below the water level (including the water transferred from the first impinger if this option was chosen), you must add a measured amount of degassed, deionized ultra-filtered water that contains 1 ppmw (1 mg/L) residual mass or less until the impinger tip is at least 1 centimeter below the surface of the water. You must record the amount of water added to the water dropout impinger (Vp)(see Figure 4 of Section 18) to correct the moisture content of the effluent gas. (Note: Prior to use, water must be degassed using a nitrogen purge bubbled through the water for at least 15 minutes to remove dissolved oxygen).

8.5.3.1.4 To perform the nitrogen purge using positive pressure nitrogen flow, you must start with no flow of gas through the clean purge line and fittings. Connect the filter outlet to the input of the impinger train and disconnect the vacuum line from the exit of the silica moisture collection impinger (see Figure 3 of Section 18). You may purge only the CPM train by disconnecting the moisture train components if you measure moisture in the field prior to the nitrogen purge. You must increase the nitrogen flow gradually to avoid over-pressurizing the impinger array. You must purge the CPM train at a minimum of 14 liters per minute for at least one hour. At the conclusion of the purge, turn off the nitrogen delivery system.

8.5.3.2 If you choose to conduct a nitrogen purge on the complete CPM sampling train using the sampling system meter box and vacuum pump, replace the short stem impinger insert with a modified Greenberg Smith impinger insert. The impinger tip length must extend below the water level in the impinger catch.

(a) You must conduct the purge on the complete CPM sampling train starting at the inlet of the condenser. If insufficient water was collected, you must add a measured amount of degassed, deionized ultra-filtered water that contains 1 ppmw (1 mg/L) residual mass or less until the impinger tip is at least 1 centimeter below the surface of the water. You must record the amount of water added to the water dropout impinger (V_p) (see Figure 4 of Section 18) to correct the moisture content of the effluent gas. *(Note:* Prior to use, water must be degassed using a nitrogen purge bubbled through the water for at least 15 minutes to remove dissolved oxygen).

(b) You must start the purge using the sampling train vacuum pump with no flow of gas through the clean purge line and fittings. Connect the filter outlet to the input of the impinger train (see Figure 2 of Section 18). To avoid over- or under-pressurizing the impinger array, slowly commence the nitrogen gas flow through the line while simultaneously opening the meter box pump valve(s). Adjust the pump bypass and/or nitrogen delivery rates to obtain the following conditions: 14 liters/min or ΔH@ and a positive overflow rate through the rotameter of less than 2 liters/min. The presence of a positive overflow rate guarantees that the nitrogen delivery system is operating at greater than ambient pressure and prevents the possibility of passing ambient air (rather than nitrogen) through the impingers. Continue the purge under these conditions for at least one hour, checking the rotameter and ΔH@ value(s) at least every 15 minutes. At the conclusion of the purge, simultaneously turn off the delivery and pumping systems.

8.5.3.3 During either purge procedure, continue operation of the condenser recirculation pump, and heat or cool the water surrounding the first two impingers to maintain the gas temperature measured at the exit of the CPM filter greater than 20 °C (greater than 65 °F), but less than or equal to 30 °C (less than or equal to 85 °F). If the volume of liquid collected in the moisture traps has not been determined prior to conducting the nitrogen purge, maintain the temperature of the moisture traps following the CPM filter to prevent removal of moisture during the purge. If necessary, add more ice during the purge to maintain the gas temperature measured at the exit of the silica gel impinger below 20 °C (68 °F). Continue the purge under these conditions for at least one hour, checking the rotameter and ΔH@ value(s) periodically. At the conclusion of the purge, simultaneously turn off the delivery and pumping systems.

8.5.3.4 Weigh the liquid, or measure the volume of the liquid collected in the dropout, impingers, and silica trap if this has not been done prior to purging the sampling train. Measure the liquid in the water dropout impinger to within 1 ml using a clean graduated cylinder or by weighing it to within 0.5 g using a balance. Record the volume or weight of liquid present to be used to calculate the moisture content of the effluent gas in the field log notebook.

8.5.3.5 If a balance is available 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 in the field log notebook.

8.5.4 Sample Recovery.

8.5.4.1 *Recovery of filterable PM.* Recovery of filterable PM involves the quantitative transfer of particles according to the filterable particulate sampling method (*i.e.*, Method 5 of appendix

A-3 to part 60, Method 17 of appendix A-6 to part 60, or Method 201A of appendix M to this part).

8.5.4.2 *CPM Container #1, Aqueous liquid impinger contents.* Quantitatively transfer liquid from the dropout and the backup impingers prior to the CPM filter into a clean, leak-proof container labeled with test identification and "CPM Container #1, Aqueous Liquid Impinger Contents." Rinse all sampling train components including the back half of the filterable PM filter holder, the probe extension, condenser, each impinger and the connecting glassware, and the front half of the CPM filter housing twice with water. Recover the rinse water, and add it to CPM Container #1. Mark the liquid level on the container.

8.5.4.3 *CPM Container #2, Organic rinses.* Follow the water rinses of the probe extension, condenser, each impinger and all of the connecting glassware and front half of the CPM filter with an acetone rinse. Recover the acetone rinse into a clean, leak-proof container labeled with test identification and "CPM Container #2, Organic Rinses." Then repeat the entire rinse procedure with two rinses of hexane, and save the hexane rinses in the same container as the acetone rinse (CPM Container #2). Mark the liquid level on the jar.

8.5.4.4 *CPM Container #3, CPM filter sample.* Use tweezers and/or clean disposable surgical gloves to remove the filter from the CPM filter holder. Place the filter in the Petri dish labeled with test identification and "CPM Container #3, Filter Sample."

8.5.4.5 *CPM Container #4, Cold impinger water.* You must weigh or measure the volume of the contents of CPM Container #4 either in the field or during sample analysis (*see* Section 11.2.4). If the water from the cold impinger has been weighed in the field, it can be discarded. Otherwise, quantitatively transfer liquid from the cold impinger that follows the CPM filter into a clean, leak-proof container labeled with test identification and "CPM Container #4, Cold Water Impinger." Mark the liquid level on the container. CPM Container #4 holds the remainder of the liquid water from the emission gases.

8.5.4.6 *CPM Container #5, Silica gel absorbent.* You must weigh the contents of CPM Container #5 in the field or during sample analysis (see Section 11.2.5). If the silica gel has been weighed in the field to measure water content, then it can be discarded or recovered for reuse. Otherwise, transfer the silica gel to its original container labeled with test identification and "CPM Container #5, Silica Gel Absorbent" and seal. You may use a funnel to make it easier to pour the silica gel without spilling. You may also use a rubber policeman as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of silica gel dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel.

8.5.4.7 *CPM Container #6, Acetone field reagent blank.* Take approximately 200 ml of the acetone directly from the wash bottle you used for sample recovery and place it in a clean, leak-proof container labeled with test identification and "CPM Container #6, Acetone Field Reagent Blank" (*see* Section 11.2.6 for analysis). Mark the liquid level on the container. Collect one acetone field reagent blank from the lot(s) of solvent used for the test.

8.5.4.8 *CPM Container #7, Water field reagent blank.* Take approximately 200 ml of the water directly from the wash bottle you used for sample recovery and place it in a clean, leak-proof container labeled with test identification and "CPM Container #7, Water Field Reagent Blank" (*see* Section 11.2.7 for analysis). Mark the liquid level on the container. Collect one water field reagent blank from the lot(s) of water used for the test.

8.5.4.9 *CPM Container #8, Hexane field reagent blank.* Take approximately 200 ml of the hexane directly from the wash bottle you used for sample recovery and place it in a clean, leak-proof container labeled with test identification and "CPM Container #8, Hexane Field Reagent Blank" (*see* Section 11.2.8 for analysis). Mark the liquid level on the container. Collect one hexane field reagent blank from the lot(s) of solvent used for the test.

8.5.4.10 *Field train proof blank.* If you did not bake the sampling train glassware as specified in Section 8.4, you must conduct a field train proof blank as specified in Sections 8.5.4.11 and 8.5.4.12 to demonstrate the cleanliness of sampling train glassware.

8.5.4.11 *CPM Container #9, Field train proof blank, inorganic rinses.* Prior to conducting the emission test, rinse the probe extension, condenser, each impinger and the connecting glassware, and the front half of the CPM filter housing twice with water. Recover the rinse water and place it in a clean, leak-proof container labeled with test identification and "CPM Container #9, Field Train Proof Blank, Inorganic Rinses." Mark the liquid level on the container.

8.5.4.12 *CPM Container #10, Field train proof blank, organic rinses.* Follow the water rinse of the probe extension, condenser, each impinger and the connecting glassware, and the front half of the CPM filter housing with an acetone rinse. Recover the acetone rinse into a clean, leak-proof container labeled with test identification and "CPM Container #10, Field Train Proof Blank, Organic Rinses." Then repeat the entire rinse procedure with two rinses of hexane and save the hexane rinses in the same container as the acetone rinse (CPM Container #10). Mark the liquid level on the container.

8.5.5 Transport procedures. Containers must remain in an upright position at all times during shipping. You do not have to ship the containers under dry or blue ice. However, samples must be maintained at or below 30 °C (85 °F) during shipping.

9.0 Quality Control

9.1 Daily Quality Checks. You must perform daily quality checks of field log notebooks and data entries and calculations using data quality indicators from this method and your site-specific test plan. You must review and evaluate recorded and transferred raw data, calculations, and documentation of testing procedures. You must initial or sign log notebook pages and data entry forms that were reviewed.

9.2 Calculation Verification. Verify the calculations by independent, manual checks. You must flag any suspect data and identify the nature of the problem and potential effect on data quality. After you complete the test, prepare a data summary and compile all the calculations and raw data sheets.

9.3 Conditions. You must document data and information on the process unit tested, the particulate control system used to control emissions, any non-particulate control system that may affect particulate emissions, the sampling train conditions, and weather conditions. Discontinue the test if the operating conditions may cause non-representative particulate emissions.

9.4 Field Analytical Balance Calibration Check. Perform calibration check procedures on field analytical balances each day that they are used. You must use National Institute of Standards and Technology (NIST)-traceable weights at a mass approximately equal to the weight of the sample plus container you will weigh.

9.5 Glassware. Use class A volumetric glassware for titrations, or calibrate your equipment against NIST-traceable glassware.

9.6 Laboratory Analytical Balance Calibration Check. Check the calibration of your laboratory analytical balance each day that you weigh CPM samples. You must use NIST Class S weights at a mass approximately equal to the weight of the sample plus container you will weigh.

9.7 Laboratory Reagent Blanks. You should run blanks of water, acetone, and hexane used for field recovery and sample analysis. Analyze at least one sample (150 ml minimum) of each lot of reagents that you plan to use for sample recovery and analysis before you begin testing. These blanks are not required by the test method, but running blanks before field use is advisable to verify low blank concentrations, thereby reducing the potential for a high field blank on test samples.

9.8 Field Reagent Blanks. You should run at least one field reagent blank of water, acetone, and hexane you use for field recovery. These blanks are not required by the test method, but running independent field reagent blanks is advisable to verify that low blank concentrations were maintained during field solvent use and demonstrate that reagents have not been contaminated during field tests.

9.9 Field Train Proof Blank. If you are not baking glassware as specified in Section 8.4, you must recover a minimum of one field train proof blank for the sampling train used for testing each new source category at a single facility. You must assemble the sampling train as it will be used for testing. You must recover the field train proof blank samples as described in Section 8.5.4.11 and 8.5.4.12.

9.10 Field Train Recovery Blank. You must recover a minimum of one field train blank for each source category tested at the facility. You must recover the field train blank after the first or second run of the test. You must assemble the sampling train as it will be used for testing. Prior to the purge, you must add 100 ml of water to the first impinger and record this data on Figure 4. You must purge the assembled train as described in Sections 8.5.3.2 and 8.5.3.3. You must recover field train blank samples as described in Section 8.5.4. From the field sample weight, you will subtract the condensable particulate mass you determine with this blank train or 0.002 g (2.0 mg), whichever is less.

10.0 Calibration and Standardization

Maintain a field log notebook of all condensable particulate sampling and analysis calibrations. Include copies of the relevant portions of the calibration and field logs in the final test report.

10.1 Thermocouple Calibration. You must calibrate the thermocouples using the procedures described in Section 10.3.1 of Method 2 of appendix A-1 to part 60 or Alternative Method 2, Thermocouple Calibration (ALT-011) (*http://www.epa.gov/ttn/emc*). Calibrate each temperature sensor at a minimum of three points over the anticipated range of use against a NIST-traceable thermometer. Alternatively, a reference thermocouple and potentiometer calibrated against NIST standards can be used.

10.2 Ammonium Hydroxide. The 0.1 N NH_4OH used for titrations in this method is made as follows: Add 7 ml of concentrated (14.8 M) NH_4OH to l liter of water. Standardize against standardized 0.1 N H_2SO_4, and calculate the exact normality using a procedure parallel to that described in Section 10.5 of Method 6 of appendix A-4 to 40 CFR part 60. Alternatively, purchase 0.1 N NH_4OH that has been standardized against a NIST reference material. Record the normality on the CPM Work Table (*see* Figure 6 of Section 18).

11.0 Analytical Procedures

11.1 Analytical Data Sheets. (a) Record the filterable particulate field data on the appropriate (*i.e.*, Method 5, 17, or 201A) analytical data sheets. Alternatively, data may be recorded electronically using software applications such as the Electronic Reporting Tool available at *http://www.epa.gov/ttn/chief/ert/ert_tool.html.* Record the condensable particulate data on the CPM Work Table (*see* Figure 6 of Section 18).

(b) Measure the liquid in all containers either volumetrically to ±1 ml or gravimetrically to ±0.5 g. Confirm on the filterable particulate analytical data sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods (subject to the approval of the Administrator) to correct the final results.

11.2 Condensable PM Analysis. See the flow chart in Figure 7 of Section 18 for the steps to process and combine fractions from the CPM train.

11.2.1 Container #3, CPM Filter Sample. If the sample was collected by Method 17 or Method 201A with a stack temperature below 30 °C (85 °F), transfer the filter and any loose PM from the sample container to a tared glass weighing dish. (See Section 3.0 for a definition of constant weight.) Desiccate the sample for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight and report the results to the nearest 0.1 mg. [Note: In-stack filter samples collected at 30 °C (85 °F) may include both filterable insoluble particulate and condensable particulate. The nozzle and front half wash and filter collected at or below 30 °C (85 °F) may not be heated and must be maintained at or below 30 °C (85 °F).] If the sample was collected by Method 202, extract the CPM filter as follows:

11.2.1.1 Extract the water soluble (aqueous or inorganic) CPM from the CPM filter by folding the filter in quarters and placing it into a 50-ml extraction tube. Add sufficient deionized, ultra-filtered water to cover the filter (e.g., 10 ml of water). Place the extractor tube into a sonication

bath and extract the water-soluble material for a minimum of two minutes. Combine the aqueous extract with the contents of Container #1. Repeat this extraction step twice for a total of three extractions.

11.2.1.2 Extract the organic soluble CPM from the CPM filter by adding sufficient hexane to cover the filter (e.g., 10 ml of hexane). Place the extractor tube into a sonication bath and extract the organic soluble material for a minimum of two minutes. Combine the organic extract with the contents of Container #2. Repeat this extraction step twice for a total of three extractions.

11.2.2 CPM Container #1, Aqueous Liquid Impinger Contents. Analyze the water soluble CPM in Container #1 as described in this section. Place the contents of Container #1 into a separatory funnel. Add approximately 30 ml of hexane to the funnel, mix well, and pour off the upper organic phase. Repeat this procedure twice with 30 ml of hexane each time combining the organic phase from each extraction. Each time, leave a small amount of the organic/hexane phase in the separatory funnel, ensuring that no water is collected in the organic phase. This extraction should yield about 90 ml of organic extract. Combine the organic extract from Container #1 with the organic train rinse in Container #2.

****

NOTE: This section (11.2.2.1 through 11.2.2.4) does not appear in the official CFR. The section was removed through an inadvertent typesetting error. It was not our intention to remove this procedure from the method. We are currently in the process of placing it back into the method. We have provided the section in line on the EMC Website version as a reference.

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11.2.2.1 Determine the inorganic fraction weight. Transfer the aqueous fraction from the extraction to a clean 500-ml or smaller beaker. Evaporate to no less than 10 ml liquid on a hot plate or in the oven at 105 °C and allow to dry at room temperature (not to exceed 30 °C (85 °F)). You must ensure that water and volatile acids have completely evaporated before neutralizing nonvolatile acids in the sample. Following evaporation, desiccate the residue for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh at intervals of at least six hours to a constant weight. (See Section 3.0 for a definition of Constant weight.) Report results to the nearest 0.1 mg on the CPM Work Table (see Figure 6 of Section 18) and proceed directly to Section 11.2.3. If the residue cannot be weighed to constant weight, re-dissolve the residue in 100 ml of deionized distilled ultra-filtered water that contains 1 ppmw (1 mg/L) residual mass or less and continue to Section 11.2.2.2.

11.2.2.2 Use titration to neutralize acid in the sample and remove water of hydration. If used, calibrate the pH meter with the neutral and acid buffer solutions. Then titrate the sample with 0.1N NH_4OH to a pH of 7.0, as indicated by the pH meter or colorimetric indicator. Record the volume of titrant used on the CPM Work Table (see Figure 6 of Section 18).

11.2.2.3 Using a hot plate or an oven at 105 °C, evaporate the aqueous phase to approximately 10 ml. Quantitatively transfer the beaker contents to a clean, 50-ml pre-tared weighing tin and evaporate to dryness at room temperature (not to exceed 30 °C (85 °F)) and pressure in a laboratory hood. Following evaporation, desiccate the residue for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh at intervals of at least six hours to a constant weight. (See Section 3.0 for a definition of Constant weight.) Report results to the nearest 0.1 mg on the CPM Work Table (see Figure 6 of Section 18).

11.2.2.4 Calculate the correction factor to subtract the NH_4^+ retained in the sample using Equation 1 in Section 12.

****

11.2.3 CPM Container #2, Organic Fraction Weight Determination. Analyze the organic soluble CPM in Container #2 as described in this section. Place the organic phase in a clean glass beaker. Evaporate the organic extract at room temperature (not to exceed 30 °C (85 °F)) and pressure in a laboratory hood to not less than 10 ml. Quantitatively transfer the beaker contents to a clean 50-ml pre-tared weighing tin and evaporate to dryness at room temperature (not to exceed 30 °C (85 °F)) and pressure in a laboratory hood. Following evaporation, desiccate the organic fraction for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh at intervals of at least six hours to a constant weight (*i.e.,* less than or equal to 0.5 mg change from previous weighing), and report results to the nearest 0.1 mg on the CPM Work Table (*see* Figure 6 of Section 18).

11.2.4 CPM Container #4, Cold Impinger Water. If the amount of water has not been determined in the field, note the level of liquid in the container, and confirm on the filterable particulate analytical data sheet whether leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods (subject to the approval of the Administrator) to correct the final results. Measure the liquid in Container #4 either volumetrically to ±1 ml or gravimetrically to ±0.5 g, and record the volume or weight on the filterable particulate analytical data sheet of the filterable PM test method.

11.2.5 CPM Container #5, Silica Gel Absorbent. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field. Record the weight on the filterable particulate analytical data sheet of the filterable PM test method.

11.2.6 Container #6, Acetone Field Reagent Blank. Use 150 ml of acetone from the blank container used for this analysis. Transfer 150 ml of the acetone to a clean 250-ml beaker. Evaporate the acetone at room temperature (not to exceed 30 °C (85 °F)) and pressure in a laboratory hood to approximately 10 ml. Quantitatively transfer the beaker contents to a clean 50-ml pre-tared weighing tin, and evaporate to dryness at room temperature (not to exceed 30 °C (85 °F)) and pressure in a laboratory hood. Following evaporation, desiccate the residue for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh at intervals of at least six hours to a constant weight (*i.e.*, less than or equal to 0.5 mg change from previous weighing), and report results to the nearest 0.1 mg on Figure 4 of Section 19.

11.2.7 Water Field Reagent Blank, Container #7. Use 150 ml of the water from the blank container for this analysis. Transfer the water to a clean 250-ml beaker, and evaporate to approximately 10 ml liquid in the oven at 105 °C. Quantitatively transfer the beaker contents to a clean 50 ml pre-tared weighing tin and evaporate to dryness at room temperature (not to exceed 30 °C (85 °F)) and pressure in a laboratory hood. Following evaporation, desiccate the residue for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh at intervals of at least six hours to a constant weight (*i.e.,* less than or equal to 0.5 mg change from previous weighing) and report results to the nearest 0.1 mg on Figure 4 of Section 18.

11.2.8 Hexane Field Reagent Blank, Container #8. Use 150 ml of hexane from the blank container for this analysis. Transfer 150 ml of the hexane to a clean 250-ml beaker. Evaporate the hexane at room temperature (not to exceed 30 °C (85 °F)) and pressure in a laboratory hood to approximately 10 ml. Quantitatively transfer the beaker contents to a clean 50-ml pre-tared weighing tin and evaporate to dryness at room temperature (not to exceed 30 °C (85 °F)) and pressure in a laboratory hood. Following evaporation, desiccate the residue for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh at intervals of at least six hours to a constant weight (*i.e.*, less than or equal to 0.5 mg change from previous weighing), and report results to the nearest 0.1 mg on Figure 4 of Section 18.

12.0 Calculations and Data Analysis

12.1 Nomenclature. Report results in International System of Units (SI units) unless the regulatory authority for testing specifies English units. The following nomenclature is used.

$\Delta H_{@}$ = Pressure drop across orifice at flow rate of 0.75 SCFM at standard conditions, inches of water column (NOTE:Specific to each orifice and meter box).

17.03 = mg/milliequivalents for ammonium ion.

ACFM = Actual cubic feet per minute.

C_{cpm} = Concentration of the condensable PM in the stack gas, dry basis, corrected to standard conditions, milligrams/dry standard cubic foot.

m_c = Mass of the NH_4^+ added to sample to form ammonium sulfate, mg.

m_{cpm} = Mass of the total condensable PM, mg.

m_{fb} = Mass of total CPM in field train recovery blank, mg.

mg = Milligrams.

mg/L = Milligrams per liter.

m_i = Mass of inorganic CPM, mg.

m_{ib} = Mass of inorganic CPM in field train recovery blank, mg.

m_o = Mass of organic CPM, mg.

m_{ob} = Mass of organic CPM in field train blank, mg.

m_r = Mass of dried sample from inorganic fraction, mg.

N = Normality of ammonium hydroxide titrant.

ppmv = Parts per million by volume.

ppmw = Parts per million by weight.

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dry standard cubic meter (dscm) or dry standard cubic foot (dscf) as defined in Equation 5-1 of Method 5.

V_t = Volume of NH_4OH titrant, ml.

V_p = Volume of water added during train purge.

12.2 Calculations. Use the following equations to complete the calculations required in this test method. Enter the appropriate results from these calculations on the CPM Work Table (*see* Figure 6 of Section 18).

12.2.1 Mass of ammonia correction. Correction for ammonia added during titration of 100 ml aqueous CPM sample. This calculation assumes no waters of hydration.

$$m_c = 17.03 \times V_t \times N \quad \text{(Eq. 1)}$$

12.2.2 Mass of the Field Train Recovery Blank (mg). Per Section 9.10, the mass of the field train recovery blank, m_{fb}, shall not exceed 2.0 mg.

$$m_{fb} = m_{ib} + m_{ob} \quad \text{(Eq. 2)}$$

12.2.3 Mass of Inorganic CPM (mg).

$$m_i = m_r - m_c \quad \text{(Eq. 3)}$$

12.2.4 Total Mass of CPM (mg).

$$m_{cpm} = m_i + m_o - m_{fb} \quad \text{(Eq. 4)}$$

12.2.5 Concentration of CPM (mg/dscf).

$$C_{cpm} = \frac{m_{cpm}}{V_{m(std)}} \quad \text{(Eq. 5)}$$

12.3 Emissions Test Report. You must prepare a test report following the guidance in EPA Guidance Document 043 (Preparation and Review of Test Reports. December 1998).

13.0 Method Performance

An EPA field evaluation of the revised Method 202 showed the following precision in the results: approximately 4 mg for total CPM, approximately 0.5 mg for organic CPM, and approximately 3.5 mg for inorganic CPM.

14.0 Pollution Prevention

[Reserved]

15.0 Waste Management

Solvent and water are evaporated in a laboratory hood during analysis. No liquid waste is generated in the performance of this method. Organic solvents used to clean sampling equipment should be managed as RCRA organic waste.

16.0 Alternative Procedures

Alternative Method 2, Thermocouple Calibration (ALT-011) for the thermocouple calibration can be found at*http://www.epa.gov/ttn/emc/approalt.html.*

17.0 References

(1) Commonwealth of Pennsylvania, Department of Environmental Resources. 1960. Chapter 139, Sampling and Testing (Title 25, Rules and Regulations, part I, Department of Environmental Resources, Subpart C, Protection of Natural Resources, Article III, Air Resources). January 8, 1960.

(2) DeWees, W.D. and K.C. Steinsberger. 1989. "Method Development and Evaluation of Draft Protocol for Measurement of Condensable Particulate Emissions." Draft Report. November 17, 1989.

(3) DeWees, W.D., K.C. Steinsberger, G.M. Plummer, L.T. Lay, G.D. McAlister, and R.T. Shigehara. 1989. "Laboratory and Field Evaluation of EPA Method 5 Impinger Catch for Measuring Condensable Matter from Stationary Sources." Paper presented at the 1989 EPA/AWMA International Symposium on Measurement of Toxic and Related Air Pollutants. Raleigh, North Carolina. May 1-5, 1989.

(4) Electric Power Research Institute (EPRI). 2008. "Laboratory Comparison of Methods to Sample and Analyze Condensable PM." EPRI Agreement EP-P24373/C11811 Condensable Particulate Methods: EPRI Collaboration with EPA, October 2008.

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(6) Richards, J., T. Holder, and D. Goshaw. 2005. "Optimized Method 202 Sampling Train to Minimize the Biases Associated with Method 202 Measurement of Condensable PM Emissions." Paper presented at Air & Waste Management Association Hazardous Waste Combustion Specialty Conference. St. Louis, Missouri. November 2-3, 2005.

(7) Texas Air Control Board, Laboratory Division. 1976. "Determination of Particulate in Stack Gases Containing Sulfuric Acid and/or Sulfur Dioxide." Laboratory Methods for Determination of Air Pollutants. Modified December 3, 1976.

(8) Puget Sound Air Pollution Control Agency, Engineering Division. 1983. "Particulate Source Test Procedures Adopted by Puget Sound Air Pollution Control Agency Board of Directors." Seattle, Washington. August 11, 1983.

(9) U.S. Environmental Protection Agency, Federal Reference Methods 1 through 5 and Method 17, 40 CFR 60, appendix A-1 through A-3 and A-6.

(10) U.S. Environmental Protection Agency. 2008. "Evaluation and Improvement of Condensable PM Measurement," EPA Contract No. EP-D-07-097, Work Assignment 2-03, October 2008.

(11) U.S. Environmental Protection Agency. 2005. "Laboratory Evaluation of Method 202 to Determine Fate of SO_2 in Impinger Water," EPA Contract No. 68-D-02-061, Work Assignment 3-14, September 30, 2005.

(12) U.S. Environmental Protection Agency. 2010. Field valuation of an Improved Method for Sampling and Analysis of Filterable and Condensable Particulate Matter. Office of Air Quality Planning and Standards, Sector Policy and Program Division Monitoring Policy Group. Research Triangle Park, NC 27711.

(13) Wisconsin Department of Natural Resources. 1988. Air Management Operations Handbook, Revision 3. January 11, 1988.

18.0 Tables, Diagrams, Flowcharts, and Validation Data

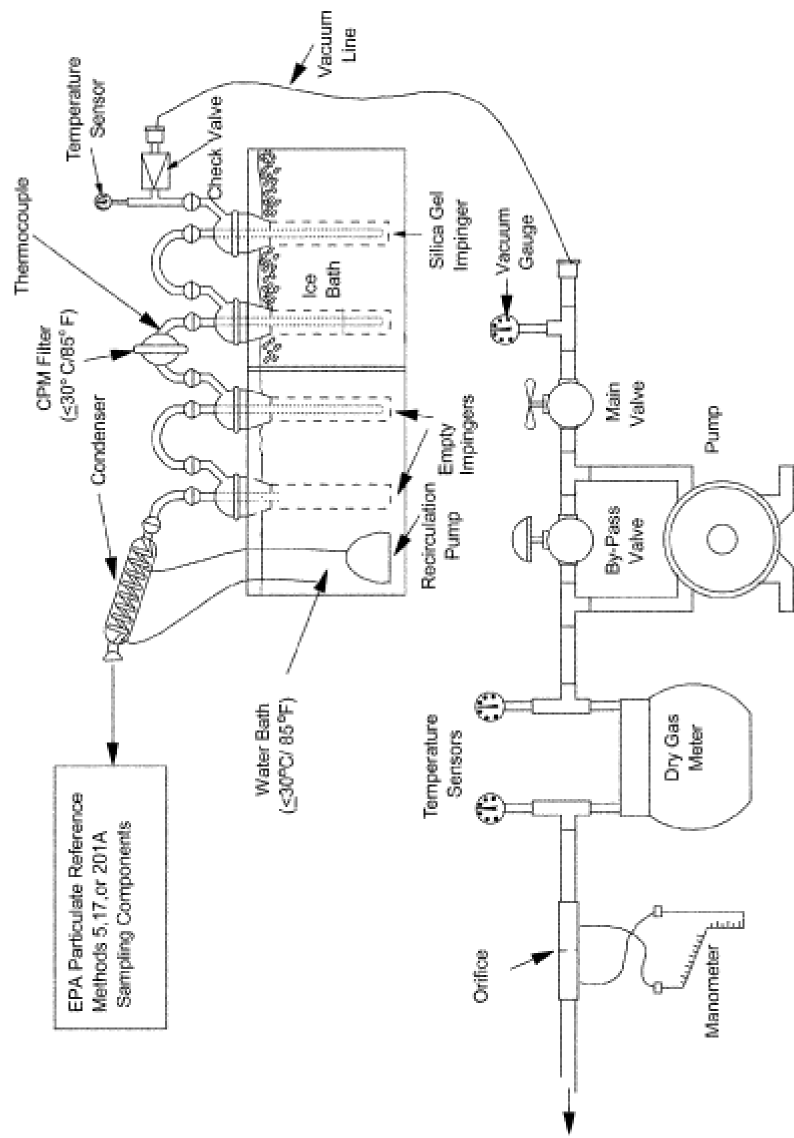

Figure 1. Schematic of Condensable Particulate Sampling Train

Figure 2. Nitrogen Purge Train Configuration (Vacuum Purge)

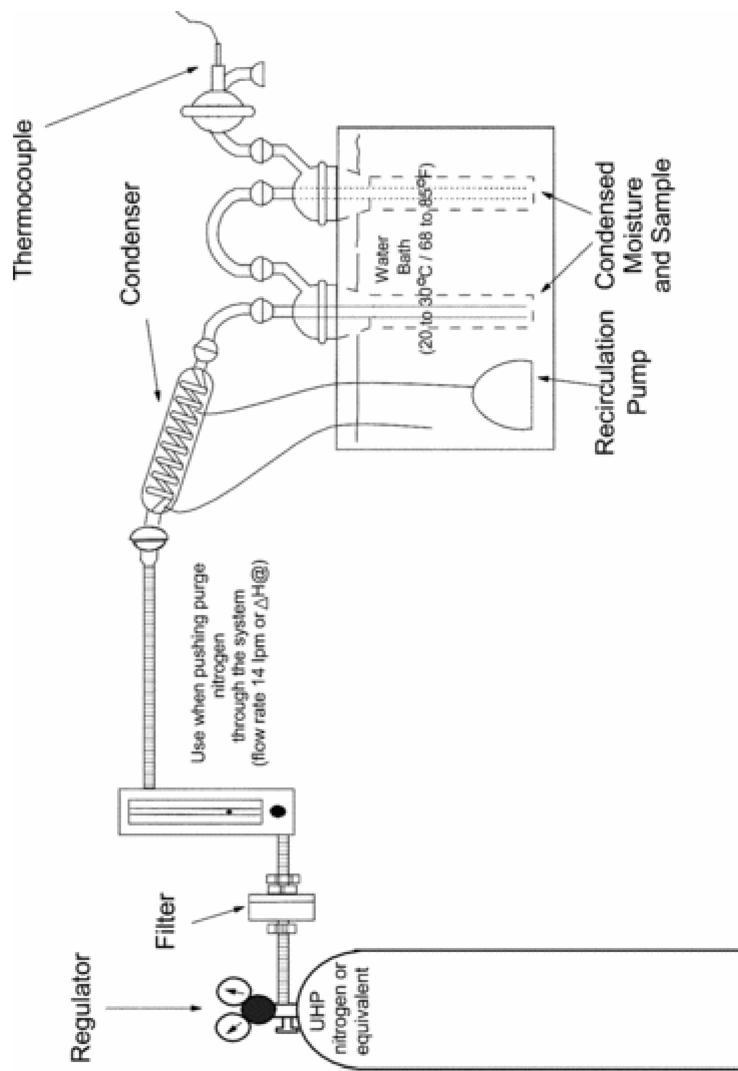

Figure 3. Nitrogen Purge Train Configuration (Pressure Purge)

Field Train Recovery Blank Condensable Particulate Calculations	
Plant	
Date	
Blank No.	
CPM Filter No.	
Water volume added to purge train (V_p)	ml
Field Reagent Blank Mass[a]	
Water (Section 11.2.7)	mg
Acetone (Section 11.2.6)	mg
Hexane (Section 11.2.8)	mg
Field Train Recovery Blank Mass	
Mass of Organic CPM (m_{ob}) (Section 11.2.3)	mg
Mass of Inorganic CPM (m_{ib}) (Equation 3)	mg
Mass of the Field Train Recovery Blank (not to exceed 2.0 mg) (Equation 2)	mg

[a]Field reagent blanks are optional and intended to provide the testing contractor with information they can use to implement corrective actions, if necessary, to reduce the residual mass contribution from reagents used in the field. Field reagent blanks are not used to correct the CPM measurement results.

Figure 4. Field Train Recovery Blank Condensable Particulate Calculations

Other Field Train Sample Condensable Particulate Data	
Plant	
Date	
Run No.	
CPM Filter No.	
Water volume added to purge train (max 50 ml) (V_p)	ml
Date	
Run No.	
CPM Filter No.	
Water volume added to purge train (max 50 ml) (V_p)	ml
Date	
Run No.	
CPM Filter No.	
Water volume added to purge train (max 50 ml) (V_p)	ml

Figure 5. Other Field Train Sample Condensable Particulate Data

Calculations for Recovery of Condensable PM (CPM)		
Plant ______		
Date ______		
Run No. ______		
Sample Preparation - CPM Containers No. 1 and 2 (Section 11.1)		
Was significant volume of water lost during transport? Yes or No	______	
If Yes, measure the volume received.	______	
Estimate the volume lost during transport.	______	ml
Was significant volume of organic rinse lost during transport? Yes or No	______	
If Yes, measure the volume received.	______	
Estimate the volume lost during transport.	______	ml
For Titration		
Normality of NH_4OH (N) (Section 10.2)	______	N
Volume of titrant (V_t) (Section 11.2.2.2)	______	ml
Mass of NH_4 added (m_c) (Equation 1)	______	mg
For CPM Blank Weights		
Inorganic Field Train Recovery Blank Mass(m_{ib}) (Section 9.9)	______	mg
Organic Field Train Recovery Blank Mass (m_{ob}) (Section 9.9)	______	mg
Mass of Field Train Recovery Blank (M_{fb}) (max. 2 mg) (Equation 2)	______	mg
For CPM Train Weights		
Mass of Organic CPM (m_o) (Section 11.2.3)	______	mg
Mass of Inorganic CPM (m_i) (Equation 3)	______	mg
Total CPM Mass (m_{cpm}) (Equation 4)	______	mg

Figure 6. CPM Work Table

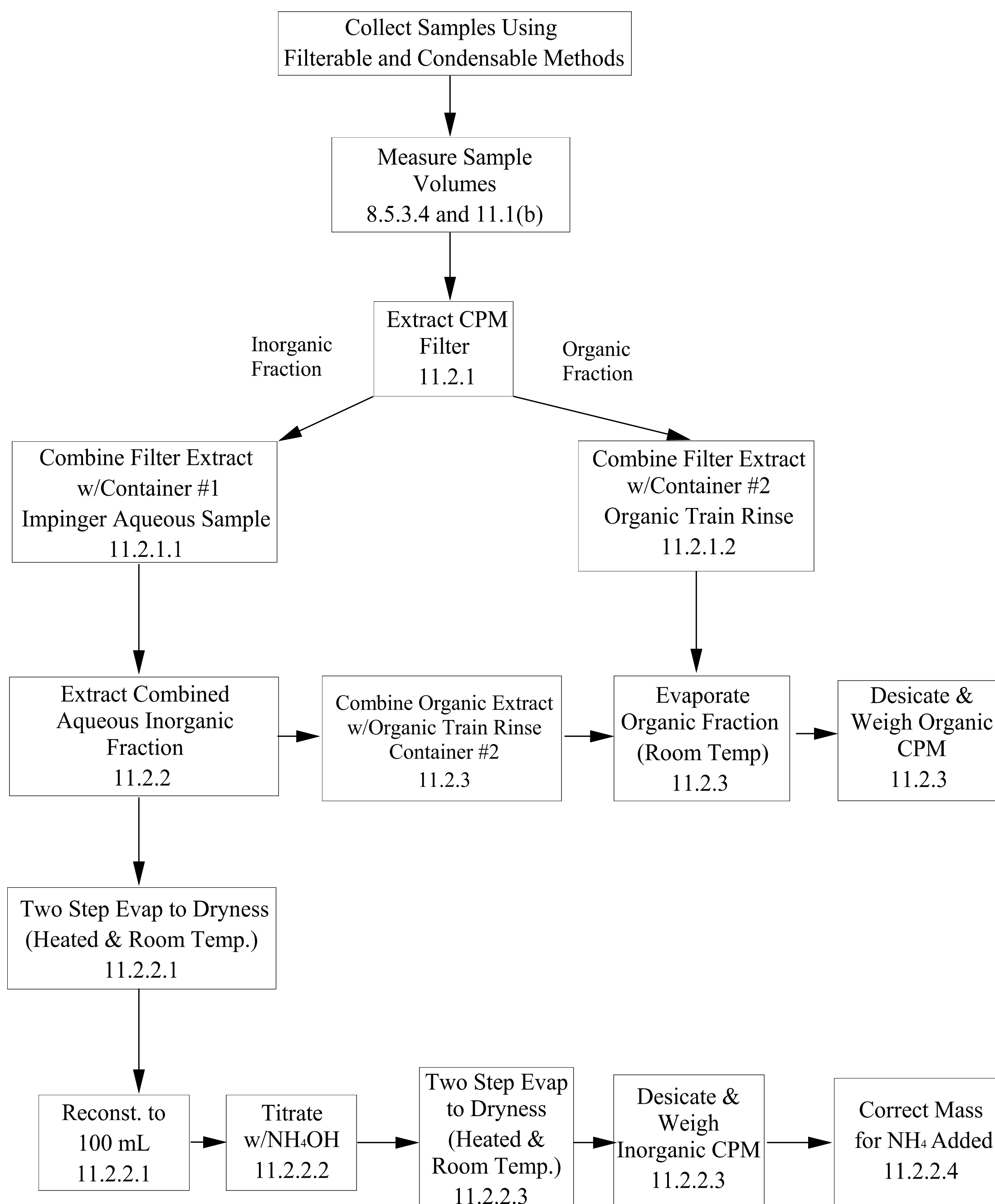

Figure 7. CPM Sample Processing Flow Chart

NOTE: This figure (Figure 7) does not appear in the official CFR. The figure was removed through an inadvertent typesetting error. It was not our intention to remove this procedure from the method. We are currently in the process of placing it back into the method. We have provided the figure in line on the EMC Website version as a reference.

METHOD 0010

MODIFIED METHOD 5 SAMPLING TRAIN

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the determination of Destruction and Removal Efficiency (DRE) of semivolatile Principal Organic Hazardous Compounds (POHCs) from incineration systems (PHS, 1967). This method also may be used to determine particulate emission rates from stationary sources as per EPA Method 5 (see References at end of 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 multicomponent sampling train. Principal components of the train include a high-efficiency glass- or quartz-fiber filter and a packed bed of porous polymeric adsorbent resin. The filter is used to collect organic-laden particulate materials and the porous polymeric resin to adsorb semivolatile organic species. Semivolatile species are defined as compounds with boiling points >100°C.

2.2 Comprehensive chemical analyses of the collected sample are conducted to determine the concentration and identity of the organic materials.

3.0 INTERFERENCES

3.1 Oxides of nitrogen (NO_x) are possible interferents in the determination of certain water-soluble compounds such as dioxane, phenol, and urethane; reaction of these compounds with NO_x in the presence of moisture will reduce their concentration. Other possibilities that could result in positive or negative bias are (1) stability of the compounds in methylene chloride, (2) the formation of water-soluble organic salts on the resin in the presence of moisture, and (3) the solvent extraction efficiency of water-soluble compounds from aqueous media. Use of two or more ions per compound for qualitative and quantitative analysis can overcome interference at one mass. These concerns should be addressed on a compound-by-compound basis before using this method.

4.0 APPARATUS AND MATERIALS

4.1 Sampling train:

4.1.1 A schematic of the sampling train used in this method is shown in Figure 1. This sampling train configuration is adapted from EPA Method 5 procedures, and, as such, the majority of the required equipment

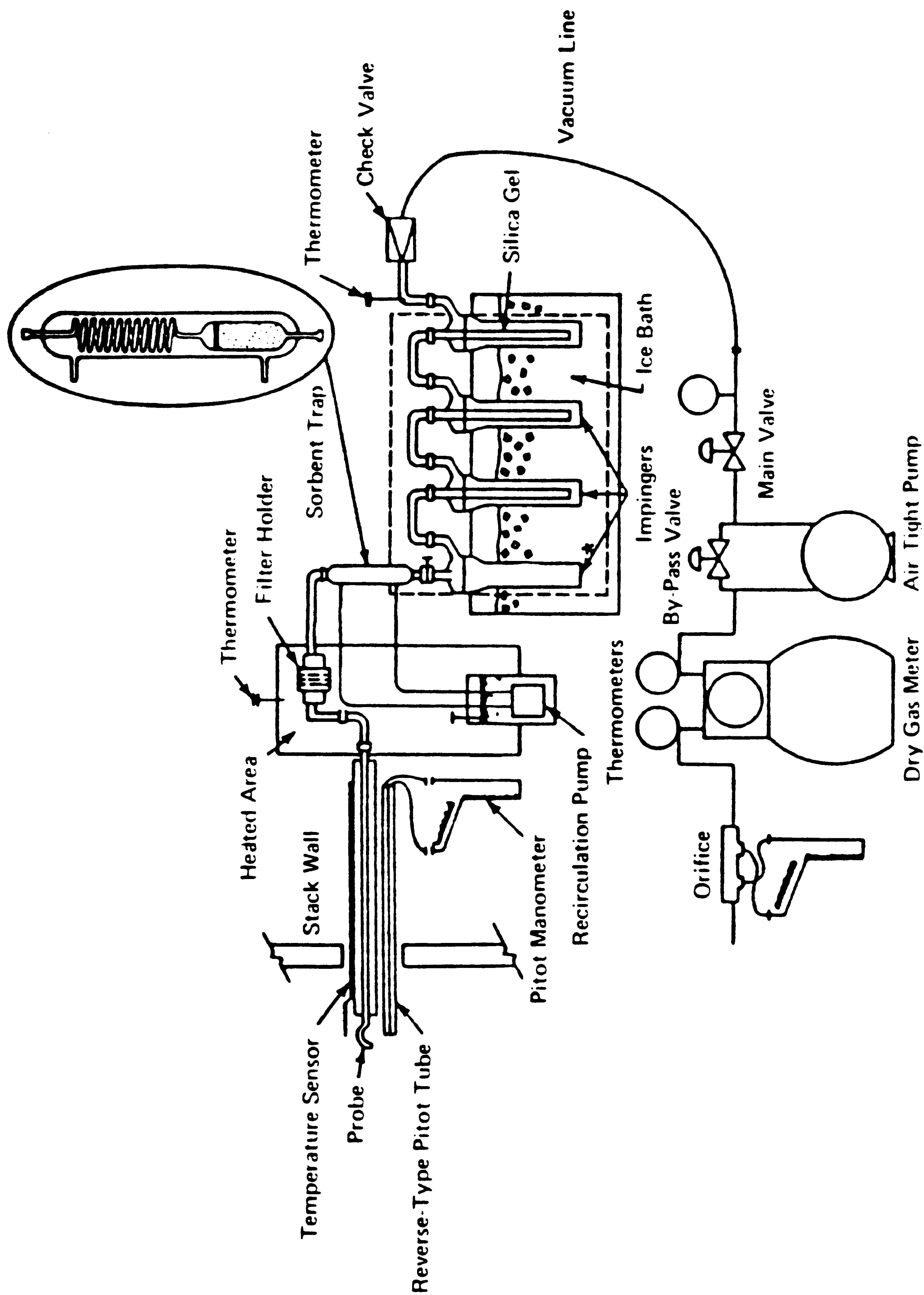

Figure 1. Modified Method 5 Sampling Train.

is identical to that used in EPA Method 5 determinations. The new components required are a condenser coil and a sorbent module, which are used to collect semivolatile organic materials that pass through the glass- or quartz-fiber filter in the gas phase.

4.1.2 Construction details for the basic train components are given in APTD-0581 (see Martin, 1971, in Section 13.0, References); commercial models of this equipment are also available. Specifications for the sorbent module are provided in the following subsections. Additionally, the following subsections list changes to APTD-0581 and identify allowable train configuration modifications.

4.1.3 Basic operating and maintenance procedures for the sampling train are described in APTD-0576 (see Rom, 1972, in Section 13.0, References). As correct usage is important in obtaining valid results, all users should refer to APTD-0576 and adopt the operating and maintenance procedures outlined therein unless otherwise specified. The sampling train consists of the components detailed below.

4.1.3.1 Probe nozzle: Stainless steel (316) or glass with sharp, tapered (30° angle) leading edge. The taper shall be on the outside to preserve a constant I.D. The nozzle shall be buttonhook or elbow design and constructed from seamless tubing (if made of stainless steel). Other construction materials may be considered for particular applications. A range of nozzle sizes suitable for isokinetic sampling should be available in increments of 0.16 cm (1/16 in.), e.g., 0.32-1.27 cm (1/8-1/2 in.), or larger if higher volume sampling trains are used. Each nozzle shall be calibrated according to the procedures outlined in Paragraph 9.1.

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

4.1.3.3 Pitot tube: Type S, as described in Section 2.1 of EPA Method 2, or other appropriate devices (Vollaro, 1976). The pitot tube shall be attached to the probe to allow constant monitoring of the stack-gas velocity. The impact (high-pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see EPA Method 2, Figure 2-6b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 4 of EPA Method 2.

4.1.3.4 Differential pressure gauge: Inclined manometer or equivalent device as described in Section 2.2 of EPA Method 2. One manometer shall be used for velocity-head (ΔP) readings and the other for orifice differential pressure (ΔH) readings.

4.1.3.5 Filter holder: Borosilicate glass, with a glass frit filter support and a sealing gasket. The sealing gasket should be made of materials that will not introduce organic material into the gas stream at the temperature at which the filter holder will be maintained. The gasket shall be constructed of Teflon or materials of equal or better characteristics. The holder design shall provide a positive seal against leakage at any point along the filter circumference. The holder shall be attached immediately to the outlet of the cyclone or cyclone bypass.

4.1.3.6 Filter heating system: Any heating system capable of maintaining a temperature of 120 $\pm$ 14°C (248 $\pm$ 25°F) around the filter holder during sampling. Other temperatures may be appropriate for particular applications. Alternatively, the tester may opt to operate the equipment at temperatures other than that specified. A temperature gauge capable of measuring temperature to within 3°C (5.4°F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling. Heating systems other than the one shown in APTD-0581 may be used.

4.1.3.7 Organic sampling module: This unit consists of three sections, including a gas-conditioning section, a sorbent trap, and a condensate knockout trap. The gas-conditioning system shall be capable of conditioning the gas leaving the back half of the filter holder to a temperature not exceeding 20°C (68°F). The sorbent trap shall be sized to contain approximately 20 g of porous polymeric resin (Rohm and Haas XAD-2 or equivalent) and shall be jacketed to maintain the internal gas temperature at 17 $\pm$ 3°C (62.5 $\pm$ 5.4°F). The most commonly used coolant is ice water from the impinger ice-water bath, constantly circulated through the outer jacket, using rubber or plastic tubing and a peristaltic pump. The sorbent trap should be outfitted with a glass well or depression, appropriately sized to accommodate a small thermocouple in the trap for monitoring the gas entry temperature. The condensate knockout trap shall be of sufficient size to collect the condensate following gas conditioning. The organic module components shall be oriented to direct the flow of condensate formed vertically downward from the conditioning section, through the adsorbent media, and into the condensate knockout trap. The knockout trap is usually similar in appearance to an empty impinger directly underneath the sorbent module; it may be oversized but should have a shortened center stem (at a minimum, one-half the length of the normal impinger stems) to collect a large volume of condensate without bubbling and overflowing into the impinger train. All surfaces of the organic module wetted by the gas sample shall be fabricated of borosilicate glass, Teflon, or other inert materials. Commercial versions of the

complete organic module are not currently available, but may be assembled from commercially available laboratory glassware and a custom-fabricated sorbent trap. Details of two acceptable designs are shown in Figures 2 and 3 (the thermocouple well is shown in Figure 2).

4.1.3.8 Impinger train: To determine the stack-gas moisture content, four 500-mL impingers, connected in series with leak-free ground-glass joints, follow the knockout trap. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with a 1.3-cm (1/2-in.) I.D. glass tube extending about 1.3 cm (1/2 in.) from the bottom of the outer cylinder. The second impinger shall be of the Greenburg-Smith design with the standard tip. The first and second impingers shall contain known quantities of water or appropriate trapping solution. The third shall be empty or charged with a caustic solution, should the stack gas contain hydrochloric acid (HCl). The fourth shall contain a known weight of silica gel or equivalent desiccant.

4.1.3.9 Metering system: The necessary components are a vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3°C (5.4°F), dry-gas meter capable of measuring volume to within 1%, and related equipment, as shown in Figure 1. At a minimum, the pump should be capable of 4 cfm free flow, and the dry-gas meter should have a recording capacity of 0-999.9 cu ft with a resolution of 0.005 cu ft. Other metering systems capable of maintaining sampling rates within 10% of isokineticity and of determining sample volumes to within 2% may be used. The metering system must be used 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.

4.1.3.10 Barometer: Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases the barometric reading may be obtained from a nearby National Weather Service station, in which case the station value (which is the absolute barometric pressure) is requested and an adjustment for elevation differences between the weather station and sampling point is applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30-m (100 ft) elevation increase (vice versa for elevation decrease).

4.1.3.11 Gas density determination equipment: Temperature sensor and pressure gauge (as described in Sections 2.3 and 2.4 of EPA Method 2), and gas analyzer, if necessary (as described in EPA Method 3). The temperature sensor ideally should be permanently attached to the pitot tube or sampling probe in a fixed configuration such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal.

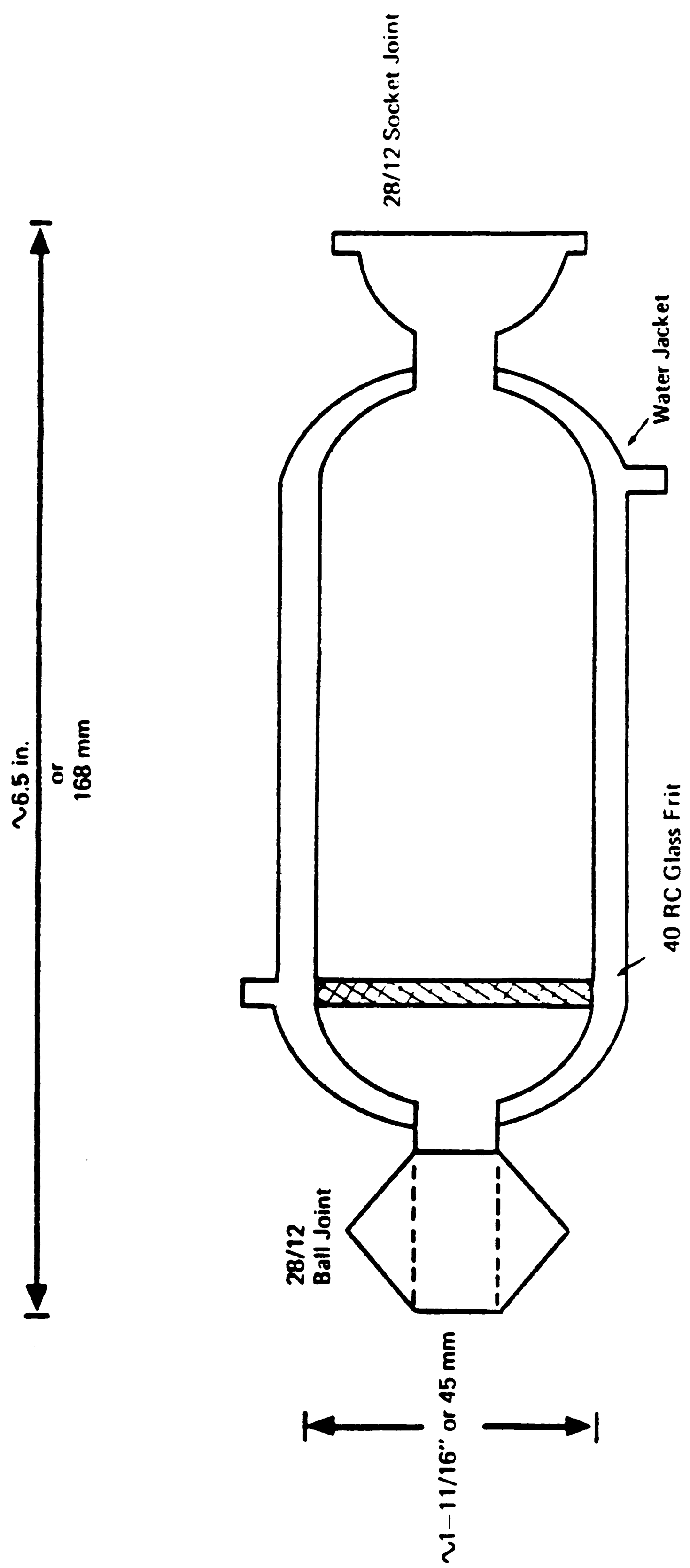

Figure 2. Adsorbent Sampling System.

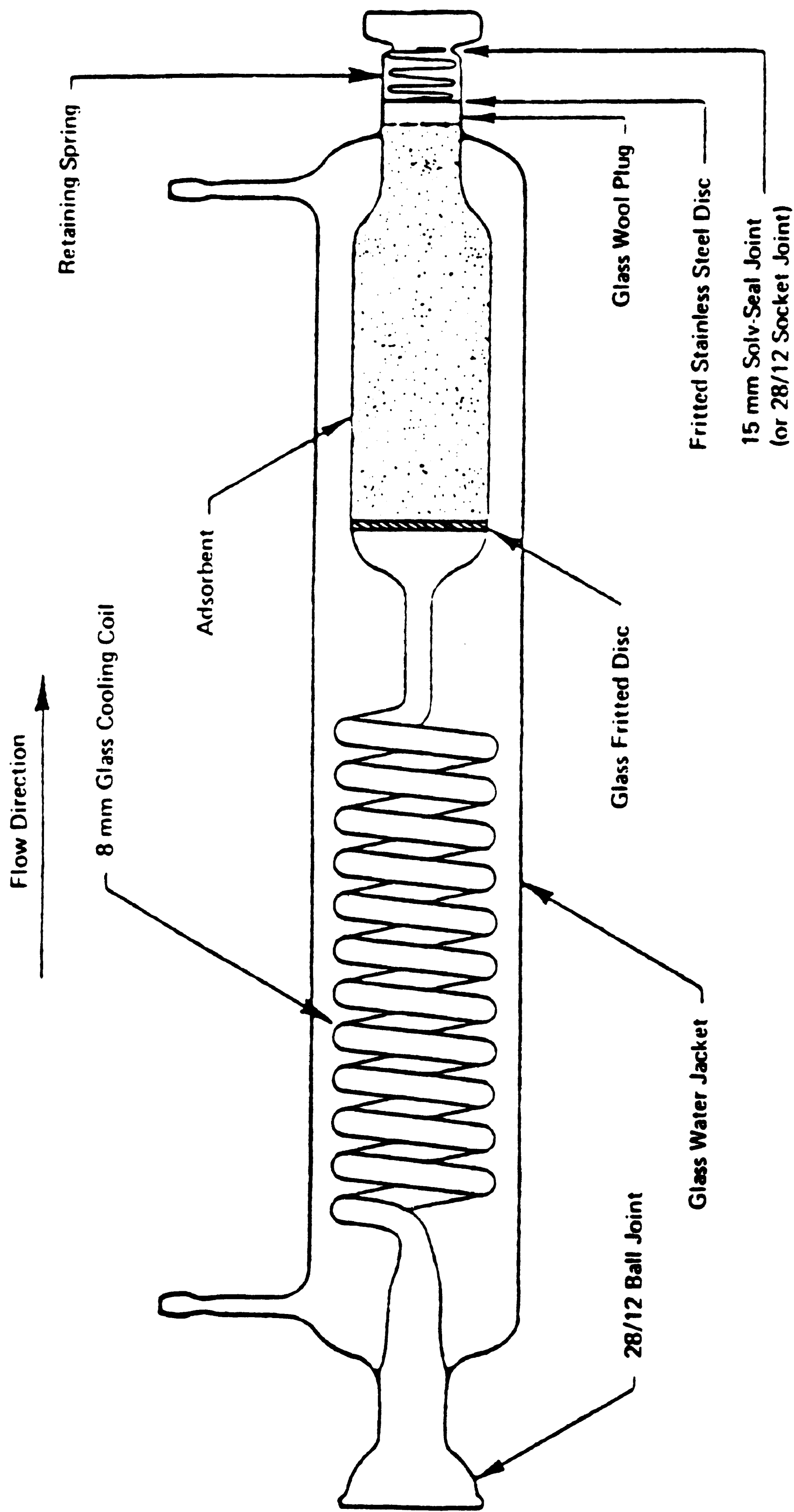

Figure 3. Adsorbent Sampling System.

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 EPA Method 2, Figure 2-7). As a second alternative, if a difference of no more than 1% in the average velocity measurement is to be introduced, the temperature gauge need not be attached to the probe or pitot tube.

4.1.3.12 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., filter and silica gel tare weights, clean XAD-2, quality assurance/quality control check results, dry-gas meter, and thermocouple calibrations, etc.). The duplicate copies should be detachable and should be stored separately in the test program archives.

4.2 Sample Recovery:

4.2.1 **Probe liner:** Probe nozzle and organic module conditioning section brushes; nylon bristle brushes with stainless steel wire handles are required. The probe brush shall have extensions of stainless steel, Teflon, or inert material at least as long as the probe. The brushes shall be properly sized and shaped to brush out the probe liner, the probe nozzle, and the organic module conditioning section.

4.2.2 **Wash bottles:** Three. Teflon or glass wash bottles are recommended; polyethylene wash bottles should not be used because organic contaminants may be extracted by exposure to organic solvents used for sample recovery.

4.2.3 **Glass sample storage containers:** Chemically resistant, borosilicate amber and clear glass bottles, 500-mL or 1,000-mL. Bottles should be tinted to prevent action of light on sample. Screw-cap liners shall be either Teflon or constructed so as to be leak-free and resistant to chemical attack by organic recovery solvents. Narrow-mouth glass bottles have been found to exhibit less tendency toward leakage.

4.2.4 **Petri dishes:** Glass, sealed around the circumference with wide (1-in.) Teflon tape, for storage and transport of filter samples.

4.2.5 **Graduated cylinder and/or balances:** To measure condensed water to the nearest 1 mL or 1 g. Graduated cylinders shall have subdivisions not >2 mL. Laboratory triple-beam balances capable of weighing to ±0.5 g or better are required.

4.2.6 **Plastic storage containers:** Screw-cap polypropylene or polyethylene containers to store silica gel.

4.2.7 **Funnel and rubber policeman:** To aid in transfer of silica gel to container (not necessary if silica gel is weighed in field).

4.2.8 **Funnels:** Glass, to aid in sample recovery.

4.3 Filters: Glass- or quartz-fiber filters, without organic binder, exhibiting at least 99.95% efficiency (<0.05% penetration) on 0.3-um dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard method D2986-71. Test data from the supplier's quality control program are sufficient for this purpose. In sources containing SO_2 or SO_3, the filter material must be of a type that is unreactive to SO_2 or SO_3. Reeve Angel 934 AH or Schleicher and Schwell #3 filters work well under these conditions.

4.4 Crushed ice: Quantities ranging from 10-50 lb may be necessary during a sampling run, depending on ambient air temperature.

4.5 Stopcock grease: Solvent-insoluble, heat-stable silicone grease. Use of silicone grease upstream of the module is not permitted, and amounts used on components located downstream of the organic module shall be minimized. Silicone grease usage is not necessary if screw-on connectors and Teflon sleeves or ground-glass joints are used.

4.6 Glass wool: Used to plug the unfritted end of the sorbent module. The glass-wool fiber should be solvent-extracted with methylene chloride in a Soxhlet extractor for 12 hr and air-dried prior to use.

5.0 REAGENTS

5.1 Adsorbent resin: Porous polymeric resin (XAD-2 or equivalent) is recommended. These resins shall be cleaned prior to their use for sample collection. Appendix A of this method should be consulted to determine appropriate precleaning procedure. For best results, resin used should not exhibit a blank of higher than 4 mg/kg of total chromatographable organics (TCO) (see Appendix B) prior to use. Once cleaned, resin should be stored in an airtight, wide-mouth amber glass container with a Teflon-lined cap or placed in one of the glass sorbent modules tightly sealed with Teflon film and elastic bands. The resin should be used within 4 wk of the preparation.

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

5.3 Impinger solutions: Distilled organic-free water (Type II) shall be used, unless sampling is intended to quantify a particular inorganic gaseous species. If sampling is intended to quantify the concentration of additional species, the impinger solution of choice shall be subject to Administrator approval. This water should be prescreened for any compounds of interest. One hundred mL will be added to the specified impinger; the third impinger in the train may be charged with a basic solution (1 N sodium hydroxide or sodium acetate) to protect the sampling pump from acidic gases. Sodium acetate should be used when large sample volumes are anticipated because sodium hydroxide will react with carbon dioxide in aqueous media to form sodium carbonate, which may possibly plug the impinger.

5.4 Sample recovery reagents:

5.4.1 **Methylene chloride:** Distilled-in-glass grade is required for sample recovery and cleanup (see Note to 5.4.2 below).

5.4.2 **Methyl alcohol:** Distilled-in-glass grade is required for sample recovery and cleanup.

NOTE: Organic solvents from metal containers may have a high residue blank and should not be used. Sometimes suppliers transfer solvents from metal to glass bottles; thus blanks shall be run prior to field use and only solvents with low blank value (<0.001%) shall be used.

5.4.3 **Water:** Water (Type II) shall be used for rinsing the organic module and condenser component.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

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

6.2 Laboratory preparation:

6.2.1 All the components shall be maintained and calibrated according to the procedure described in APTD-0576, unless otherwise specified.

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

6.2.3 Check filters visually against light for irregularities and flaws or pinhole leaks. Label the shipping containers (glass Petri dishes) and keep the filters in these containers at all times except during sampling and weighing.

6.2.4 Desiccate the filters at 20 $\pm$ 5.6°C (68 $\pm$ 10°F) and ambient pressure for at least 24 hr, and weigh at intervals of at least 6 hr to a constant weight (i.e., <0.5-mg change from previous weighing), recording results to the nearest 0.1 mg. During each weighing the filter must not be exposed for more than a 2-min period to the laboratory atmosphere and relative humidity above 50%. Alternatively (unless otherwise specified by the Administrator), the filters may be oven-dried at 105°C (220°F) for 2-3 hr, desiccated for 2 hr, and weighed.

6.3 Preliminary field determinations:

6.3.1 Select the sampling site and the minimum number of sampling points according to EPA Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and range of velocity heads using EPA Method 2. It is recommended that a leak-check of the pitot lines (see EPA Method 2, Section 3.1) be performed. Determine the stack-gas moisture content using EPA Approximation Method 4 or its alternatives to establish estimates of isokinetic sampling-rate settings. Determine the stack-gas dry molecular weight, as described in EPA Method 2, Section 3.6. If integrated EPA Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the sample run.

6.3.2 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 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 EPA Method 2).

6.3.3 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.

6.3.4 A minimum of 3 dscm (105.9 dscf) of sample volume is required for the determination of the Destruction and Removal Efficiency (DRE) of POHCs from incineration systems. Additional sample volume shall be collected as necessitated by analytical detection limit constraints. To determine the minimum sample volume required, refer to sample calculations in Section 10.0.

6.3.5 Determine the total length of sampling time needed to obtain the identified minimum volume by comparing the anticipated average sampling rate with the volume requirement. Allocate the same time to all traverse points defined by EPA Method 1. To avoid timekeeping errors, the length of time sampled at each traverse point should be an integer or an integer plus one-half min.

6.3.6 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-sample volumes. In these cases, the Administrator's approval must first be obtained.

6.4 Preparation of collection train:

6.4.1 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.

6.4.2 Fill the sorbent trap section of the organic module with approximately 20 g of clean adsorbent resin. While filling, ensure that the trap packs uniformly, to eliminate the possibility of channeling. When freshly cleaned, many adsorbent resins carry a static charge, which will cause clinging to trap walls. This may be minimized by filling the trap in the presence of an antistatic device. Commercial antistatic devices include Model-204 and Model-210 manufactured by the 3M Company, St. Paul, Minnesota.

6.4.3 If an impinger train is used to collect moisture, place 100 mL of water in each of the first two impingers, leave the third impinger empty (or charge with caustic solution, as necessary), and transfer approximately 200-300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the 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.

6.4.4 Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

6.4.5 When glass liners are used, install the selected nozzle using a Viton-A O-ring when stack temperatures are <260°C (500°F) and a woven glass-fiber gasket when temperatures are higher. See APTD-0576 (Rom, 1972) for details. Other connecting systems utilizing either 316 stainless steel or Teflon ferrules may be used. When metal liners are used, install the nozzle as above, or by a leak-free direct mechanical connection. Mark the probe with heat-resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

6.4.6 Set up the train as in Figure 1. During assembly, do not use any silicone grease on ground-glass joints that are located upstream of the organic module. A very light coating of silicone grease may be used on all ground-glass joints that are located downstream of the organic module, but it should be limited to the outer portion (see APTD-0576) of the ground-glass joints to minimize silicone-grease contamination. Subject to the approval of the Administrator, a glass cyclone may be used between the probe and the filter holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the stack. The organic module condenser must be maintained at a temperature of 17 $\pm$ 3°C. Connect all temperature sensors to an appropriate potentiometer/display unit. Check all temperature sensors at ambient temperature.

6.4.7 Place crushed ice around the impingers and the organic module condensate knockout.

6.4.8 Turn on the sorbent module and condenser coil coolant recirculating pump and begin monitoring the sorbent module gas entry temperature. Ensure proper sorbent module gas entry temperature before proceeding and again before any sampling is initiated. It is extremely important that the XAD-2 resin temperature never exceed 50°C (122°F), because thermal decomposition will occur. During testing, the XAD-2 temperature must not exceed 20°C (68°F) for efficient capture of the semivolatile species of interest.

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

6.5 Leak-check procedures

6.5.1 **Pre-test leak-check:**

6.5.1.1 Because the number of additional intercomponent connections in the Semi-VOST train (over the M5 Train) increases the possibility of leakage, a pre-test leak-check is required.

6.5.1.2 After the sampling train has been assembled, turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 381-mm Hg (15-in. Hg) vacuum.
(NOTE: A lower vacuum may be used, provided that it is not exceeded during the test.)

6.5.1.3 If an asbestos string is used, do not connect the probe to the train during the leak-check. Instead, leak-check the train by first attaching a carbon-filled leak-check impinger (shown in Figure 4) to the inlet of the filter holder (cyclone, if applicable) and then plugging the inlet and pulling a 381-mm Hg (15-in. Hg) vacuum. (Again, a lower vacuum may be used, provided that it is not exceeded during the test.) Then, connect the probe to the train and leak-check at about 25-mm Hg (1-in. Hg) vacuum; alternatively, leak-check the probe with the rest of the sampling train in one step at 381-mm Hg (15-in. Hg) vacuum. Leakage rates in excess of 4% of the average sampling rate or >0.00057 m^3/min (0.02 cfm), whichever is less, are unacceptable.

6.5.1.4 The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with 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; this will cause water to back up into the organic module. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak-check, as shown below, and start over.

CROSS SECTIONAL VIEW

Leak Testing Apparatus

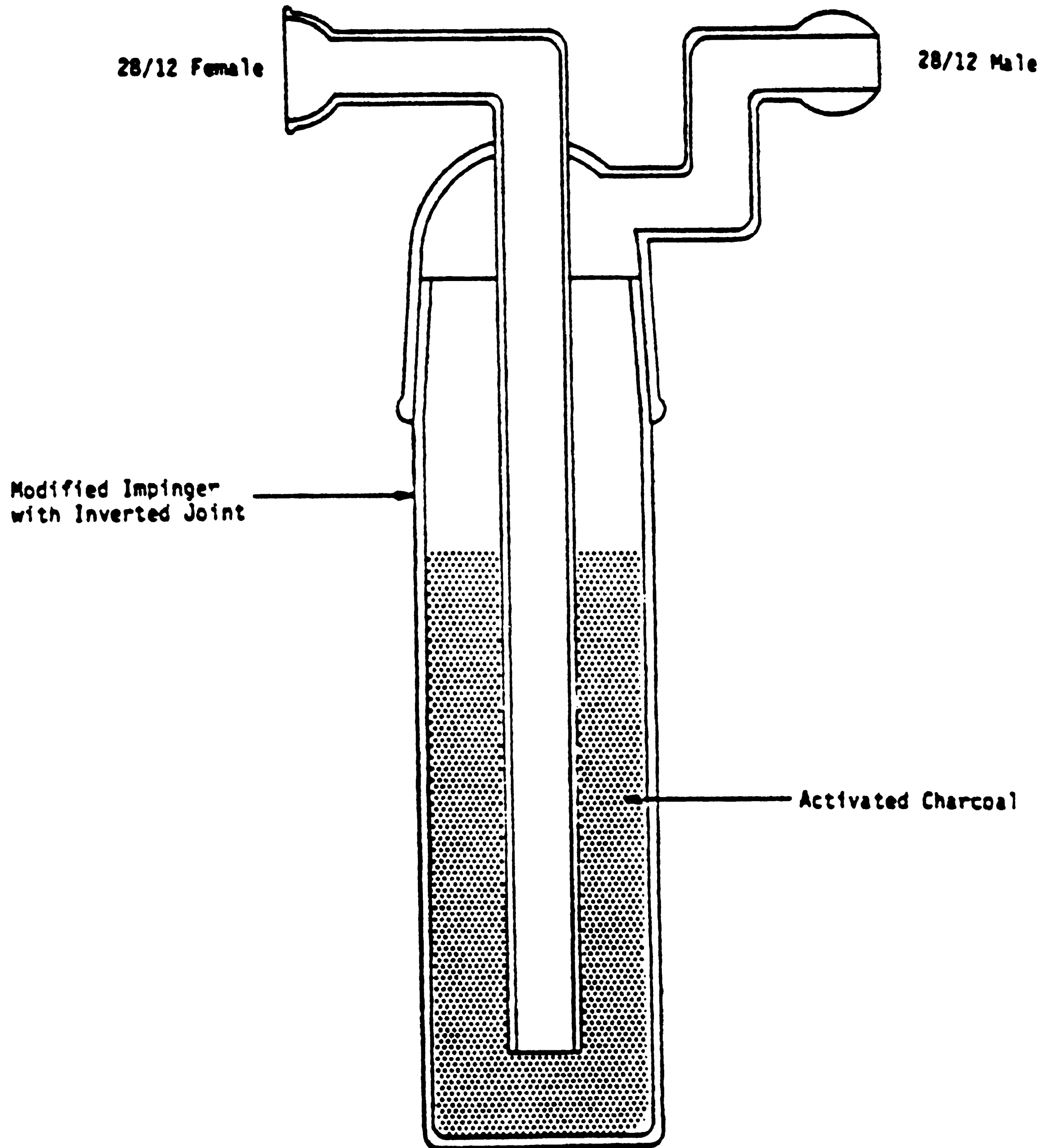

Figure 4. Leak-check Impinger

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

6.5.2 **Leak-checks during sampling run:**

6.5.2.1 If, during the sampling run, a component (e.g., filter assembly, impinger, or sorbent trap) change becomes necessary, a leak-check shall be conducted immediately after the interruption of sampling and before the change is made. The leak-check shall be done according to the procedure outlined in Paragraph 6.5.1, except that it shall be done at a vacuum greater than or equal to the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered. If a higher leakage rate is obtained, the tester shall void the sampling run. (It should be noted that any "correction" of the sample volume by calculation by calculation reduces the integrity of the pollutant concentrations data generated and must be avoided.)

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

6.5.3 **Post-test leak-check:**

6.5.3.1 A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done with the same procedures as those with the pre-test leak-check, except that it shall be conducted at a vacuum greater than or equal to the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate, correct the sample volume (as shown in the calculation section of this method), and consider the data obtained of questionable reliability, or void the sampling run.

6.6 Sampling-train operation:

6.6.1 During the sampling run, maintain an isokinetic sampling rate to within 10% of true isokinetic, unless otherwise specified by the Administrator. Maintain a temperature around the filter of 120 $\pm$ 14°C (248 $\pm$ 25°F) and a gas temperature entering the sorbent trap at a maximum of 20°C (68°F).

6.6.2 For each run, record the data required on a data sheet such as the one shown in Figure 5. 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 required by Figure 5 at least once at each sample point during each time increment and additional readings when significant changes (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.

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

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

6.6.5 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.

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

6.6.7 During the test run, make periodic adjustments to keep the temperature around the filter holder and the organic module at the proper levels; add more ice and, if necessary, salt to maintain a temperature of <20°C (68°F) at the condenser/silica gel outlet. Also, periodically check the level and zero of the manometer.

Plant ______________________

Location ______________________

Operator ______________________

Date ______________________

Run No. ______________________

Sample Box No. ______________________

Meter Box No. ______________________

Meter $H@$ ______________________

C Factor ______________________

Pitot Tube Coefficient C_p ______________________

Schematic of Stack Cross Section

Ambient Temperature ______________________

Barometric Pressure ______________________

Assumed Moisture % ______________________

Probe Length, m (ft) ______________________

Nozzle Identification No. ______________________

Average Calibrated Nozzle Diameter, cm (in) ______________________

Probe Heater Setting ______________________

Leak Rate, m^3/min, (cfm) ______________________

Probe Liner Material ______________________

Static Pressure, mm Hg (in. Hg) ______________________

Filter No. ______________________

Traverse Point Number	Sampling Time (θ) min.	Vacuum mm Hg (in. Hg)	Stack Temperature (T_s) °C(°F)	Velocity Head (ΔP_s) mm (in) H_2O	Pressure Differential Across Orifice Meter mm (H_2O) (in H_2O)	Gas Sample Volume m^3 (ft^3)	Gas Sample Temp. at Dry Gas Meter		Filter Holder Temperature °C(°F)	Temperature of Gas Entering Sorbent Trap °C(°F)	Temperature of Gas Leaving Condenser or Last Impinger
							Inlet °C(°F)	Outlet °C(°F)			
Total							Avg.	Avg.			
Average											

Figure 5. Particulate field data.

6.6.8 If the pressure drop across the filter or sorbent trap becomes too high, making isokinetic sampling difficult to maintain, the filter/sorbent trap may be replaced in the midst of a sample run. Using another complete filter holder/sorbent trap assembly is recommended, rather than attempting to change the filter and resin themselves. After a new filter/sorbent trap assembly is installed, conduct a leak-check. The total particulate weight shall include the summation of all filter assembly catches.

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

6.6.10 Note that when two or more trains are used, separate analysis of the front-half (if applicable) organic-module and impinger (if applicable) catches from each train shall be performed, unless identical nozzle sizes were used on all trains. In that case, the front-half catches from the individual trains may be combined (as may the impinger catches), and one analysis of front-half catch and one analysis of impinger catch may be performed.

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

6.6.12 Calculate percent isokineticity (see Section 10.8) to determine whether the run was valid or another test run should be made.

7.0 SAMPLE RECOVERY

7.1 <u>Preparation</u>:

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 safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over the tip to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling down because this will create a vacuum in the filter holder, drawing water from the impingers into the sorbent module.

7.1.2 Before moving the sample train to the cleanup site, remove the probe from the sample train and cap the open outlet, being careful not to lose any condensate that might be present. Cap the filter inlet.

Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the organic module and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the organic module.

7.1.3 Cap the filter-holder outlet and the inlet to the organic module. Separate the sorbent trap section of the organic module from the condensate knockout trap and the gas-conditioning section. Cap all organic module openings. Disconnect the organic-module knockout trap from the impinger train inlet and cap both of these openings. Ground-glass stoppers, Teflon caps, or caps of other inert materials may be used to seal all openings.

7.1.4 Transfer the probe, the filter, the organic-module components, and the impinger/condenser assembly to the cleanup area. This area should be clean and protected from the weather to minimize sample contamination or loss.

7.1.5 Save a portion of all washing solutions (methanol/methylene chloride, Type II water) used for cleanup as a blank. Transfer 200 mL of each solution directly from the wash bottle being used and place each in a separate, prelabeled glass sample container.

7.1.6 Inspect the train prior to and during disassembly and note any abnormal conditions.

7.2 Sample containers:

7.2.1 **Container no. 1:** Carefully remove the filter from the filter holder and place it in its identified Petri dish container. Use a pair or pairs of tweezers to handle the filter. If it is necessary to fold the filter, ensure that the particulate cake is inside the fold. Carefully transfer to the Petri dish any particulate matter or filter fibers that adhere to the filter-holder gasket, using a dry nylon bristle brush or sharp-edged blade, or both. Label the container and seal with 1-in.-wide Teflon tape around the circumference of the lid.

7.2.2 **Container no. 2:** Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components first with methanol/methylene chloride (1:1 v/v) into a glass container. Distilled water may also be used. Retain a water and solvent blank and analyze in the same manner as with the samples. Perform rinses as follows:

7.2.2.1 Carefully remove the probe nozzle and clean the inside surface by rinsing with the solvent mixture (1:1 v/v methanol/-methylene chloride) from a wash bottle and brushing with a nylon bristle brush. Brush until the rinse shows no visible particles; then make a final rinse of the inside surface with the solvent mix. Brush and rinse the inside parts of the Swagelok fitting with the solvent mix in a similar way until no visible particles remain.

7.2.2.2 Have two people rinse the probe liner with the solvent mix by tilting and rotating the probe while squirting solvent into its upper end so that all inside surfaces will be wetted with solvent. Let the solvent drain from the lower end into the sample container. A glass funnel may be used to aid in transferring liquid washes to the container.

7.2.2.3 Follow the solvent rinse with a probe brush. Hold the probe in an inclined position and squirt solvent into the upper end while pushing the probe brush through the probe with a twisting action; place a sample container underneath the lower end of the probe and catch any solvent and particulate matter that is brushed from the probe. Run the brush through the probe three times or more until no visible particulate matter is carried out with the solvent or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above-prescribed manner at least six times (metal probes have small crevices in which particulate matter can be entrapped). Rinse the brush with solvent and quantitatively collect these washings in the sample container. After the brushing, make a final solvent rinse of the probe as described above.

7.2.2.4 It is recommended that two people work together to clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination.

7.2.2.5 Clean the inside of the front half of the filter holder and cyclone/cyclone flask, if used, by rubbing the surfaces with a nylon bristle brush and rinsing with methanol/methylene chloride (1:1 v/v) mixture. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. Carefully rinse out the glass cyclone and cyclone flask (if applicable). Brush and rinse any particulate material adhering to the inner surfaces of these components into the front-half rinse sample. After all solvent washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that solvent will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the container to identify its contents.

7.2.3 **Container no. 3:** The sorbent trap section of the organic module may be used as a sample transport container, or the spent resin may be transferred to a separate glass bottle for shipment. If the sorbent trap itself is used as the transport container, both ends should be sealed with tightly fitting caps or plugs. Ground-glass stoppers or Teflon caps may be used. The sorbent trap should then be labeled, covered with aluminum foil, and packaged on ice for transport to the laboratory. If a separate bottle is used, the spent resin should be quantitatively transferred from the trap into the clean bottle. Resin that adheres to the walls of the trap should be recovered using a rubber policeman or spatula and added to this bottle.

7.2.4 **Container no. 4:** Measure the volume of condensate collected in the condensate knockout section of the organic module to within ±1 mL by using a graduated cylinder or by weighing to within ±0.5 g using a triple-beam balance. Record the volume or weight of liquid present and note any discoloration or film in the liquid catch. Transfer this liquid to a prelabeled glass sample container. Inspect the back half of the filter housing and the gas-conditioning section of the organic module. If condensate is observed, transfer it to a graduated or weighing bottle and measure the volume, as described above. Add this material to the condensate knockout-trap catch.

7.2.5 **Container no. 5:** All sampling train components located between the high-efficiency glass- or quartz-fiber filter and the first wet impinger or the final condenser system (including the heated Teflon line connecting the filter outlet to the condenser) should be thoroughly rinsed with methanol/methylene chloride (1:1 v/v) and the rinsings combined. This rinse shall be separated from the condensate. If the spent resin is transferred from the sorbent trap to a separate sample container for transport, the sorbent trap shall be thoroughly rinsed until all sample-wetted surfaces appear clean. Visible films should be removed by brushing. Whenever train components are brushed, the brush should be subsequently rinsed with solvent mixture and the rinsings added to this container.

7.2.6 **Container no. 6:** Note the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere strongly to the impinger wall. Because the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, weigh the container and its contents to 0.5 g or better.

7.3 Impinger water:

7.3.1 Make a notation of any color or film in the liquid catch. Measure the liquid in the first three impingers to within ±1 mL by using a graduated cylinder or by weighing it to within ±0.5 g by using a balance (if one is available). Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

7.3.2 Discard the liquid after measuring and recording the volume or weight, unless analysis of the impinger catch is required (see Paragraph 4.1.3.7). Amber glass containers should be used for storage of impinger catch, if required.

7.3.3 If a different type of condenser is used, measure the amount of moisture condensed either volumetrically or gravimetrically.

7.4 Sample preparation for shipment: Prior to shipment, recheck all sample containers to ensure that the caps are well secured. Seal the lids of all containers around the circumference with Teflon tape. Ship all liquid samples upright on ice and all particulate filters with the particulate catch facing upward. The particulate filters should be shipped unrefrigerated.

8.0 ANALYSIS

8.1 Sample preparation:

8.1.1 **General:** The preparation steps for all samples will result in a finite volume of concentrated solvent. The final sample volume (usually in the 1- to 10-mL range) is then subjected to analysis by GC/MS. All samples should be inspected and the appearance documented. All samples are to be spiked with surrogate standards as received from the field prior to any sample manipulations. The spike should be at a level equivalent to 10 times the MDL when the solvent is reduced in volume to the desired level (i.e., 10 mL). The spiking compounds should be the stable isotopically labeled analog of the compounds of interest or a compound that would exhibit properties similar to the compounds of interest, be easily chromatographed, and not interfere with the analysis of the compounds of interest. Suggested surrogate spiking compounds are: deuterated naphthalene, chrysene, phenol, nitrobenzene, chlorobenzene, toluene, and carbon-13-labeled pentachlorophenol.

8.1.2 **Condensate:** The "condensate" is the moisture collected in the first impinger following the XAD-2 module. Spike the condensate with the surrogate standards. The volume is measured and recorded and then transferred to a separatory funnel. The pH is to be adjusted to pH 2 with 6 N sulfuric acid, if necessary. The sample container and graduated cylinder are sequentially rinsed with three successive 10-mL aliquots of the extraction solvent and added to the separatory funnel. The ratio of solvent to aqueous sample should be maintained at 1:3. Extract the sample by vigorously shaking the separatory funnel for 5 min. After complete separation of the phases, remove the solvent and transfer to a Kuderna-Danish concentrator (K-D), filtering through a bed of precleaned, dry sodium sulfate. Repeat the extraction step two additional times. Adjust the pH to 11 with 6 N sodium hydroxide and reextract combining the acid and base extracts. Rinse the sodium sulfate into the K-D with fresh solvent and discard the desiccant. Add Teflon boiling chips and concentrate to 10 mL by reducing the volume to slightly less than 10 mL and then bringing to volume with fresh solvent. In order to achieve the necessary detection limit, the sample volume can be further reduced to 1 mL by using a micro column K-D or nitrogen blow-down. Should the sample start to exhibit precipitation, the concentration step should be stopped and the sample redissolved with fresh solvent taking the volume to some finite amount. After adding a standard (for the purpose of quantitation by GC/MS), the sample is ready for analysis, as discussed in Paragraph 8.2.

8.1.3 **Impinger:** Spike the sample with the surrogate standards; measure and record the volume and transfer to a separatory funnel. Proceed as described in Paragraph 8.1.2.

8.1.4 **XAD-2:** Spike the resin directly with the surrogate standards. Transfer the resin to the all-glass thimbles by the following procedure (care should be taken so as not to contaminate the thimble by touching it with anything other than tweezers or other solvent-rinsed mechanical holding devices). Suspend the XAD-2 module directly over the thimble. The glass frit of the module (see Figure 2) should be in the up position. The thimble is contained in a clean beaker, which will serve to catch the solvent rinses. Using a Teflon squeeze bottle, flush the XAD-2 into the thimble. Thoroughly rinse the glass module with solvent into the beaker containing the thimble. Add the XAD-2 glass-wool plug to the thimble. Cover the XAD-2 in the thimble with a precleaned glass-wool plug sufficient to prevent the resin from floating into the solvent reservoir of the extractor. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. If a question arises concerning the completeness of the extraction, a second extraction, without a spike, is advised. The thimble is placed in the extractor and the rinse solvent contained in the beaker is added to the solvent reservoir. Additional solvent is added to make the reservoir approximately two-thirds full. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle 5-6 times per hr. Extract the resin for 16 hr. Transfer the solvent and three 10-mL rinses of the reservoir to a K-D and concentrate as described in Paragraph 8.1.2.

8.1.5 **Particulate filter (and cyclone catch):** If particulate loading is to be determined, weigh the filter (and cyclone catch, if applicable). The particulate filter (and cyclone catch, if applicable) is transferred to the glass thimble and extracted simultaneously with the XAD-2 resin.

8.1.6 **Train solvent rinses:** All train rinses (i.e., probe, impinger, filter housing) using the extraction solvent and methanol are returned to the laboratory as a single sample. If the rinses are contained in more than one container, the intended spike is divided equally among the containers proportioned from a single syringe volume. Transfer the rinse to a separatory funnel and add a sufficient amount of organic-free water so that the methylene chloride becomes immiscible and its volume no longer increases with the addition of more water. The extraction and concentration steps are then performed as described in Paragraph 8.1.2.

8.2 Sample analysis:

8.2.1 The primary analytical tool for the measurement of emissions from hazardous waste incinerators is GC/MS using fused-silica capillary GC columns, as described in Method 8270 in Chapter Four of this manual. Because of the nature of GC/MS instrumentation and the cost associated

with sample analysis, prescreening of the sample extracts by gas chromatography/flame ionization detection (GC/FID) or with electron capture (GC/ECD) is encouraged. Information regarding the complexity and concentration level of a sample prior to GC/MS analysis can be of enormous help. This information can be obtained by using either capillary columns or less expensive packed columns. However, the FID screen should be performed with a column similar to that used with the GC/MS. Keep in mind that GC/FID has a slightly lower detection limit than GC/MS and, therefore, that the concentration of the sample can be adjusted either up or down prior to analysis by GC/MS.

8.2.2 The mass spectrometer will be operated in a full scan (40-450) mode for most of the analyses. The range for which data are acquired in a GC/MS run will be sufficiently broad to encompass the major ions, as listed in Chapter Four, Method 8270, for each of the designated POHCs in an incinerator effluent analysis.

8.2.3 For most purposes, electron ionization (EI) spectra will be collected because a majority of the POHCs give reasonable EI spectra. Also, EI spectra are compatible with the NBS Library of Mass Spectra and other mass spectral references, which aid in the identification process for other components in the incinerator process streams.

8.2.4 To clarify some identifications, chemical ionization (CI) spectra using either positive ions or negative ions will be used to elucidate molecular-weight information and simplify the fragmentation patterns of some compounds. In no case, however, should CI spectra alone be used for compound identification. Refer to Chapter Four, Method 8270, for complete descriptions of GC conditions, MS conditions, and quantitative and quantitative identification.

9.0 CALIBRATION

9.1 Probe nozzle: Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make measurements at three separate places across the diameter and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

9.2 Pitot tube: The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Section 4 of EPA Method 2, or assigned a nominal coefficient of 0.84 if it is not visibly nicked, dented, or corroded and if it meets design and intercomponent spacing specifications.

9.3 Metering system:

9.3.1 Before its initial use in the field, the metering system shall be calibrated according to the procedure outlined in APTD-0576. Instead of physically adjusting the dry-gas meter dial readings to correspond to the wet-test meter readings, calibration factors may be used to correct the gas meter dial readings mathematically to the proper values. Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: Make a 10-min calibration run at 0.00057 m^3/min (0.02 cfm); at the end of the run, take the difference of the measured wet-test and dry-gas meter volumes and divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.02 cfm).

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

9.3.3 **Leak-check of metering system:** That 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. The following procedure is suggested (see Figure 6): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13-18 cm (5-7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for 1 min. A loss of pressure on the manometer indicates a leak in the meter box. Leaks, if present, must be corrected.

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

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

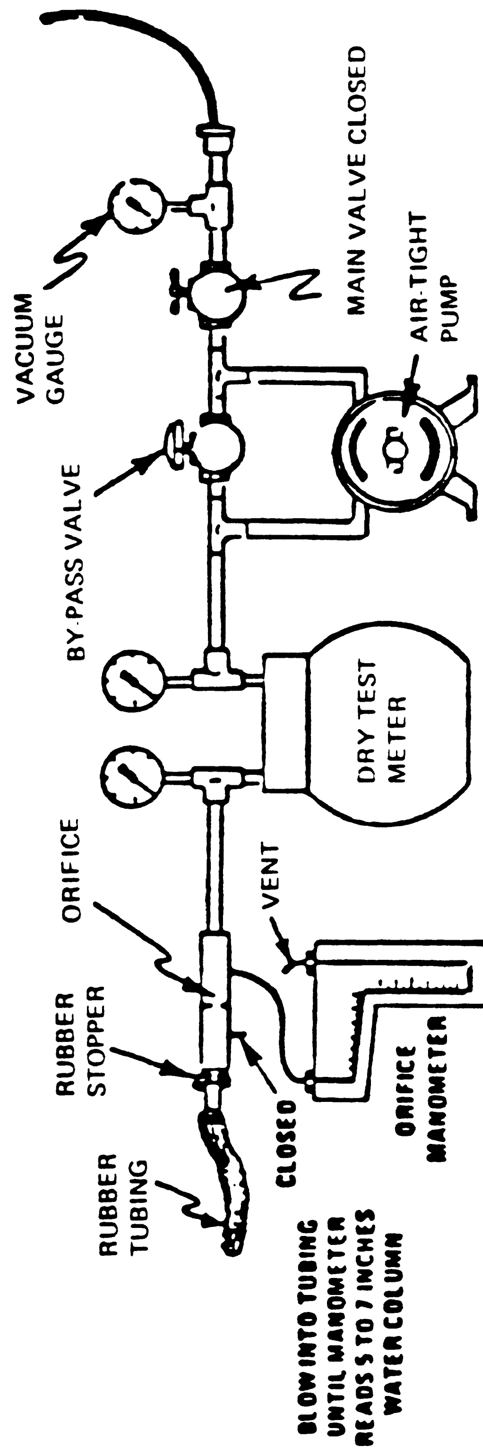

Figure 6. Leak-check of meter box.

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

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

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

9.6 Barometer: Adjust the barometer initially and before each test series to agree to within ±25 mm Hg (0.1 in. Hg) of the mercury barometer or the corrected barometric pressure value reported by a nearby National Weather Service Station (same altitude above sea level).

9.7 Triple-beam balance: Calibrate the triple-beam 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.

10.0 CALCULATIONS

10.1 Carry out calculations. Round off figures after the final calculation to the correct number of significant figures.

10.2 Nomenclature:

A_n = Cross-sectional area of nozzle, m^2 (ft^2).

B_{ws} = Water vapor in the gas stream, proportion by volume.

C_d = Type S pitot tube coefficient (nominally 0.84 ± 0.02), dimensionless.

I = Percent of isokinetic sampling.

L_a = Maximum acceptable leakage rate for a leak-check, either pre-test or following a component change; equal to 0.00057 m^3/min (0.02 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_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_s = Absolute stack-gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 mm Hg-m^3/K-g-mole (21.85 in. Hg-ft^3/°R-lb-mole).

T_m = Absolute average dry-gas meter temperature (see Figure 6), K (°R).

T_s = Absolute average stack-gas temperature (see Figure 6), K (°R).

T_{std} = Standard absolute temperature, 293K (528°R).

V_{lc} = Total volume of liquid collected in the organic module condensate knockout trap, 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).

W_a = Weight of residue in acetone wash, mg.

γ = Dry-gas-meter calibration factor, dimensionless.

ΔH = Average pressure differential across the orifice meter (see Figure 2), 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.

10.3 Average dry-gas-meter temperature and average orifice pressure drop: See data sheet (Figure 5, above).

10.4 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:

$$V_{m(std)} = V_m Y \frac{T_{std}}{T_m} \frac{P_{bar} + \Delta H/13.6}{P_{std}} = K_1 V_m Y \frac{P_{bar} + \Delta H/13.6}{T_m} \quad (1)$$

where:

K_1 = 0.3858 K/mm Hg for metric units, or
K_1 = 17.64°R/in. Hg for English units.

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

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

$$V_m - (L_p - L_a)$$

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

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

and substitute only for those leakage rates (L_1 or L_p) that exceed L_a.

10.5 Volume of water vapor:

$$V_{w(std)} = V_{1c} \frac{P_w}{M_w} \frac{RT_{std}}{P_{std}} = K_2 V_{1c} \qquad (2)$$

where:

K_2 = 0.001333 m^3/mL for metric units, or
K_2 = 0.04707 ft^3/mL for English units.

10.6 Moisture content:

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}} \qquad (3)$$

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 3) and a second from the assumption of saturated conditions. The lower of the two values of B_w 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 Method 4. For the purposes of this method, the average stack-gas temperature from Figure 6 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is $\pm$1°C (2°F).

10.7 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

10.8 Isokinetic variation:

10.8.1 **Calculation from raw data:**

$$I = \frac{100\ T_s[K_3 F_{lc} + (V_m/T_m)\ (P_{bar} + \Delta H/13.6)]}{60\theta V_s P_s A_n} \quad (4)$$

where:

K_3 = 0.003454 mm Hg-m^3/mL-K for metric units, or
K_3 = 0.002669 in. Hg-ft^3/mL-°R for English units.

10.8.2 **Calculation for intermediate values:**

$$I = \frac{T_s V_{m(std)} P_{std} 100}{T_{std} V_s \theta A_n P_s 60(1-B_{ws})} \quad (5)$$

$$= K_4 \frac{T_s V_{m(std)}}{P_s V_s A_n \theta(1-B_{ws})}$$

where:

K_4 = 4.320 for metric units, or
K_4 = 0.09450 for English units.

10.8.3 **Acceptable results:** If 90% $\leq$ I $\leq$ 110%, the results are acceptable. If the results are low in comparison with the standard and I is beyond the acceptable range, or if I is less than 90%, the Administrator may opt to accept the results.

10.9 To determine the minimum sample volume that shall be collected, the following sequence of calculations shall be used.

10.9.1 From prior analysis of the waste feed, the concentration of POHCs introduced into the combustion system can be calculated. The degree of destruction and removal efficiency that is required is used to determine the maximum amount of POHC allowed to be present in the effluent. This may be expressed as:

$$\frac{(WF)\ (POHC_i\ conc)}{100}\ \frac{(100\text{-}\%DRE)}{100} = \text{Max } POHC_i \text{ Mass} \quad (6)$$

where:

WF = mass flow rate of waste feed per hr, g/hr (lb/hr).

$POHC_i$ = concentration of Principal Organic Hazardous Compound (wt %) introduced into the combustion process.

DRE = percent Destruction and Removal Efficiency required.

Max POHC = mass flow rate (g/hr [lb/hr]) of POHC emitted from the combustion source.

10.9.2 The average discharge concentration of the POHC in the effluent gas is determined by comparing the Max POHC with the volumetric flow rate being exhausted from the source. Volumetric flow rate data are available as a result of preliminary Method 1-4 determinations:

$$\frac{\text{Max POHC}_i \text{ Mass}}{DV_{eff(std)}} = \text{Max POHC}_i \text{ conc} \qquad (7)$$

where:

$DV_{eff(std)}$ = volumetric flow rate of exhaust gas, dscm (dscf).

$POHC_i$ conc = anticipated concentration of the POHC in the exhaust gas stream, g/dscm (lb/dscf).

10.9.3 In making this calculation, it is recommended that a safety margin of at least ten be included:

$$\frac{LDL_{POHC} \times 10}{POHC_i \text{ conc}} = V_{TBC} \qquad (8)$$

where:

LDL_{POHC} = detectable amount of POHC in entire sampling train.

NOTE: The whole extract from an XAD-2 cartridge is seldom if ever, injected at once. Therefore, if aliquoting factors are involved, the LDL_{POHC} is not the same as the analytical (or column) detection limit.

V_{TBC} = minimum dry standard volume to be collected at dry-gas meter.

10.10 Concentration of any given POHC in the gaseous emissions of a combustion process:

1) Multiply the concentration of the POHC as determined in Method 8270 by the final concentration volume, typically 10 mL.

$$C_{POHC} \text{ (ug/mL)} \times \text{sample volume (mL)} = \text{amount (ug) of POHC in sample} \qquad (9)$$

where:

C_{POHC} = concentration of POHC as analyzed by Method 8270.

2) Sum the amount of POHC found in all samples associated with a single train.

Total (ug) = XAD-2 (ug) + condensate (ug) + rinses (ug) + impinger (ug) (10)

3) Divide the total ug found by the volume of stack gas sampled (m^3).

(Total ug)/(train sample volume) = concentration of POHC (ug/m^3) (11)

11.0 QUALITY CONTROL

11.1 Sampling: See EPA Manual 600/4-77-027b for Method 5 quality control.

11.2 Analysis: The quality assurance program required for this study includes the analysis of field and method blanks, procedure validations, incorporation of stable labeled surrogate compounds, quantitation versus stable labeled internal standards, capillary column performance checks, and external performance tests. The surrogate spiking compounds selected for a particular analysis are used as primary indicators of the quality of the analytical data for a wide range of compounds and a variety of sample matrices. The assessment of combustion data, positive identification, and quantitation of the selected compounds are dependent on the integrity of the samples received and the precision and accuracy of the analytical methods employed. The quality assurance procedures for this method are designed to monitor the performance of the analytical method and to provide the required information to take corrective action if problems are observed in laboratory operations or in field sampling activities.

11.2.1 **Field Blanks:** Field blanks must be submitted with the samples collected at each sampling site. The field blanks include the sample bottles containing aliquots of sample recovery solvents, unused filters, and resin cartridges. At a minimum, one complete sampling train will be assembled in the field staging area, taken to the sampling area, and leak-checked at the beginning and end of the testing (or for the same total number of times as the actual test train). The filter housing and probe of the blank train will be heated during the sample test. The train will be recovered as if it were an actual test sample. No gaseous sample will be passed through the sampling train.

11.2.2 **Method blanks:** A method blank must be prepared for each set of analytical operations, to evaluate contamination and artifacts that can be derived from glassware, reagents, and sample handling in the laboratory.

11.2.3 Refer to Method 8270 for additional quality control considerations.

12.0 METHOD PERFORMANCE

12.1 Method performance evaluation: Evaluation of analytical procedures for a selected series of compounds must include the sample-preparation procedures and each associated analytical determination. The analytical procedures should be challenged by the test compounds spiked at appropriate levels and carried through the procedures.

12.2 Method detection limit: The overall method detection limits (lower and upper) must be determined on a compound-by-compound basis because different compounds may exhibit different collection, retention, and extraction efficiencies as well as instrumental minimum detection limit (MDL). The method detection limit must be quoted relative to a given sample volume. The upper limits for the method must be determined relative to compound retention volumes (breakthrough).

12.3 Method precision and bias: The overall method precision and bias must be determined on a compound-by-compound basis at a given concentration level. The method precision value would include a combined variability due to sampling, sample preparation, and instrumental analysis. The method bias would be dependent upon the collection, retention, and extraction efficiency of the train components. From evaluation studies to date using a dynamic spiking system, method biases of -13% and -16% have been determined for toluene and 1,1,2,2-tetrachloroethane, respectively. A precision of 19.9% was calculated from a field test data set representing seven degrees of freedom which resulted from a series of paired, unspiked Semivolatile Organic Sampling trains (Semi-VOST) sampling emissions from a hazardous waste incinerator.

13.0 REFERENCES

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METHOD 0010, APPENDIX A

PREPARATION OF XAD-2 SORBENT RESIN

1.0 SCOPE AND APPLICATION

1.1 XAD-2 resin as supplied by the manufacturer is impregnated with a bicarbonate solution to inhibit microbial growth during storage. Both the salt solution and any residual extractable monomer and polymer species must be removed before use. The resin is prepared by a series of water and organic extractions, followed by careful drying.

2.0 EXTRACTION

2.1 Method 1: The procedure may be carried out in a giant Soxhlet extractor. An all-glass thimble containing an extra-coarse frit is used for extraction of XAD-2. The frit is recessed 10-15 mm above a crenellated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass-wool plug and stainless steel screen because it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse: Place resin in a beaker, rinse once with Type II water, and discard. Fill with water a second time, let stand overnight, and discard.
Water	Extract with H_2O for 8 hr.
Methyl alcohol	Extract for 22 hr.
Methylene chloride	Extract for 22 hr.
Methylene chloride (fresh)	Extract for 22 hr.

2.2 Method 2:

2.2.1 As an alternative to Soxhlet extraction, a continuous extractor has been fabricated for the extraction sequence. This extractor has been found to be acceptable. The particular canister used for the apparatus shown in Figure A-1 contains about 500 g of finished XAD-2. Any size may be constructed; the choice is dependent on the needs of the sampling programs. The XAD-2 is held under light spring tension between a pair of coarse and fine screens. Spacers under the bottom screen allow for even distribution of clean solvent. The three-necked flask should be of sufficient size (3-liter in this case) to hold solvent

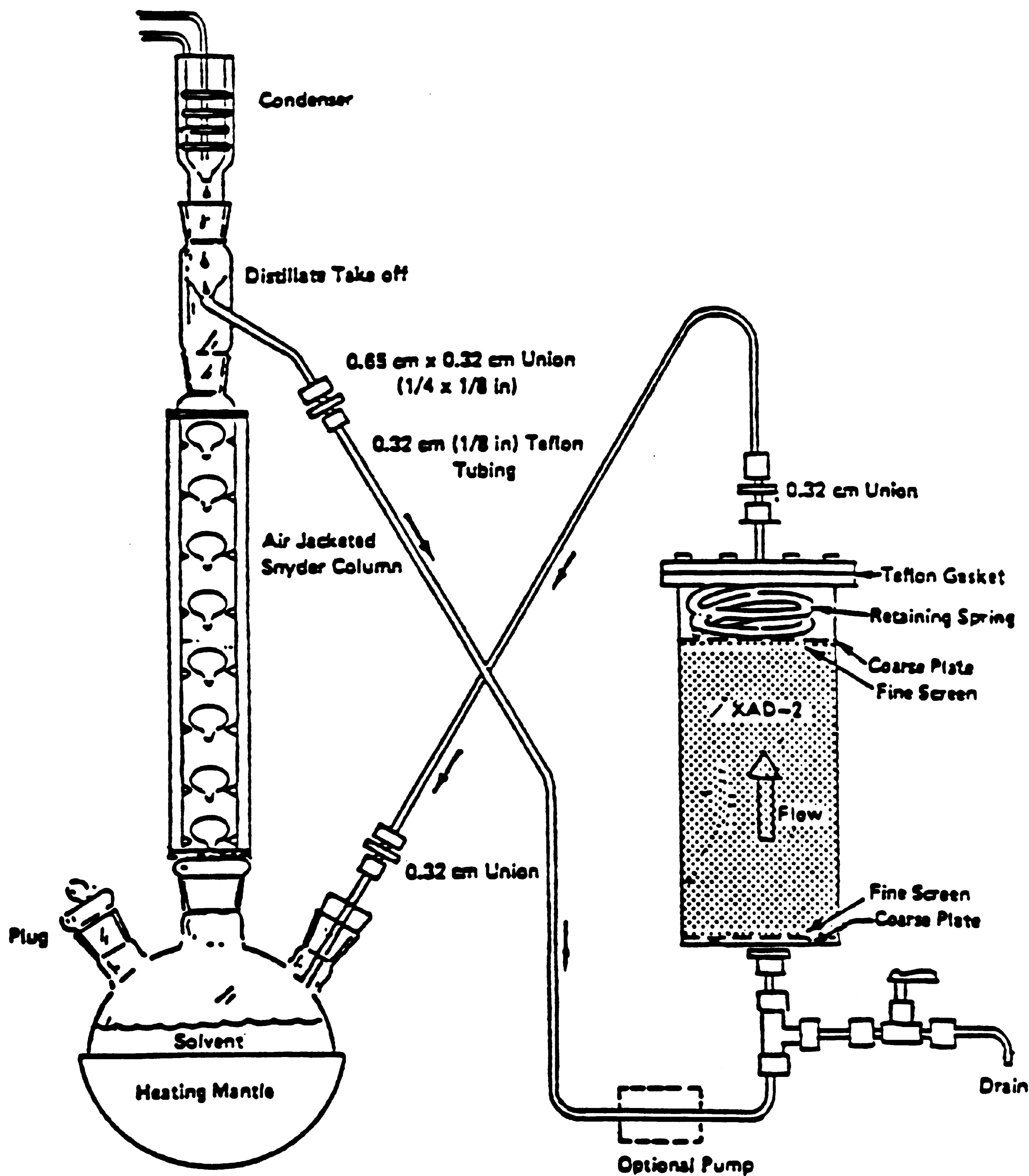


Figure A-1. XAD-2 cleanup extraction apparatus.

equal to twice the dead volume of the XAD-2 canister. Solvent is refluxed through the Snyder column, and the distillate is continuously cycled up through the XAD-2 for extraction and returned to the flask. The flow is maintained upward through the XAD-2 to allow maximum solvent contact and prevent channeling. A valve at the bottom of the canister allows removal of solvent from the canister between changes.

2.2.2 Experience has shown that it is very difficult to cycle sufficient water in this mode. Therefore the aqueous rinse is accomplished by simply flushing the canister with about 20 liters of distilled water. A small pump may be useful for pumping the water through the canister. The water extraction should be carried out at the rate of about 20-40 mL/min.

2.2.3 After draining the water, subsequent methyl alcohol and methylene chloride extractions are carried out using the refluxing apparatus. An overnight or 10- to 20-hr period is normally sufficient for each extraction.

2.2.4 All materials of construction are glass, Teflon, or stainless steel. Pumps, if used, should not contain extractable materials. Pumps are not used with methanol and methylene chloride.

3.0 DRYING

3.1 After evaluation of several methods of removing residual solvent, a fluidized-bed technique has proved to be the fastest and most reliable drying method.

3.2 A simple column with suitable retainers, as shown in Figure A-2, will serve as a satisfactory column. A 10.2-cm (4-in.) Pyrex pipe 0.6 m (2 ft) long will hold all of the XAD-2 from the extractor shown in Figure A-1 or the Soxhlet extractor, with sufficient space for fluidizing the bed while generating a minimum resin load at the exit of the column.

3.3 Method 1: The gas used to remove the solvent is the key to preserving the cleanliness of the XAD-2. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has routinely proved to be a reliable source of large volumes of gas free from organic contaminants. The liquid nitrogen cylinder is connected to the column by a length of precleaned 0.95-cm (3/8-in.) copper tubing, coiled to pass through a heat source. As nitrogen is bled from the cylinder, it is vaporized in the heat source and passes through the column. A convenient heat source is a water bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40°C. Experience has shown that about 500 g of XAD-2 may be dried overnight by consuming a full 160-liter cylinder of liquid nitrogen.

3.4 Method 2: As a second choice, high-purity tank nitrogen may be used to dry the XAD-2. The high-purity nitrogen must first be passed through a bed

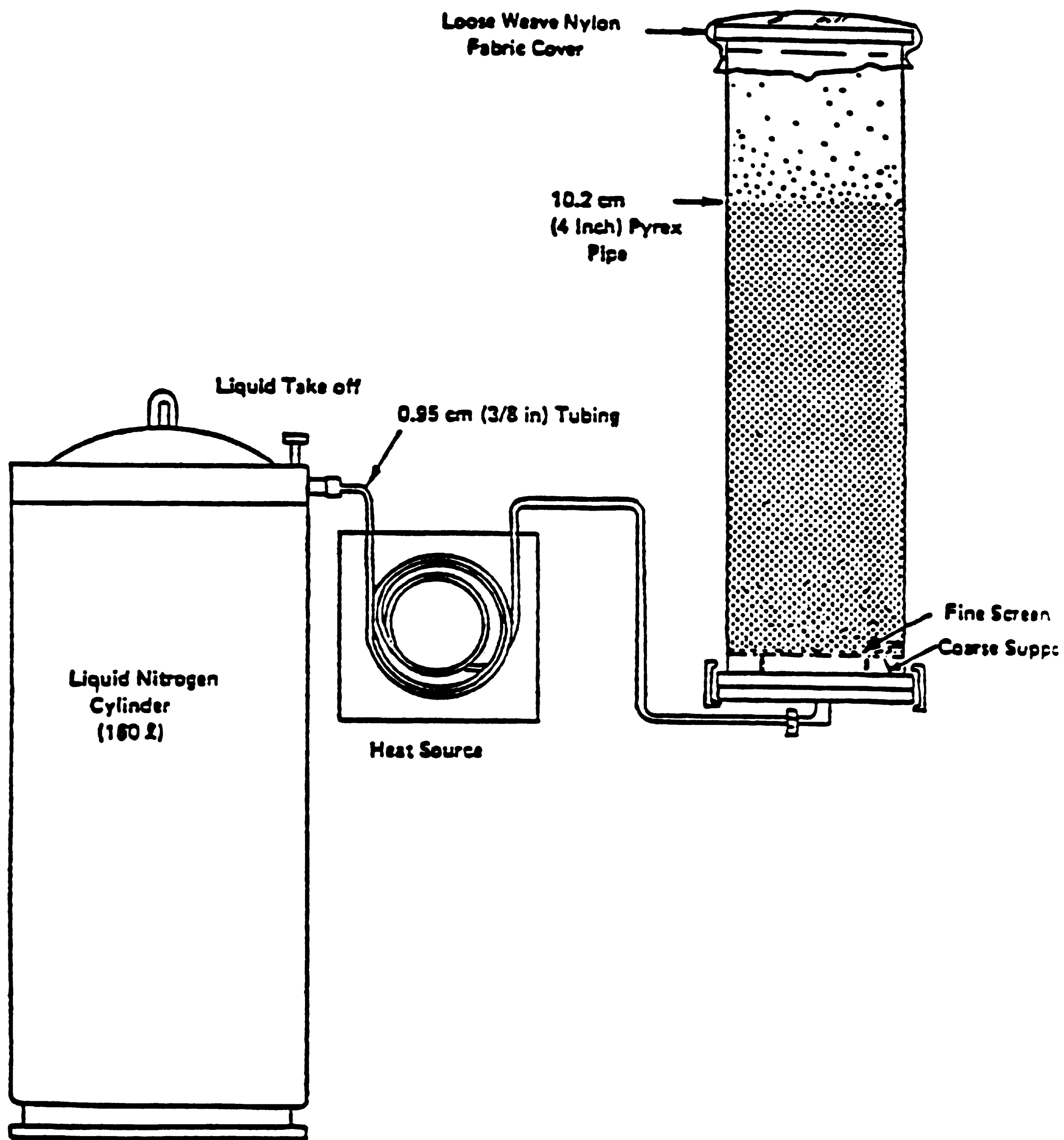


Figure A-2. XAD-2 fluidized-bed drying apparatus.

of activated charcoal approximately 150 mL in volume. With either type of drying method, the rate of flow should gently agitate the bed. Excessive fluidization may cause the particles to break up.

4.0 QUALITY CONTROL PROCEDURES

4.1 For both Methods 1 and 2, the quality control results must be reported for the batch. The batch must be reextracted if the residual extractable organics are >20 ug/mL by TCO analysis or the gravimetric residue is >0.5 mg/20 g XAD-2 extracted. (See also section 5.1, Method 0010.)

4.2 Four control procedures are used with the final XAD-2 to check for (1) residual methylene chloride, (2) extractable organics (TCO), (3) specific compounds of interest as determined by GC/MS, as described in Section 4.5 below, and (4) residue (GRAV).

4.3 Procedure for residual methylene chloride:

4.3.1 **Description:** A 1±0.1-g sample of dried resin is weighed into a small vial, 3 mL of toluene are added, and the vial is capped and well shaken. Five uL of toluene (now containing extracted methylene chloride) are injected into a gas chromatograph, and the resulting integrated area is compared with a reference standard. The reference solution consists of 2.5 uL of methylene chloride in 100 mL of toluene, simulating 100 ug of residual methylene chloride on the resin. The acceptable maximum content is 1,000 ug/g resin.

4.3.2 **Experimental:** The gas chromatograph conditions are as follows:

6-ft x 1/8-in. stainless steel column containing 10% OV-101 on 100/120 Supelcoport;

Helium carrier at 30 mL/min;

FID operated on 4 x 10^{-11} A/mV;

Injection port temperature: 250°C;

Detector temperature: 305°C;

Program: 30°C(4 min) 40°C/min 250°C (hold); and

Program terminated at 1,000 sec.

4.4 Procedure for residual extractable organics:

4.4.1 **Description:** A 20±0.1-g sample of cleaned, dried resin is weighed into a precleaned alundum or cellulose thimble which is plugged with cleaned glass wool. (Note that 20 g of resin will fill a thimble, and the

resin will float out unless well plugged.) The thimble containing the resin is extracted for 24 hr with 200-mL of pesticide- grade methylene chloride (Burdick and Jackson pesticide-grade or equivalent purity). The 200-mL extract is reduced in volume to 10-mL using a Kuderna-Danish concentrator and/or a nitrogen evaporation stream. Five uL of that solution are analyzed by gas chromatography using the TCO analysis procedure. The concentrated solution should not contain >20 ug/mL of TCO extracted from the XAD-2. This is equivalent to 10 ug/g of TCO in the XAD-2 and would correspond to 1.3 mg of TCO in the extract of the 130-g XAD-2 module. Care should be taken to correct the TCO data for a solvent blank prepared (200 mL reduced to 10 mL) in a similar manner.

4.4.2 **Experimental:** Use the TCO analysis conditions described in the revised Level 1 manual (EPA 600/7-78-201).

4.5 GC/MS Screen: The extract, as prepared in paragraph 4.4.1, is subjected to GC/MS analysis for each of the individual compounds of interest. The GC/MS procedure is described in Chapter Four, Method 8270. The extract is screened at the MDL of each compound. The presence of any compound at a concentration >25 ug/mL in the concentrated extract will require the XAD-2 to be recleaned by repeating the methylene chloride step.

4.6 Methodology for residual gravimetric determination: After the TCO value and GC/MS data are obtained for the resin batch by the above procedures, dry the remainder of the extract in a tared vessel. There must be <0.5 mg residue registered or the batch of resin will have to be extracted with fresh methylene chloride again until it meets this criterion. This level corresponds to 25 ug/g in the XAD-2, or about 3.25 mg in a resin charge of 130 g.

TOTAL CHROMATOGRAPHABLE ORGANIC MATERIAL ANALYSIS

1.0 SCOPE AND APPLICATION

1.1 In this procedure, gas chromatography is used to determine the quantity of lower boiling hydrocarbons (boiling points between 90° and 300°C) in the concentrates of all organic solvent rinses, XAD-2 resin and LC fractions - when Method 1 is used (see References, Method 0010) - encountered in Level 1 environmental sample analyses. Data obtained using this procedure serve a twofold purpose. First, the total quantity of the lower boiling hydrocarbons in the sample is determined. Then whenever the hydrocarbon concentrations in the original concentrates exceed 75 ug/m^3, the chromatography results are reexamined to determine the amounts of individual species.

The extent of compound identification is limited to representing all materials as normal alkanes based upon comparison of boiling points. Thus the method is not qualitative. In a similar manner, the analysis is semiquantitative; calibrations are prepared using only one hydrocarbon. They are replicated but samples routinely are not.

1.2 Application: This procedure applies solely to the Level 1 C7-C16 gas chromatographic analysis of concentrates of organic extracts, neat liquids, and of LC fractions. Throughout the procedure, it is assumed the analyst has been given a properly prepared sample.

1.3 Sensitivity: The sensitivity of this procedure, defined as the slope of a plot of response versus concentration, is dependent on the instrument and must be verified regularly. TRW experience indicates the nominal range is of the order of 77 uV·V·sec·uL/ng of n-heptane and 79 uV·sec·ul/ng of n-hexadecane. The instrument is capable of perhaps one hundredfold greater sensitivity. The level specified here is sufficient for Level 1 analysis.

1.4 Detection limit: The detection limit of this procedure as written is 1.3 ng/uL for a 1 uL injection of n-decane. This limit is arbitrarily based on defining the minimum detectable response as 100 uv·sec. This is an easier operational definition than defining the minimum detection limit to be that amount of material which yields a signal twice the noise level.

1.5 Range: The range of the procedure will be concentrations of 1.3 ng/uL and greater.

1.6 Limitations

1.6.1 **Reporting limitations:** It should be noted that a typical environmental sample will contain compounds which: (a) will not elute in the specified boiling ranges and thus will not be reported, and/or (b)

will not elute from the column at all and thus will not be reported. Consequently, the organic content of the sample as reported is a lower bound and should be regarded as such.

1.6.2 **Calibration limitations:** Quantitation is based on calibration with n-decane. Data should therefore be reported as, e.g., mg C8/m^3 as n-decane. Since response varies linearly with carbon number (over a wide range the assumption may involve a 20% error), it is clear that heptane (C7) detected in a sample and quantitated as decane will be overestimated. Likewise, hexadecane (C16) quantitated as decane will be underestimated. From previous data, it is estimated the error involved is on the order of 6-7%.

1.6.3 **Detection limitations:** The sensitivity of the flame ionization detector varies from compound to compound. However, n-alkanes have a greater response than other classes. Consequently, using an n-alkane as a calibrant and assuming equal responses of all other compounds tends to give low reported values.

2.0 SUMMARY OF METHOD

2.1 A mL aliquot of all 10-mL concentrates is disbursed for GC-TCO analysis. With boiling point-retention time and response-amount calibration curves, the data (peak retention times and peak areas) are interpreted by first summing peak areas in the ranges obtained from the boiling point-retention time calibration. Then, with the response-amount calibration curve, the area sums are converted to amounts of material in the reported boiling point ranges.

2.2 After the instrument is set up, the boiling point-retention time calibration is effected by injecting a mixture of n-C7 through n-C16 hydrocarbons and operating the standard temperature program. Response-quantity calibrations are accomplished by injecting n-decane in n-pentane standards and performing the standard temperature program.

2.3 Definitions

2.3.1 **GC:** Gas chromatography or gas chromatograph.

2.3.2 **C7-C16 n-alkanes:** Heptane through hexadecane.

2.3.3 **GCA temperature program:** 4 min isothermal at 60°C, 10°C/min from 60° to 220°C.

2.3.4 **TRW temperature program:** 5 min isothermal at room temperature, then program from 30°C to 250°C at 15°C/min.

3.0 INTERFERENCES

Not applicable.

4.0 APPARATUS AND MATERIALS

4.1 Gas chromatograph: This procedure is intended for use on a Varian 1860 gas chromatograph, equipped with dual flame ionization detectors and a linear temperature programmer. Any equivalent instrument can be used provided that electrometer settings, etc., be changed appropriately.

4.2 Gases:

4.2.1 **Helium:** Minimum quality is reactor grade. A 4A or 13X molecular sieve drying tube is required. A filter must be placed between the trap and the instrument. The trap should be recharged after every third tank of helium.

4.2.2 **Air:** Zero grade is satisfactory.

4.2.3 **Hydrogen:** Zero grade.

4.3 Syringe: Syringes are Hamilton 701N, 10 uL, or equivalent.

4.4 Septa: Septa will be of such quality as to produce very low bleed during the temperature program. An appropriate septum is Supelco Microsep 138, which is Teflon-backed. If septum bleed cannot be reduced to a negligible level, it will be necessary to install septum swingers on the instrument.

4.5 Recorder: The recorder of this procedure must be capable of not less than 1 mV full-scale display, a 1-sec time constant and 0.5 in. per min chart rate.

4.6 Integrator: An integrator is required. Peak area measurement by hand is satisfactory but too time-consuming. If manual integration is required, the method of "height times width at half height" is used.

4.7 Columns:

4.7.1 **Preferred column:** 6 ft x 1/8 in. O.D. stainless steel column of 10% OV-101 on 100/120 mesh Supelcoport.

4.7.2 **Alternate column:** 6 ft x 1/8 in. O.D. stainless steel column of 10% OV-1 (or other silicon phase) on 100/120 mesh Supelcoport.

4.8 Syringe cleaner: Hamilton syringe cleaner or equivalent connected to a suitable vacuum source.

5.0 REAGENTS

5.1 Pentane: "Distilled-in-Glass" (reg. trademark) or "Nanograde" (reg. trademark) for standards and for syringe cleaning.

5.2 Methylene chloride: "Distilled-in-Glass" (reg. trademark) or "Nanograde" (reg. trademark) for syringe cleaning.

6.0 SAMPLING HANDLING AND PRESERVATION

6.1 The extracts are concentrated in a Kuderna-Danish evaporator to a volume less than 10 mL. The concentrate is then quantitatively transferred to a 10-mL volumetric flask and diluted to volume. A 1-mL aliquot is taken for both this analysis and possible subsequent GC/MS analysis and set aside in the sample bank. For each GC-TCO analysis, obtain the sample sufficiently in advance to allow it to warm to room temperature. For example, after one analysis is started, return that sample to the sample bank and take the next sample.

7.0 PROCEDURES

7.1 Setup and checkout: Each day, the operator will verify the following:

7.1.1 That supplies of carrier gas, air and hydrogen are sufficient, i.e., that each tank contains > 100 psig.

7.1.2 That, after replacement of any gas cylinder, all connections leading to the chromatograph have been leak-checked.

7.1.3 That the carrier gas flow rate is 30 $\pm$ 2 mL/min, the hydrogen flow rate is 30 $\pm$ 2 mL/min, and the air flow rate is 300 $\pm$ 20 mL/min.

7.1.4 That the electrometer is functioning properly.

7.1.5 That the recorder and integrator are functioning properly.

7.1.6 That the septa have been leak-checked (leak-checking is effected by placing the soap bubble flow meter inlet tube over the injection port adaptors), and that no septum will be used for more than 20 injections.

7.1.7 That the list of samples to be run is ready.

7.2 Retention time calibration:

7.2.1 To obtain the temperature ranges for reporting the results of the analyses, the chromatograph is given a normal boiling point-retention time calibration. The n-alkanes, their boiling points, and data reporting ranges are given in the table below:

	NBP, °C	Reporting Range, °C	Report As
n-heptane	98	90-110	C7
n-octane	126	110-140	C8
n-nonane	151	140-160	C9
n-decane	174	160-180	C10
n-undecane	194	180-200	C11
n-dodecane	214	200-220	C12
n-tridecane	234	220-240	C13
n-tetradecane	252	240-260	C14
n-pentadecane	270	260-280	C15
n-hexadecane	288	280-300	C16

7.2.2 **Preparation of standards:** Preparing a mixture of the C7-C16 alkanes is required. There are two approaches: (1) use of a standards kit (e.g., Polyscience Kit) containing bottles of mixtures of selected n-alkanes which may be combined to produce a C7-C16 standard; or (2) use of bottles of the individual C7-C16 alkanes from which accurately known volumes may be taken and combined to give a C7-C16 mixture.

7.2.3 **Procedure for retention time calibration:** This calibration is performed at the start of an analytical program; the mixture is chromatographed at the start of each day. To attain the required retention time precision, both the carrier gas flow rate and the temperature program specifications must be observed. Details of the procedure depend on the instrument being used. The general procedure is as follows:

7.2.3.1 Set the programmer upper limit at 250°C. If this setting does not produce a column temperature of 250°C, find the correct setting.

7.2.3.2 Set the programmer lower limit at 30°C.

7.2.3.3 Verify that the instrument and samples are at room temperature.

7.2.3.4 Inject 1 uL of the n-alkane mixture.

7.2.3.5 Start the integrator and recorder.

7.2.3.6 Allow the instrument to run isothermally at room temperature for five min.

7.2.3.7 Shut the oven door.

7.2.3.8 Change the mode to Automatic and start the temperature program.

7.2.3.9 Repeat Steps 1-9 a sufficient number of times so that the relative standard deviation of the retention times for each peak is <5%.

7.3 Response calibration:

7.3.1 For the purposes of a Level 1 analysis, response-quantity calibration with n-decane is adequate. A 10-uL volume of n-decane is injected into a tared 10 mL volumetric flask. The weight injected is obtained and the flask is diluted to the mark with n-pentane. This standard contains about 730 ng n-decane per uL n-pentane. The exact concentration depends on temperature, so that a weight is required. Two serial tenfold dilutions are made from this standard, giving standards at about 730, 73, and 7.3 ng n-decane per uL n-pentane, respectively.

7.3.2 **Procedure for response calibration:** This calibration is performed at the start of an analytical program and monthly thereafter. The most concentrated standard is injected once each day. Any change in calibration necessitates a full calibration with new standards. Standards are stored in the refrigerator locker and are made up monthly.

7.3.2.1 Verify that the instrument is set up properly.

7.3.2.2 Set electrometer at 1×10^{-10} A/mV.

7.3.2.3 Inject 1 uL of the highest concentration standard.

7.3.2.4 Run standard temperature program as specified above.

7.3.2.5 Clean syringe.

7.3.2.6 Make repeated injections of all three standards until the relative standard deviations of the areas of each standard are ≤5%.

7.4 Sample analysis procedure:

7.4.1 The following apparatus is required:

7.4.1.1 **Gas chromatograph** set up and working.

7.4.1.2 **Recorder, integrator** working.

7.4.1.3 **Syringe and syringe cleaning apparatus.**

7.4.1.4 **Parameters:** Electrometer setting is 1×10^{-10} A/mV; recorder is set at 0.5 in./min and 1 mV full-scale.

7.4.2 Steps in the procedure are:

7.4.2.1 Label chromatogram with the data, sample number, etc.

7.4.2.2 Inject sample.

7.4.2.3 Start integrator and recorder.

7.4.2.4 After isothermal operation for 5 min, begin temperature program.

7.4.2.5 Clean syringe.

7.4.2.6 Return sample; obtain new sample.

7.4.2.7 When analysis is finished, allow instrument to cool. Turn chromatogram and integrator output and data sheet over to data analyst.

7.5 Syringe cleaning procedure:

7.5.1 Remove plunger from syringe.

7.5.2 Insert syringe into cleaner; turn on aspirator.

7.5.3 Fill pipet with pentane; run pentane through syringe.

7.5.4 Repeat with methylene chloride from a separate pipet.

7.5.5 Flush plunger with pentane followed by methylene chloride.

7.5.6 Repeat with methylene chloride.

7.6 Sample analysis decision criterion: The data from the TCO analyses of organic extract and rinse concentrates are first used to calculate the total concentration of C7-C16 hydrocarbon-equivalents (Paragraph 7.7.3) in the sample with respect to the volume of air actually sampled, i.e., ug/m^3. On this basis, a decision is made both on whether to calculate the quantity of each n-alkane equivalent present and on which analytical procedural pathway will be followed. If the total organic content is great enough to warrant continuing the analysis -- >500 ug/m^3 -- a TCO of less than 75 ug/m^3 will require only LC fractionation and gravimetric determinations and IR spectra to be obtained on each fraction. If the TCO is greater than 75 ug/m^3, then the first seven LC fractions of each sample will be reanalyzed using this same gas chromatographic technique.

7.7 Calculations:

7.7.1 **Boiling Point - Retention Time Calibration:** The required data for this calibration are on the chromatogram and on the data sheet. The data reduction is performed as follows:

7.7.1.1 Average the retention times and calculate relative standard deviations for each n-hydrocarbon.

7.7.1.2 Plot average retention times as abscissae versus normal boiling points as ordinates.

7.7.1.3 Draw in calibration curve.

7.7.1.4 Locate and record retention times corresonding to boiling ranges 90-100, 110-140, 140-160, 160-180, 180-200, 200-220, 220-240, 240-260, 260-280, 280-300°C.

7.7.2 **Response-amount calibration:** The required data for this calibration are on the chromatogram and on the data sheet. The data reduction is performed as follows:

7.7.2.1 Average the area responses of each standard and calculate relative standard deviations.

7.7.2.2 Plot response (uv·sec) as ordinate versus ng/uL as abscissa.

7.7.2.3 Draw in the curve. Perform least squares regression and obtain slope (uV·sec·uL/ng).

7.7.3 **Total C7-C16 hydrocarbons analysis:** The required data for this calculation are on the chromatogram and on the data sheet. The data reduction is performed as follows:

7.7.3.1 Sum the areas of all peaks within the retention time range of interest.

7.7.3.2 Convert this area (uV·sec) to ng/uL by dividing by the weight response for n-decane (uV·sec.uL/ng).

7.7.3.3 Multiply this weight by the total concentrate volume (10 mL) to get the weight of the C7-C16 hydrocarbons in the sample.

7.7.3.4 Using the volume of gas sampled or the total weight of sample acquired, convert the result of Step 7.7.3.3 above to ug/m^3.

7.7.3.5 If the value of total C7-C16 hydrocarbons from Step 7.7.3.4 above exceeds 75 ug/m^3, calculate individual hydrocarbon concentrations in accordance with the instructions in Paragraph 7.7.5.5 below.

7.7.4 **Individual C7-C16 n-Alkane Equivalent Analysis:** The required data from the analyses are on the chromatogram and on the data sheet. The data reduction is performed as follows:

7.7.4.1 Sum the areas of peaks in the proper retention time ranges.

7.7.4.2 Convert areas (uV·sec) to ng/uL by dividing by the proper weight response (uV·sec·uL/ng).

7.7.4.3 Multiply each weight by total concentrate volume (10 mL) to get weight of species in each range of the sample.

7.7.4.4 Using the volume of gas sampled on the total weight of sample acquired, convert the result of Step 7.7.4.3 above to ug/m^3.

8.0 QUALITY CONTROL

8.1 Appropriate QC is found in the pertinent procedures throughout the method.

9.0 METHOD PERFORMANCE

9.1 Even relatively comprehensive error propagation analysis is beyond the scope of this procedure. With reasonable care, peak area reproducibility of a standard should be of the order of 1% RSD. The relative standard deviation of the sum of all peaks in a fairly complex waste might be of the order of 5-10%. Accuracy is more difficult to assess. With good analytical technique, accuracy and precision should be of the order of 10-20%.

10.0 REFERENCES

1. Emissions Assessment of Conventional Stationary Combustion Systems: Methods and Procedure Manual for Sampling and Analysis, Interagency Energy/Environmental R&D Program, Industrial Environmental Research Laboratory, Research Triangle Park, NC 27711, EPA-600/7-79-029a, January 1979.

SAMPLING METHOD FOR VOLATILE ORGANIC COMPOUNDS (SMVOC)

1.0 SCOPE AND APPLICATION

1.1 Method 0031 is used to determine volatile organic compounds in gaseous emissions from a wide variety of stationary sources including hazardous waste incinerators. The following compounds may be determined by this method:

Compound	Boiling Point (°C)	CAS No.[a]
Acrylonitrile[b]	77	107-13-1
Benzene	80	71-43-2
Bromodichloromethane	87	75-27-4
Carbon disulfide	46	75-15-0
Carbon tetrachloride	77	56-23-5
Chlorodibromomethane	119-120 @ 748 mm Hg	124-48-1
Chloroform	61	67-66-3
Chloroprene[c]	59	126-99-8
Dibromomethane	97	74-95-3
1,1-Dichloroethane	57	75-34-3
1,2-Dichloroethane	83	107-06-2
1,1-Dichloroethene	32	75-35-4
trans-1,2-Dichloroethene	48	156-60-5
1,2-Dichloropropane	96	78-87-5
1,3-Dichloropropene	106 @ 730 mm Hg	542-75-6
Methylene chloride	39	75-09-2
Tetrachloroethene	121	127-18-4
Toluene	111	108-88-3
1,1,1-Trichloroethane	75	71-55-6
1,1,2-Trichloroethane	113	79-00-5
Trichloroethene	87	79-01-6
Trichlorofluoromethane	24	75-69-4

[a] Chemical Abstract Services Registry Number.
[b] The water solubility and reactivity of this compound may cause problems with some stationary sources.
[c] Reactive compound; may interact with the test matrix.

1.2 Method 0031 may be used to prepare volatile organic compounds that have a boiling point between -15°C and 121°C. Field application for volatile organic compounds with boiling points less than 0°C should be supported by data obtained from laboratory gaseous dynamic spiking and gas chromatographic/mass spectrometric (GC/MS) analysis according to Methods 5041 and 8260 to demonstrate the efficiency of the sampling and analysis method.

1.3 The method is not applicable to particulates or aerosols since isokinetic sampling is not performed. Isokinetic sampling is not required because the volatile organic compounds are in the gas phase when they are sampled.

1.4 Application of Method 0031 is not restricted to those compounds in the target analyte list, however, detection limits have been determined for these compounds and acceptable method performance data have been obtained. Method 0031 may also be applied to the compounds listed in Table 1 if extra care is taken because of the high volatility of these compounds.

1.5 Method 0031 is generally not applicable to polar water-soluble and reactive volatile organic compounds. Examples of polar water-soluble and reactive compounds are shown in Table 2. Other examples where Method 0030 (VOST) sampling and analytical methodology has been used inappropriately include: bromoform (boiling point 137°C, above the maximum limit allowed by the methodology), ethylbenzene (136°C), 1,2,3-trichloropropane (156°C), xylenes (~140°C), styrene (146°C), 1,1,2,2-tetrachloroethane (146°C at 746 mm Hg), and the dichlorobenzenes (~175°C). Although successful analysis for these compounds can be demonstrated by spiking sorbent tubes, the compounds will not be collected quantitatively at the upper temperature limit for the operation of the SMVOC train.

1.6 This method is applicable to the determination of volatile organic compounds in the gaseous effluent of stationary sources such as hazardous waste incinerators with an upper concentration limit per compound in the emissions of approximately 1.5 parts per million (ppm). Method 0031 is not appropriate for gaseous volatile organic compound concentrations above this limit, since saturation of the analytical system or compound breakthrough in the field may occur. Modifications of analytical methods to reduce the concentration of compounds entering the gas chromatograph/mass spectrometer (GC/MS), such as splitters or dilutions, may prevent saturation of the analytical system, but the analytical data are not accurate if breakthrough has occurred during sampling. The analysis of screening samples or distributive volume samples is recommended to prevent analytical system saturation when high analyte concentrations may be encountered.

1.7 The sensitivity of this method is dependent upon the level of interferences in the sample matrix and the presence of detectable levels of volatile organic compounds in the blanks. The target detection limit of this method is 0.1 $\mu g/m^3$ (ng/L) of gaseous effluent. The upper end of the range of applicability of this method is limited by breakthrough of the volatile organic compounds on the sorbent traps used to collect the sample and the ability of the analytical system to respond within the linear range of the instrumentation. Laboratory method development data have demonstrated a range of 0.1 to 100 $\mu g/m^3$ (ng/L) for selected volatile organic compounds collected on a set of sorbent traps using a total sample volume of 20 L or less (see Sec. 2.3).

1.8 The SMVOC is designed to be operated at a sampling rate of 1 L/min with traps being replaced every 20 min for a total sampling time of 2 hrs. Analysis of the traps is carried out by thermal desorption purge-and-trap gas chromatography/mass spectrometry (see Methods 5041 and 8260). Traps may be analyzed separately or combined onto one trap to improve detection limits. Additional flow rates and sampling times are acceptable. For example, when less than maximum detection ability is needed, it is acceptable to operate the SMVOC at 0.5 L/min for a total of three 40-minute periods (two-hour total sampling time). In this example, a two-hour sampling time is maintained, but the number of sampling tubes which must be changed in the field is minimized, as is the number of analyses which must be performed.

NOTE: The SMVOC sampling train may be operated no slower than 0.25 L/min, and no faster than 1 L/min.

1.9 This method is restricted to use by, or under close supervision of, trained analytical personnel experienced in sampling volatile organic compounds in air. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 This method employs a sampling module and meter box to withdraw a 20-L sample of effluent gas containing volatile organic compounds from a stationary source at a flow rate of 1 L/min, using a glass-lined probe heated to 130 ± 5°C and a sampling method for volatile organic compounds (SMVOC) train.

2.2 The gas stream is cooled to 20°C by passage through a water-cooled condenser and volatile organic compounds are collected on a set of sorbent traps (Tenax®-GC/Tenax®-GC/Anasorb®-747). Liquid condensate is collected in an impinger placed between the two Tenax®-GC traps and the Anasorb®-747 trap. The first and second traps contain 1.6 g of Tenax®-GC each and the third trap (back trap) contains 5.0 g of Anasorb®-747. A total number of sorbent tube sets to encompass a total sampling time of 2 hrs is collected: i.e., if a sampling rate of 1 L/min for 20 minutes is used, a total of six sorbent tube sets will be collected in 2 hr of sampling.

2.3 Alternative conditions for sample collection may be used, collecting a sample volume of 20 L or less at a flow rate reduced from 1 L/min. (Operation of the SMVOC under these conditions is referred to as SLO-SMVOC.) The SLO-SMVOC may be used to collect 5 L of sample (0.25 mL/min for 20 min) or 20 L of sample (0.5 L/min for 40 min) on each set of sorbent tubes. These smaller sample volumes collected at lower flow rates should be considered when the boiling points of the volatile organic compounds of interest are below 0°C (see Table 1) to prevent breakthrough. Refer to Sec. 2.2 for the total number of tube sets collected per run.

3.0 INTERFERENCES

3.1 Interferences are encountered in the analytical methodology and arise primarily from background contamination of sorbent traps prior to or after sample collection. Other interferences may arise from exposure of the sorbent materials to solvent vapors prior to assembly and exposure to significant concentrations of volatile organic compounds in the ambient air at a stationary source site. To avoid or minimize the low-level contamination of train components with volatile organic compounds, care should be taken to avoid contact of all interior surfaces or train components with synthetic organic materials such as organic solvents, and lubricating and sealing greases. Train components should be carefully cleaned and conditioned according to the procedures described in this protocol. The use of a sealed/enclosed sampling train is suggested but not required (for example, a purged glove bag may be used). The use of blanks (Sec. 6.6) is essential to assess the extent of any contamination. Refer to Method 5041 for additional information on analytical interferences.

3.2 If the emission source has a high level of organic compounds in the emissions matrix (for example, hydrocarbons present at levels of hundreds of ppm), the presence of these volatile organic compounds may interfere with the performance of the SMVOC analytical methodology. If the probability of saturation of the analytical instrumentation exists, preliminary SMVOC screening samples with distributive volumes may be necessary to help ensure that valid and usable data will be obtained. To perform sampling according to distributive volumes, samples of different volumes are collected (typically 5 L, 10 L, and 20 L) to verify that analyte concentrations are 1X, 2X, and 4X.

4.0 APPARATUS AND MATERIALS

4.1 Sampling train - A schematic of the principal components of the SMVOC is shown in Figure 1. The SMVOC consists of a heated glass-lined probe, followed by an isolation valve and charcoal trap, a water-cooled glass condenser, two sorbent tubes containing Tenax®-GC (1.6 ± 0.1 g each), an empty knock-out trap for condensate removal, a second water-cooled glass condenser, a third sorbent tube containing Anasorb®-747 (5.0 g ± 0.1 g), a silica gel drying tube, a calibrated rotameter, a sampling pump, and a dry gas meter. The vacuum during sampling and for leak-checking is monitored by pressure gauges which are in-line with and downstream from the silica gel drying tube. The components of the sampling train are described below.

4.1.1 Probe - The probe is made of stainless steel with a borosilicate or quartz glass liner. The temperature of the probe is maintained at 130°C ± 5°C or higher, but not so high that the sorbent temperature exceeds 20°C. A water-cooled probe may be necessary at elevated source temperatures to protect the probe and meet the required sorbent temperature maximum. Isokinetic sample collection is not a requirement for the use of SMVOC since the compounds of interest are in the vapor phase at the point of sample collection. No nozzle is required, but a plug of clean quartz wool (approximately 2.5 cm. (1 in.)) is inserted in the probe to remove particulate matter.

NOTE: No stainless steel components should be in contact with the sample stream.

4.1.2 Isolation valve - The isolation valve is a greaseless stopcock (0.25 in. outer diameter stem is recommended) with a glass bore and sliding Teflon® plug with Teflon® washers (Ace Glass 8193 or equivalent).

4.1.3 Condensers - The condensers (Ace Glass 5979-14 or equivalent) must be of sufficient capacity to cool the gas stream to 20°C or less prior to passage through the first sorbent tube. The top connection of the condenser must form a leak-free, vacuum-tight seal without using sealing greases. Solverall® tube fittings and screw caps with Solverall® washers (¼ in. OD, or equivalent) are recommended.

4.1.4 Sorbent tubes - See Figure 2 for a diagram of a SMVOC tube.

4.1.4.1 The first and second tubes of a three-tube set of sorbent tubes should each be packed with 1.6 ± 0.1 g of Tenax®-GC resin and the third tube of the set should be packed with 5.0 ± 0.1 g of Anasorb®-747. The tubes should be marked with an arrow to indicate the direction of flow during sampling.

4.1.4.2 The sorbent tubes are glass tubes with approximate dimensions of 10 cm x 1.6 cm ID. The tube is a single glass tube which has the ends reduced in size to accommodate a ¼-in. Swagelok® fitting. The sorbent is held in place by unsilanized clean glass wool at each end of the sorbent layer. Threaded end caps are placed on the sorbent tube after packing with sorbent to protect the sorbent from contamination during storage and transport. In order to minimize tube breakage, fittings are finger-tight plus an additional quarter of a turn. Ceramic-filled Teflon® ferrules (Supeltex M2A or equivalent) are used for tubes. Graphite ferrules (Supeltex M4 or equivalent) are used if reconditioning of the tubes is necessary. The Swagelok® end caps should be finger-tightened with the ferrules in place so that the entire cap assembly may be turned as a unit. In order to seal the assembly and avoid glass breakage, the cap assembly should be pushed to the end of the glass and then backed off slightly before tightening

the cap with a wrench one quarter of a turn. Backing the cap assembly off from the end of the tube will prevent chipping, cracking, or breaking of the glass.

4.1.4.3 The sorbent tubes are placed in transport tubes (capped culture tubes with glass wool and charcoal) for shipment. A layer of clean charcoal is placed in the bottom of the transport tube to absorb any volatile organics in the air in the transport tube. A plug of cleaned glass wool (approximately 2.5 cm. (1 in.)) is placed above the charcoal. The SMVOC tube, with both ends capped, is placed in the transport tube, and a plug of cleaned glass wool (approximately 2.5 cm. (1 in.)) is placed on top of the SMVOC tube. The two glass wool plugs cushion the SMVOC tube during shipping. The transport tube is then sealed tightly with a Teflon®-lined screw cap. At no time, should the samples contained in the sorbent tubes be exposed to large pressure differentials such as might be caused by shipping in unpressurized aircraft cargo compartments.

4.1.5 Metering system - The metering system for SMVOC consists of a vacuum gauge, a pump, a calibrated rotameter for monitoring the sampling flow rate, a dry gas meter (2% accuracy, with a minimum resolution of 0.01 L) at the required sampling rate, needle valves, and a temperature readout device. Provisions should be made for monitoring the temperature of the sample gas stream between the first condenser and the first sorbent tube, since this temperature should not exceed 20°C. The temperature can be monitored by placing a thermocouple on the exterior glass surface of the outlet from the first condenser. The temperature at that point should be less than 20°C. If the cooling is not sufficient, an alternative condenser providing the necessary cooling capacity must be used.

4.1.6 Sample transfer lines - All sample transfer lines connecting the probe to the SMVOC shall be less than 1.52 m. (5 ft.) in length. All sample transfer lines ahead of the first condenser shall be heat-traced Teflon® or glass maintained at 130 ± 5°C. Connecting fittings must be capable of forming leak-free, vacuum-tight connections without the use of sealing grease. All other sample transfer lines used with the SMVOC shall be Teflon® with connecting fittings that are capable of forming leak-free, vacuum-tight connections without the use of sealing grease. These sample transfer lines should not be reused at other emission sources.

4.2 Solverall® washers - All washers or gaskets used in SMVOC shall be Teflon®-coated (Solverall® washers or equivalent; ¼ in. stainless steel Swagelok® fittings with Supeltex M2A ferrules may also be used). Prior to use, these gaskets should be ultrasonically-cleaned with methanol and air-dried in a contained/isolated organic vapor-free area. Gaskets should be stored in clean, screw-capped containers prior to use.

4.3 Glass wool - Glass wool shall be Soxhlet-extracted for 8 to 16 hours using methanol, and oven dried at 110°C before use. Glass wool should not be silanized to prevent contamination of samples with siloxanes. Quartz wool is recommended for high temperature applications.

4.4 Cold packs/ice - Ice or any commercially-available reusable liquids or gels that can be frozen repeatedly are acceptable. These reusable liquids are typically sold in plastic containers as "Blue Ice" or "Ice-Packs". Enough cold packs or ice should be used to maintain tubes less than 10°C. If ice is used as a coolant for the tubes, the tubes should be shielded from direct contact with the ice so they will not become wet when the ice melts. Use of dry ice (solid CO_2) for cooling tubes should be avoided; the sorbent tubes take up carbon dioxide as the solid coolant vaporizes and the analytical system is vented when the tubes are desorbed and analyzed. The tubes should not be stored at freezing temperatures, since the seal between the glass and Teflon® fittings will be compromised and diffusion of volatile organic compounds into the sorbent may occur.

4.5 VOA vials - 40-mL glass vials with Teflon®-lined screw caps are required for recovery of condensate.

4.6 Teflon® squeeze bottles -Teflon® squeeze bottles should be washed with a solution of a laboratory detergent, rinsed with hot tap water, then with distilled water, then rinsed with clean purged water prior to use.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that 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 it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. It is recommended that blanks be taken of all reagents used in testing.

5.2 2,6-Diphenyl-p-phenylene oxide polymer (Tenax®-GC, 35/60 mesh, or equivalent).

5.2.1 New Tenax®-GC is Soxhlet-extracted for 24 hours with methanol. The Tenax®-GC is dried for 6 hours in a vacuum oven at 50°C before use. Thermal conditioning (Sec. 7.1.1) of the Tenax®-GC should be done prior to blanking.

5.2.2 If reuse of Tenax®-GC is necessary, the polymer may be extracted sequentially with methanol and pentane, dried in a vacuum oven, and thermally reconditioned as described above. However, reused tubes must meet the same criteria for cleanliness as new tubes. Reuse of sorbents is not recommended. Common practice in laboratories where SMVOC tubes are prepared commercially or where SMVOC sampling and analysis are done extensively is not to reuse sorbents.

5.3 Anasorb®-747 - New Anasorb®-747 is used as it is received from the manufacturer without preparation other than thermal conditioning pending a Quality Control check (Sec. 7.1.1). Anasorb®-747 must not be reused. The Anasorb®-747 should not be extracted with organic solvent prior to use as a sorbent in the SMVOC.

5.4 Silica gel - Indicating type, 6-16 mesh. New silica gel may be used as received from the vendor. Silica gel should not be reused for SMVOC.

5.5 Methanol, CH_3OH - The methanol used for extracting the Tenax®-GC and glass wool should be pesticide grade or equivalent.

5.6 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 SMVOC glassware cleaning- All glass components of the train should be cleaned thoroughly. The following procedure has been found to be effective, but any protocol which consistently results in contamination-free glassware is acceptable.

6.1.1 Sonicate for 1 hour in a solution of a laboratory detergent such as Alconox®.

6.1.2 Rinse with copious amounts of hot tap water to remove all detergent residue.

6.1.3 Rinse three times with HPLC grade water.

6.1.4 Oven dry at 110°C.

6.1.5 Cap for shipment using Teflon® tape or aluminum foil.

6.2 Assembly

The assembly and packing of the sorbent tubes should be carried out in an area free of volatile organic material, such as a laboratory in which no organic solvents are handled or stored and in which the laboratory air is charcoal filtered. Alternatively, an air-tight sealed glove box is suggested.

6.3 Tenax®-GC tubes

6.3.1 The Tenax®-GC glass tubes and metal tube parts are cleaned and stored (see Sec. 6.1). Ferrules are discarded but the metal unions are cleaned by sonication in methanol. Tenax®-GC (1.6 ± 0.1 g) is weighed and packed into each of the first two sorbent tubes which have unsilanized cleaned glass wool in the downstream end. The Tenax®-GC is held in place by inserting unsilanized cleaned glass wool. Each tube should be marked, using an engraving tool, permanent marker or diamond-tipped pencil, with an arrow to indicate the direction of sample flow during sampling, and a serial number.

6.3.2 Conditioned sorbent tubes are capped and placed on cold packs or ice for storage and transport. The temperature of the tubes during storage and transport is maintained at a temperature of less than 10°C. Conditioned tubes should be held for no more than 14 days before sampling, to prevent the possibility of contamination. At no time, should the samples contained in the sorbent tubes be exposed to large pressure differentials such as might be caused by shipping in unpressurized aircraft cargo compartments.

6.4 Anasorb®-747 tubes - Anasorb®-747 (5.0 ± 0.1 g) is weighed and packed into the third sorbent tube which also has unsilanized cleaned glass wool in the downstream end. The Anasorb®-747 is held in place by inserting unsilanized cleaned glass wool. Special care should be taken to conspicuously mark the Anasorb®-747 tube with an arrow to indicate the direction of flow during sampling, and a serial number.

6.5 Sample collection

6.5.1 For sample collection, place the inlet of the probe at the centroid of the stack or at a point no closer to the walls than 1 meter. After leak checking (see Sec. 6.5.3) but before the initiation of sample collection, the probe shall be purged with stack gas. This purge can be accomplished by attaching a pump to the isolation valve upstream of the first condenser and drawing stack gas through the probe via the isolation valve, so that the probe is purged of ambient air at the initiation of sample collection.

6.5.2 Sample collection is accomplished by opening the valve at the inlet to the first condenser (see Figure 1), turning on the pump, and sampling at a rate of 1 L/min (or slower rate, if desired, according to the guidelines for SLO-SMVOC) for 20 minutes (or an appropriately longer period, if slower sampling rates are used). The volume of sample for any

set of traps should not exceed 20 liters. The end caps of the sorbent tubes should be placed in a clean screw-capped glass container during sample collection to prevent contamination.

6.5.3 Following completion of sample collection, the SMVOC is leak-checked a second time at the highest vacuum encountered during the sampling run to minimize the chance of vacuum desorption of volatile organic compounds from Tenax®-GC. The sample is considered invalid if the leak test does not meet specifications. The train is returned to atmospheric pressure and the set of sorbent tubes is removed. The end caps are replaced and the tubes are placed in an organic-free environment and maintained at a temperature less than 10°C for storage and transport. The set of tubes and any condensate collected (see Sec. 6.5.4) are placed in self-sealing plastic storage bags.

In the laboratory, tubes are maintained in a clean, organic vapor-free environment at a temperature less than 10°C until analysis. The maximum storage time between sampling and analysis of the tubes should be 14 days. The rate of loss of sorbed volatile organic compounds from the tubes is both compound-specific and source-specific. A 14-day period is chosen for the holding time before analysis to provide a reasonably conservative guideline for quantitative analysis of the volatile organic compounds which have been sampled.

NOTE: To prevent breakage and/or loosening of the seals at the end of the tubes, SMVOC tubes should not be stored in a freezer or over dry ice. A solvent-free refrigerator (no cooler than 4°C) is appropriate for storage of the tubes until analysis.

6.5.4 Depending upon condensate volume collected, recovery may be performed with each tube change, or at the end of each run (nominally 2 hrs). Collection of a single composite sample for the run may be especially appropriate when minimal condensate is being collected. If not all the sorbent tubes are analyzed, the total amount of analyte in the composite condensate should be added to the total amount for the run. The condensate is recovered by transferring any liquid contained in the knock-out trap to a 40-mL VOA vial and rinsing the knock-out trap three times with a minimum volume of organic-free reagent water (Sec. 5.6) and adding the rinses to the VOA vial. If necessary, water should be added to eliminate headspace in the vial. If there is sufficient condensate to fill more than one vial, two vials should be used. The VOA vials containing the condensate are placed, with the set of tubes, in a self-sealing plastic storage bag and maintained at a temperature less than 10°C for storage and transport until analysis. The condensate is analyzed by Method 8260. Refer to Method 8260 for details on analytical procedures. Condensate samples, like the sorbent tubes, must be analyzed within 14 days.

6.5.5 A new set of tubes is placed in the SMVOC, the SMVOC is leak-checked, and the sample collection process repeated as described above. To avoid removing the probe from the stack, it is sufficient to perform a glassware leak check using the three way valve just downstream of the probe. Sample collection continues until sufficient samples to encompass a two-hour sampling period have been collected. If samples are taken at a sampling rate of 1 L/minute, a two hour sampling period will result in the collection of six sets of tubes. If SLO-SMVOC procedures are used, fewer than six sets of tubes will be sampled over a two-hour period.

6.6 Blanks

6.6.1 Field blanks - Blank Tenax®-GC and Anasorb®-747 tubes are attached to the sampling train while the train is leak-checked. The tubes are removed and stored with the sample tubes. At least one field blank should be collected for every two-hour sampling period.

6.6.2 Trip blanks - At least one set of blank tubes (two Tenax®-GC, one Anasorb®-747) should be included with each shipment of tubes to a stationary source sampling site. These trip blanks should be treated like any other tubes except that the end caps will not be removed during storage at the site. This set of tubes should be analyzed to assess contamination which may occur during storage and shipment.

6.6.3 Laboratory blanks - One set of blank tubes (two Tenax®-GC, one Anasorb®-747) should remain in the laboratory using the method of storage which is used for field samples. These laboratory blanks should be from the same batch of sorbent as used for the field blanks, trip blanks and collected samples. If the field and trip blanks contain high concentrations of contaminants (e.g., greater than 2 ng of a particular volatile organic compound), the laboratory blank should be analyzed in order to identify the source of contamination.

7.0 PROCEDURE

7.1 Tube conditioning

7.1.1 In a desorption oven, the sorbent tubes are connected to a source of organic-free nitrogen. Nitrogen is passed through each tube at a flow rate of 80-100 mL/min while the tubes are heated. Anasorb®-747 is thermally conditioned for 18-24 hours at 300°C, under a nitrogen flow rate of 80-100 mL/min. Tenax®-GC is thermally conditioned at 220°C for 8-12 hours at a nitrogen flow rate of 80-100 mL/min. The actual length of time required for the conditioning period may be determined based on the adequacy of the resulting blank checks of the conditioned tubes. Method 5041 (modified to use a sorbent desorption temperature of 250°C) and Method 8260 may be used to perform a blank check of each set of sampling tubes to ensure cleanliness.

7.1.2 An acceptable blank level is less than or equal to ($\leq$) Method Detection Limits for Method 5041/8260 (see Method 8260 for Method Detection Limits). A general guideline of analyte values less than 2 ng for any volatile organic compound may be used as a criterion of cleanliness.

7.1.3 After conditioning, tubes are sealed and placed on cold packs or ice (maintained at a temperature less than 10°C) until sampling is completed. Conditioned tubes should be held for no more than 14 days before sampling, to prevent the possibility of contamination.

7.2 Pretest preparation

7.2.1 All train components should be cleaned and assembled as previously described. A dry gas meter should be calibrated within 30 days prior to use, using a standard orifice, or other approved calibration device/meter.

7.2.2 The SMVOC is assembled according to the schematic diagram in Figure 1. Cooling water should be circulated to the condensers and the temperature of the cooling water must be low enough to maintain the temperature of the gas entering the sorbent below 20°C.

7.3 Leak-checking

7.3.1 To leak-check the entire train, it is necessary to leak-check from the probe to the pump. In order to adequately represent actual sampling conditions, a leak-check should be performed with the pump on and the leak rate measured in liters per minute (Lpm) on the dry gas meter. After the desired vacuum is reached, the pump is isolated from the train to check for leaks.

7.3.2 Ensure that all connections are tight and that the train is assembled correctly with sorbent cartridges properly assembled and in the right direction for sampling. Seal the end of the probe and turn the isolation valve to the sample open position. Turn on the pump and adjust the vacuum to 25.4 cm above normal operating pressure (38 cm Hg should be sufficient as 12.7 cm or less is normal). Prior to leak-checking, verify that both the coarse and fine adjust valves on the meter box are partially opened to prevent backflushing of any condensate during final leak checks as the fine adjust valve will need to be adjusted to increase vacuum rather than decrease vacuum. Allow the rotameter on the meter box to drop to zero, allow the dry gas meter to stop, and the pressure on the water column gauge (represents the pressure inside the dry gas meter) to stabilize. The pump is isolated from the train by shutting off the coarse adjust valve. Record the leak rate directly from the vacuum gauge and time for one minute. The leak rate must be less than 0.02 Lpm for 1 Lpm sampling and 0.01 Lpm for sampling at a lower rate.

7.3.3 Upon completion of the leak check, turn off the pump and release the pressure/vacuum in the train by turning the isolation valve to the vacuum release position and allowing ambient air (filtered with charcoal or equivalent) to enter the train. The initial leak check should be above normal operating pressure. The final leak check (following collection of 20 L of sample) should be at least at the highest vacuum encountered during the run.

NOTE: The volume of air pulled through the SMVOC during leak-checking procedures prior to sampling should be less than 2.5% of the total volume sampled. If a volume greater than 2.5% of the total sampling volume is pulled through the SMVOC in obtaining a successful leak check, the sorbent tubes used during this leak check must be discarded and a successful leak check with a minimum volume of gas pulled through the train must be obtained with a new set of sampling tubes in place.

7.4 Sample collection - Sample collection procedures are described in Sec. 6.5.

7.5 Analytical procedure - Samples are analyzed by Methods 5041 and 8260. In these methods, adapted for a three-tube SMVOC, the Tenax® sorbent tubes are spiked with surrogates, internal standards are spiked into the purge water, and the tube(s) thermally desorbed at 250°C under a purge of organic-free helium. The tubes may all be analyzed individually, or the Tenax® tubes may be analyzed as a pair with the Anasorb® tube analyzed separately, or multiple tubes may be combined on one trap for analysis in order to decrease detection limits. The gaseous effluent from the tubes is bubbled through purged organic-free reagent water (Sec. 5.6) and trapped on an analytical sorbent trap in a purge-and-trap unit. After desorption, the analytical sorbent trap is heated rapidly and the gas flow from the analytical trap is directed to the head of a wide-bore capillary column (Method 5041) under subambient conditions. The volatile organic compounds desorbed

from the analytical trap are separated by temperature-programmed gas chromatography and detected by continuously-scanning low resolution mass spectrometry (Method 8260). Concentrations of volatile organic compounds are calculated from a multipoint calibration curve, using the method of response factors. Refer to Method 8260 for details.

7.6 Calculations

7.6.1 The following nomenclature is used in the calculation of sample volume:

P_{bar} = Barometric pressure at the exit orifice of the dry gas meter, mm (in.) Hg.

P_{std} = Standard absolute pressure, 760 mm Hg.

T_m = Dry gas meter average absolute temperature, °K (°R)

T_{std} = Standard absolute temperature, 293°K (528°R)

V_m = Dry gas volume measured by dry gas meter, dcm (dcf)

γ = Dry gas meter calibration factor

$V_{m(std)}$ = Dry gas volume measured by dry gas meter, corrected to standard conditions, dscm (dscf)

7.6.2 The volume of gas sampled is calculated as follows:

$$V_{m_{std}} = V_m \ \gamma \ \frac{T_{std} \ P_{bar}}{T_m \ P_{std}} = K_1 \ \gamma \ \frac{V_m \ P_{bar}}{T_m}$$

where:

K_1 = 0.3858°K/mm Hg for metric units or

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

7.6.3 The concentration of volatile organic compound (CPD) in the stack sample (C_g) is calculated as follows:

$$C_g = \frac{\text{Total weight of CPD in sample, µg (i.e., VOST tubes + condensate)}}{\text{Volume of sample at standard conditions, dscm}}$$

If all three sorbent tubes and the condensate are analyzed separately, four sample results (fewer if some tubes are analyzed together) must be added together to obtain the total weight of CPD. If a measurable amount of the compound is found in one or more fractions of the sample, but the amount in one or more of the other fractions is below detection limit, the following strategy is recommended, but is subject to being overruled by regulatory authorities. Count the "sum of the nondetects" as zero if the sum of the detection limits (in nondetect fractions) is less than 10% of the total of the detected amount from the other fractions. In

cases where the sum of the detection limits in the nondetect fractions is greater than 10% of the amount quantitated in the other fractions, then report the total CPD as greater than the detected amount but less than the detected amount plus the sum of nondetect fraction detection limits.

8.0 QUALITY CONTROL

8.1 Prior to actual sampling on-site, all of the applicable sampling equipment should be thoroughly checked to ensure that each component is clean and operable. Each of the equipment calibration data forms should be reviewed for completeness and adequacy to ensure the acceptability of the equipment. Each component of the sampling system should be carefully packed for shipment. Upon arrival on-site, the equipment should be unloaded, inspected for possible damage, and then assembled for use.

8.2 The following quality control (QC) checks are applicable to the sampling procedures:

8.2.1 Each sampling train must be visually inspected for proper assembly before every use.

8.2.2 All sampling data should be recorded on standard data forms which may serve as a pretest checklist.

8.2.3 The temperature measurement system should be visually checked for damage and operability by measuring the ambient temperature.

8.2.4 All sampling data and calculations should be recorded on preformatted data sheets.

8.2.5 All glassware for SMVOC should be cleaned according to the procedure in Sec. 6.1.

8.2.6 Ten percent of the SMVOC tubes should be subjected to GC/MS QC measurements. No analytes should be detected at concentrations above method detection limits in unused SMVOC tubes. If these quality control tests are performed by the manufacturer, documentation should be obtained from the commercial supplier and retained.

8.2.7 All cleaned glassware, hardware, and prepared sorbent traps should be kept closed with ground-glass caps or Teflon® tape until assembly of the sampling train in the field. The sorbent traps should be recapped immediately after each set of samples is collected.

8.2.8 Prior to sampling, the Tenax®-GC and Anasorb®-747 tubes should be spiked with the compounds of interest to ensure that they can be thermally desorbed under laboratory conditions. This spiking is necessary but not sufficient. The compound must still be sampled from the source.

8.2.9 Assembly and recovery of the sampling trains must be performed in an environment as free from uncontrolled dust and solvent vapors as possible.

8.2.10 Blanks (field, trip, laboratory) must be collected.

8.2.11 The entire sampling train should be leak-checked before and after each run. If the sampling train is moved from one sampling port to another during a run, the train should be leak-checked before and after the move.

8.2.12 Dry gas meter readings, temperature readings, and pump vacuum readings should be made during sampling and recorded in intervals no greater than 5 minutes.

8.2.13 Sorbent traps should be used for sampling within two weeks of preparation.

8.2.14 During sample collection, the gas stream temperature at the inlet to the first sorbent trap must be maintained at or below 20°C.

8.2.15 All sample traps should be stored under refrigeration or on ice or cold packs (temperature maintained less than 10°C) until ready for analysis.

8.3 QC for analytical procedures

8.3.1 Calibration standards should be prepared at five different concentration levels for each analyte of interest. Compounds of interest, surrogate compounds, and internal standards are spiked into the purge water for generation of a multipoint calibration curve. When samples are analyzed, surrogate compounds are spiked onto the sampling tubes using flash vaporization techniques (Method 5041), but internal standards are spiked into the purge water. Response factors for each compound are calculated and these response factors are used for the calculation of analytical results. Refer to Methods 5041 and 8260 for detailed analytical QC procedures for analysis of samples.

8.3.2 To establish the precision and accuracy of the analysis, triplicate paired Tenax®-GC tubes should be spiked with analytical surrogate volatile organic compounds using flash evaporation and analyzed immediately following the initial calibration and before sample analysis. The spiking level should be at the expected level of volatile organic compounds in the stationary source. The spiking standard must be prepared from stock standards separate from those used for calibration. Recovery for each volatile organic compound and surrogate should be within 50% to 150% of spiked value. The relative standard deviation associated with each analyte should be less than 25 percent.

8.3.3 The average recovery from the initial precision and accuracy determinations should be used as an acceptance criterion for sample results. The surrogate recovery in each sample should be within three standard deviations of the average recovery obtained from the initial precision and accuracy determinations.

8.3.4 An EPA performance audit should be completed during a trial burn as a check on the entire SMVOC system. The audit results should agree within 50% to 150% of the expected value for each specific compound of interest. This audit consists of collecting a gas sample containing one or more volatile organic compounds in the SMVOC from an EPA audit gas cylinder. Collection of the audit sample in the SMVOC may be conducted either in the laboratory or at the field test site. Analysis of the SMVOC audit sample must be by the same person, at the same time, and with the same analytical procedure as used for the regular SMVOC samples from the field test.

9.0 METHOD PERFORMANCE

See Method 8260.

10.0 REFERENCES

1. McGaughey, J.F., Bursey, J.T., Merrill, R. G., "Field Test of a Generic Method for Halogenated Hydrocarbons: A VOST Test at a Chemical Manufacturing Facility Using a Modified VOST Sampling Method", EPA-600/R-94/130, PB95-142055, U.S. EPA, Research Triangle Park, NC, July 1994,

2. Johnson, L.D., Fuerst, R.G., Foster, A.L. and Bursey, J.T.,"Replacement of Charcoal Sorbent in the Sampling of Volatile Organics from Stationary Sources," Intern. J. Environ. Anal. Chem.,Vol 62, pp. 231-244 (1996).

3. Foster, A.L. and Bursey, J.T., VOST Charcoal Specification Study, EPA-600/R-96/051, PB96-175252, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1996.

TABLE 1

HIGH VOLATILITY ORGANIC COMPOUNDS[a]

Compound	Boiling Point
Bromomethane	4°C
Chloroethane	12°C
Vinyl bromide	16°C, at 750 mm
Vinyl chloride	-13.4°C

[a]Use of SLO-SMVOC may be helpful.

TABLE 2

COMPOUNDS FOR WHICH METHOD 0031 IS NOT APPLICABLE

Compounds	Boiling Point	Comment
Allyl chloride	45°C	Reactive compounds; interacts with test matrix to yield poor recoveries and poor reproducibility
Acetone	56°C	Polar, water soluble
Methyl ethyl ketone	80°C	Polar, water soluble
Chloromethane	-24°C	Reactive compounds; interacts with test matrix to yield poor recoveries and poor reproducibility
Epichlorohydrin	116°C	Not amenable to SMVOC analytical procedure
Chloromethyl methyl ether	56°C	Not amenable to SMVOC analytical procedure
Bis(chloromethyl) ether	106°C	Not amenable to SMVOC analytical procedure
Acetonitrile	82°C	Polar, water soluble
Acetaldehyde	21°C	Polar, water soluble, reactive
Acrolein	53°C	Polar, water soluble, reactive
Methanol	65°C	Polar, water soluble
Ethanol	78°C	Polar, water soluble
Isopropyl alcohol	82°C	Polar, water soluble

FIGURE 1
SCHEMATIC OF SAMPLING METHOD FOR VOLATILE
ORGANIC COMPOUNDS (SMVOC) TRAIN

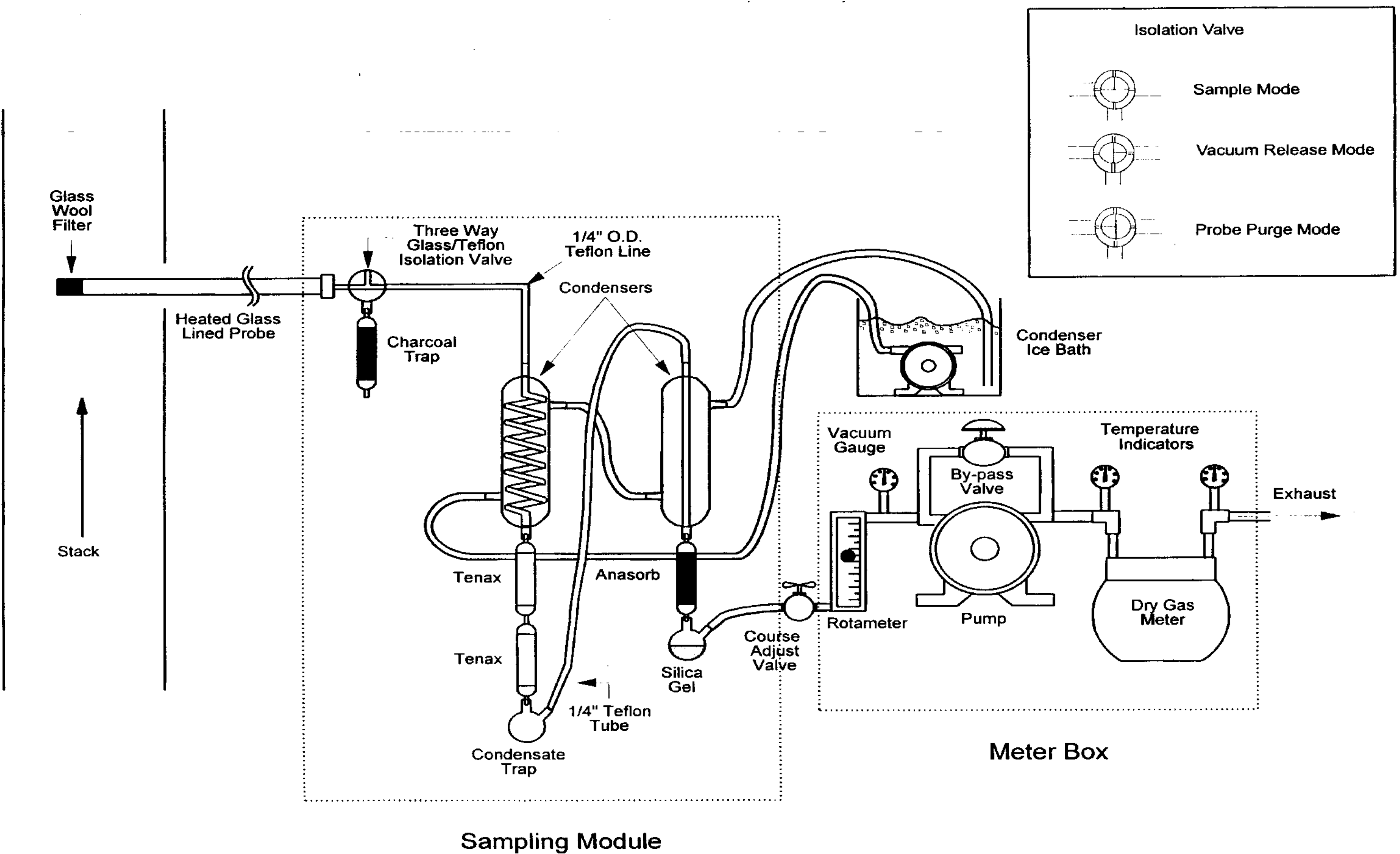
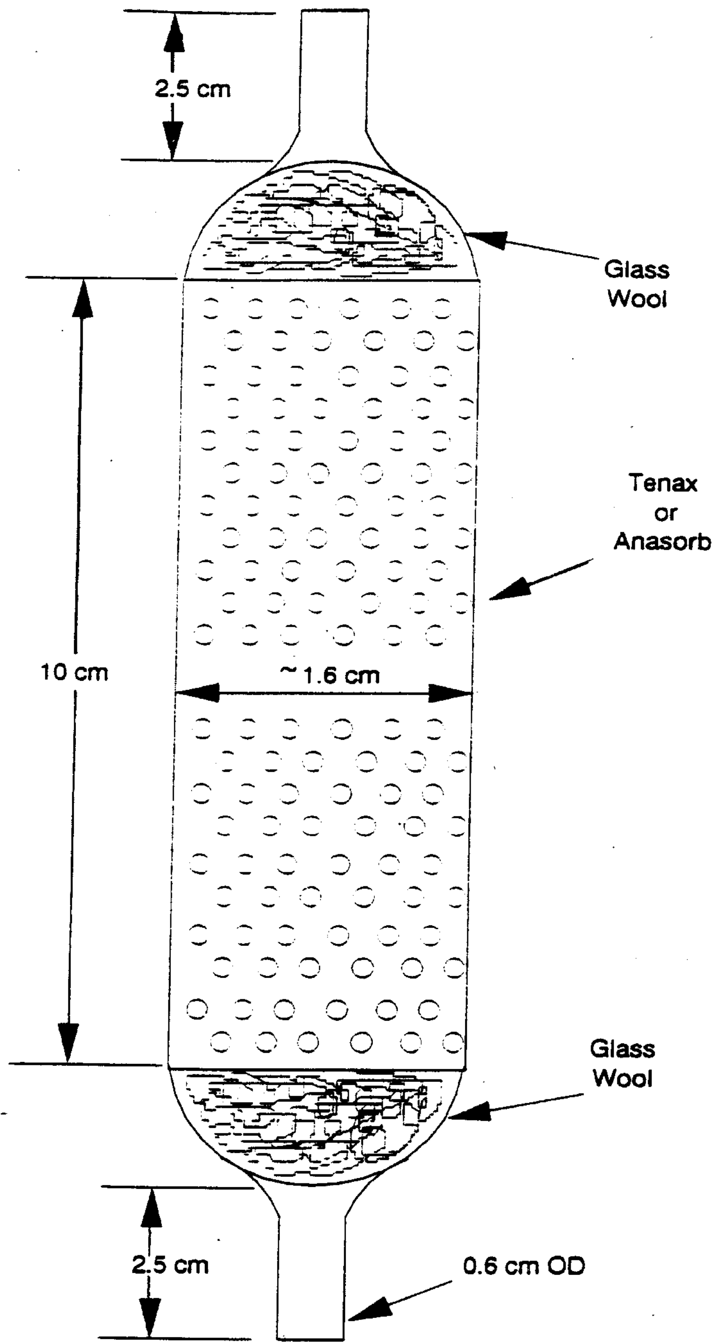


FIGURE 2
SMVOC TUBE



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 ≥ 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).
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.
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:

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

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):

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

12.4 Volume of Water Vapor Condensed.

$$V_{w(std)} = V_{lc} \frac{\rho_w R T_{std}}{M_w P_{std}} = K_2 V_{lc} \quad \text{Eq. 3}$$

12.5 Moisture Content.

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

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	2.205×10^{-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:

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

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.***

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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.

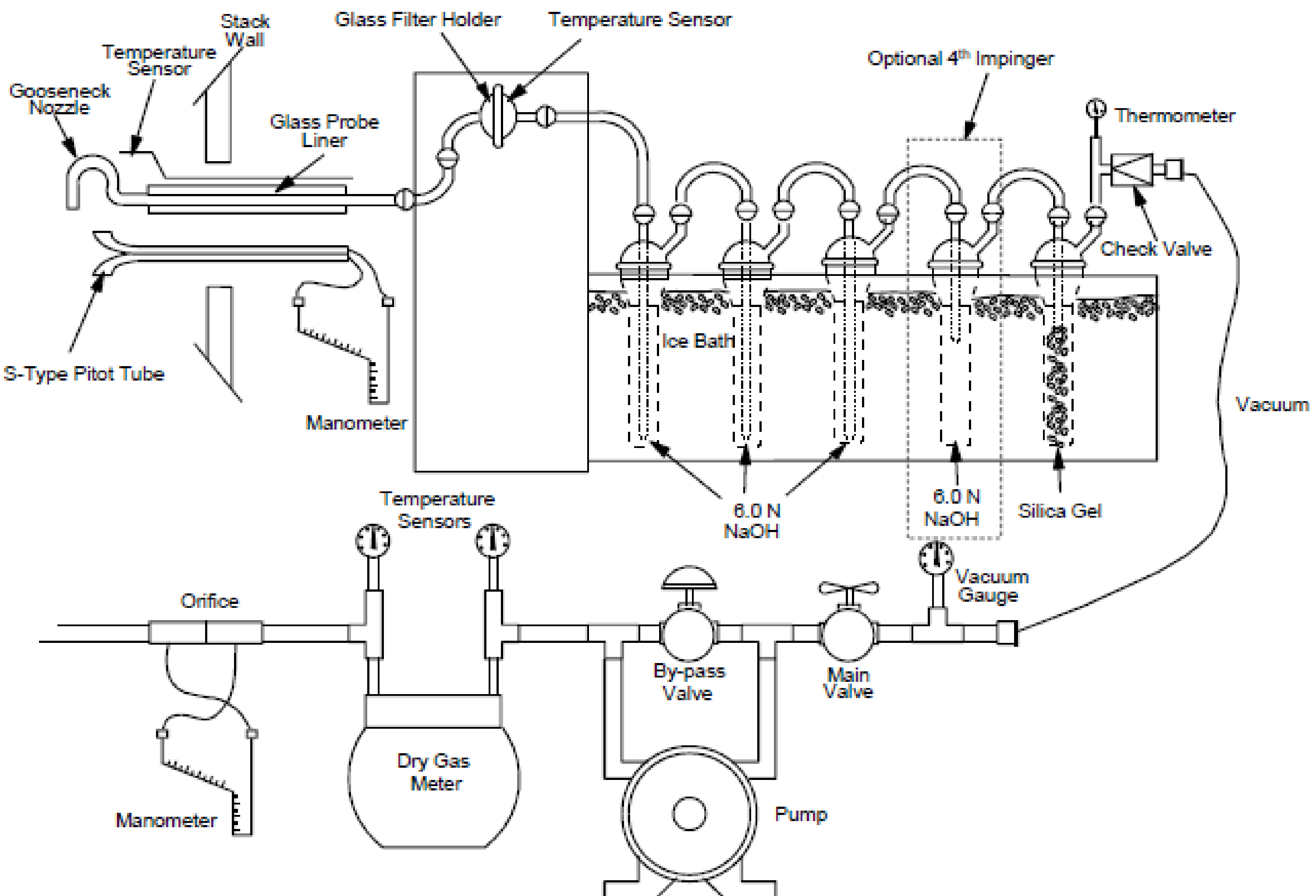

Figure 1. HCN Sampling Train, NaOH Configuration

FIELD DATA SHEET

Run Number ______
Page ____ of ____

Plant	Nozzle Type & ID (in)	Meter Box Number	Diagram of Duct
Date	Filter Holder Setting (°F)	Meter delta H @	
Operator	Probe Heater Setting (°F)	DGM Factor (gamma)	
Sampling Location	Heater Box Setting (°F)	K Factor	
Sample Type	Minimum Sample Volume (ft^3)	Moisture Collected (g)	
Ambient Temperature (°F)	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 (°F)	Orfice Pressure Differential (Delta H . In H_2O)		Probe Temp (°F)	Filter#1 Temp (°F)	Dry Gas Meter Temperature		Impinger Exit Temp (°F)	Pump Vacuum (in Hg)
						Desired	Actual			Inlet (Tm in)	Outlet (Tm out)		
Averages													
Total													
Comments:													

Figure 2: Example Sampling Field Data Form

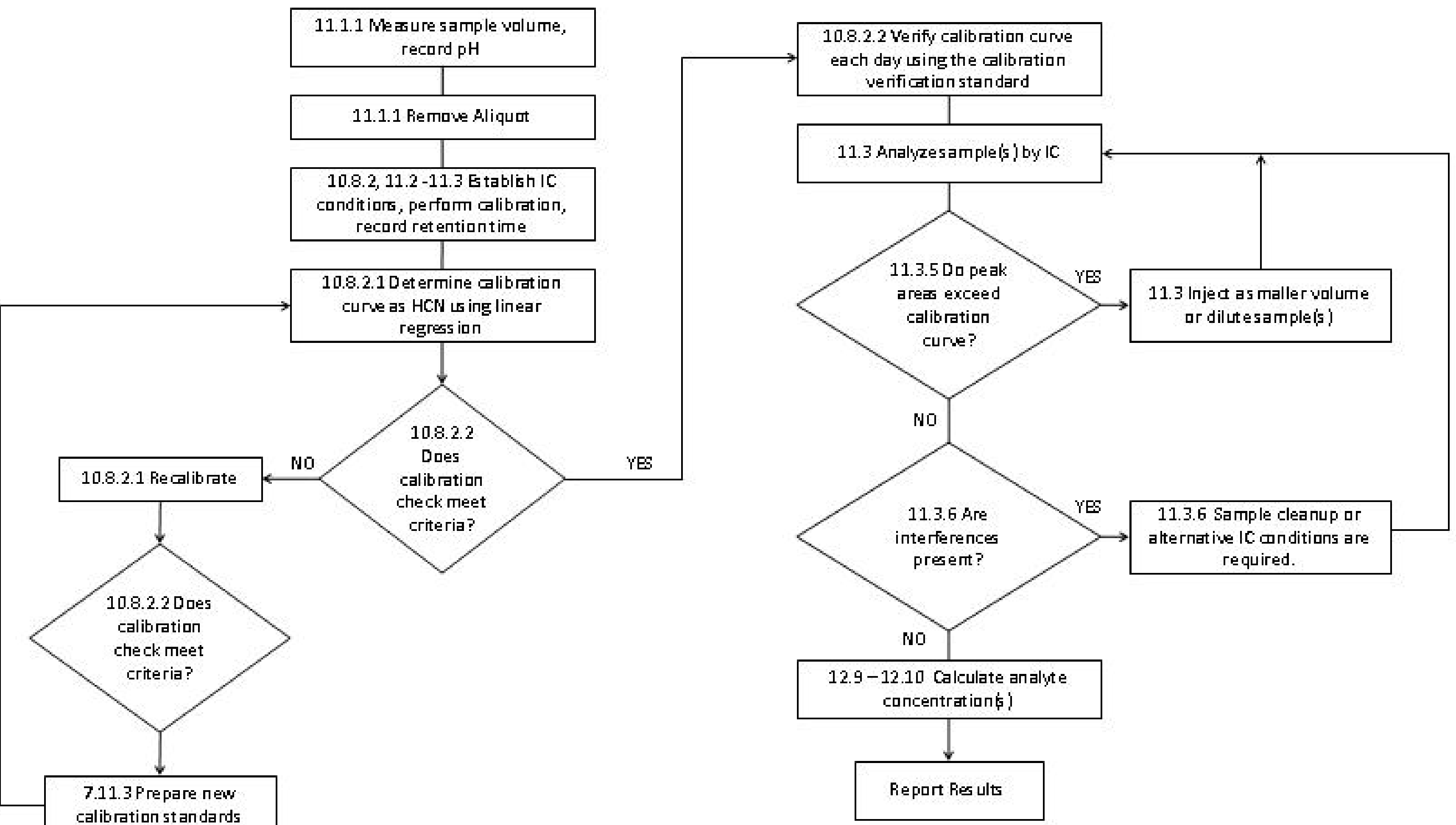

Figure 3. Hydrogen Cyanide by Ion Chromatography (IC)

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 (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 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

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NCASI METHOD ISS/FP-A105.01

IMPINGER SOURCE SAMPLING METHOD FOR ALDEHYDES, KETONES, AND POLAR COMPOUNDS

1.0 Introduction

1.1 Quality Assurance - This method shall be considered conducted only if all quality assurance procedures have been performed and all the results clearly reported in the sampling report. Sufficient data must be presented such that the QA results and calculations are transparent. A summary of QA procedures is provided in the appendix.

1.2 Caveats

This method has not been field validated via EPA Method 301 and is considered a self-validating method.

NCASI strongly suggests that sampling contractors and laboratories conduct train spikes and conduct full trial runs of all sample train configurations prior to use of this method in the field. Failure to do so will greatly increase the probability that quality assurance criteria will not be achieved.

NCASI recommends that mills, sampling contractors, and laboratories carefully review this method and all quality assurance procedures and criteria prior to source sampling. Since spikes will be used as one of the quality assurance procedures, evaluation of source concentration for the analytes of interest needs to be carefully undertaken prior to formulation of the spike solutions. If multiple and varied sources (for example, inlets and outlets of control systems) are to be sampled, multiple spike solutions or varied spike volumes will likely be necessary to meet spiking criteria.

This method was developed to sample the six compounds referred to as “Total HAPs” in the Plywood and Composite Wood Products MACT Rule (Subpart DDDD of 40 CFR Part 63, National Emission Standards for Hazardous Air Pollutants). These six compounds are methanol, phenol, acetaldehyde, acrolein, formaldehyde and propionaldehyde. The method should be capable of measuring a wider range of aldehydes, ketones, and polar organics. The method’s fairly extensive quality assurance procedures will provide feedback on the methods ability to accurately measure a given compound.

1.3 Feedback

NCASI welcomes feedback on this method. Feedback on alternate sampling configurations, alternate lab and field techniques, alternate internal standards, sample handling procedures,

etc. will be appreciated. Feedback on the quality assurance criteria and procedures is also welcome, but keep in mind that this method is a self-validating method. Please submit feedback by e-mail to D_Word@src-ncasi.org.

1.4 Terminology

Procedural steps outlined by this method range from optional to mandated. Actions that are not to be performed are also specified. The following terms will be used within the text of this method in order to clarify these activities:

Term:	The action, activity, or procedural step is…
…must not….	Prohibited
…may…	Optional
…should…	Suggested
…must…	Required

1.4.1 Sample Batch – A grouping of samples.

1.4.2 mg/L - Milligrams per liter.

1.4.3 Sample Run – A sample collection period preceded and followed by quality assurance checks, such as flow rate measurements and leak checks, as specified in this method. The recommended sampling run duration is one hour. However other sample run times may be used if required by the specific sampling or source conditions. If very short or long sample runs are conducted, the minimum measurement level and the capacity of the BHA solution should be considered.

1.4.4 Sampling Event – Three or more consecutive sample runs conducted at a sample location or source type. The term "sampling event" is used in this method primarily with respect to quality assurance (QA) procedures or requirements.

1.4.5 Source Type – Used to describe emissions from a distinct process unit or a group of process units tested at a single location. For example, a rotary dryer and a press, each vented separately, are two distinct source types. Combined exhausts from a dryer and press sampled at a single location is a single source type.

1.4.6 Sample Location – An emissions sampling point or location. For the purposes of the field quality assurance requirements of this method, multiple emission points may be considered to be the same sample location if the emission characteristics (sample matrices) are similar. For example, an exhaust stream split so that it vents to two locations can be considered a single sample location. A press exhausted at three vents can be considered a single sample location. (Since the field quality assurance procedures for a self-validating method are primarily designed to assure the user that the sample method is valid for each source type or sample matrix

sampled, duplication of quality assurance procedures at a single source type with multiple, similar emission points is not required. For a three vent press, for example, only one duplicate sample run, and one run spike (or two bracketed run spikes) would need to be conducted for all three vents.) Note that this definition applies to the quality assurance procedures of this method only and does not imply that a single sample location can be used to adequately characterize a source's mass emission rate.

Control device inlets and outlets cannot be considered a single sample location with similar emission characteristics.

1.4.7 [AQU] – [AQU] indicates analytes in an aqueous matrix.

1.4.8 [HEX] – [HEX] indicates analytes in a hexane matrix.

1.4.9 Minimum Measurement Level (MML) – For this method, NCASI has established a MML of 0.4 mg/L for the [AQU] GC/FID analysis and 0.5 mg/L for the [HEX] GC/NPD analysis. This is a measurement level that all labs should be able to achieve for the six primary analytes: [AQU] methanol, phenol, [HEX] acrolein, acetaldehyde, formaldehyde, and propionaldehyde. Laboratories that wish to conduct a detection limit study and use lower detection limits may do so. Records of the detection limit study should be maintained.

1.4.10 Sampling System Minimum Measurement Level (SSMML) – For this proposed method, the SSMML is calculated based on the MML and source sampling parameters (sample volume, BHA solution volume, and hexane volume). The SSMML will, therefore, vary by sample run. An example is provided in the appendix.

1.4.11 Equivalency – This method allows labs and testers to use alternate procedures if equivalency is established. Equivalency may be established using the criteria provided in EPA Method 301 for paired sample systems ("Comparison with a Validated Method Using Paired Sample Systems"). For this comparison, assume the "Validated Method" is the procedure provided in this method. The proposed, alternative procedure is the "alternative test method." Follow the steps provided in Section 12.0 of EPA Proposed Method 301 (Federal Register, Vol. 69, No. 245, December 22, 2004, pages 76642-76655.

1.4.12 Second Source Standard - A second source or reference standard is a compound or material purchased from a different vendor than that used to prepare the primary stock solution or materials used to make the calibration curves. The second source standard provides a check on the reagents used to make the calibration curves.

2.0 Method ISS/FP-A.105.01

2.1 Principle and Applicability

This method was developed to capture six compounds termed "Total HAPs" in the PCWP MACT. These six compounds are comprised of two alcohols, methanol [67-56-1] and phenol [108-95-2], and four aldehydes, acetaldehyde [75-07-0], acrolein [107-02-8], formaldehyde [50-0-0], and propionaldehyde [123-38-6]. Theoretically, the method can capture a wide variety of aldehydes, ketones, alcohols, and other polar compounds. The method can be used for other compounds provided all QA criteria are met.

The field sampling equipment is relatively simple and very similar to the equipment used for NCASI Method CI/WP-98.01. Sample gas passes through three chilled aqueous impingers containing an o-benzylhydroxylamine (BHA) solution. The carbonyl group of aldehyde compounds reacts with the amine group of BHA forming aldehyde oximes and splitting off water. The alcohols are simply captured by the water and unaffected by the BHA. The aldehyde oximes have limited water solubility and form an emulsion in the bubbling impingers. The oximes may form a slight, somewhat oily layer at the water surface and may also coat the glass walls of the impingers.

The impingers and impinger contents are washed with hexane to extract the oximes. An aliquot of the hexane solution is introduced into a gas chromatograph with a nitrogen-phosphorous detector (GC/NPD) for quantification. The alcohols are determined by direct aqueous injection into a GC with a flame ionization detector (GC/FID).

Since this method contains self-validating procedures and criteria, the applicability is not restricted in terms of compounds or sources. The user must demonstrate the method's precision and accuracy on each source for each compound by conducting train spikes, run spikes, duplicate sample runs, and other procedures as required by the method.

This method is not appropriate for compounds that are insoluble in water or are slightly soluble in water (e.g., benzene). This method should only be used for water soluble compounds.

This method may be used for high moisture sources. But, extremely high moisture sources (greater than 90% moisture content, v/v) should be sampled with consideration to the volume of water that will be collected and the capacity of the BHA solution. Note that condensers, if used, will not contain BHA and the aldehydes captured in the condenser will not react with BHA until the condenser contents and the impinger solution are mixed in the sample bottle. Sufficient BHA must be available in the final mixture to derivitize the aldehydes and ketones.

This method should not be used on sources where significant amounts of entrained water droplets are present unless it is used in an isokinetic manner. There is potential, within the source ducts or stacks, for alcohols and aldehydes to concentrate in water droplets. Failure to capture a representative amount of water droplets can bias the results. Theoretically, isokinetic sampling will capture a representative portion of the water droplets. This method

may be used isokinetically if all QA/QC procedures are conducted and all QA/QC criteria are met. The flow rate to BHA solution volume ratio must be within the range discussed in Section 2.2.5, and care must be taken to avoid exceeding the capacity of the BHA solution. If the flow rate to BHA solution volume ratio exceeds 1000:1, it is recommended that train spikes be conducted prior to any field work and that the spiking solution be near or above the upper limits of the expected source. Additionally, BHA capacity calculations should be conducted.

Lab analyses must be conducted by or under the supervision of analysts experienced in the use of gas chromatographs and skilled in the interpretation of chromatograms.

2.2 Apparatus

This method allows substantial flexibility, but certain equipment or equipment operational parameters are mandated. Follow the nomenclature discussed in Section 1.4 (i.e., must, should, etc.) relative to field equipment, laboratory equipment and operational parameters. The sample train used in development of this method is based on NCASI Method CI/WP-98.01 and uses midget impingers and a critical orifice to regulate the sample flow rate. However, this method allows the use of alternative equipment and/or train configurations. For example, the midget impingers could be replaced with Greenburg-Smith design impingers or a dry gas meter could be used to measure sample gas volume. The following description, therefore, applies to the sample train as used by NCASI in Method CI/WP-98.01. Alternative configurations must incorporate components that will achieve the basic premise of the sample train design of filtering the sample gas stream at 250 ± 25°F followed by sample capture by the BHA solution in impingers.

2.2.1 Heated Sample Probe – The sample system must have a heated probe maintained at 250 ± 25°F. The probe must be constructed of stainless steel tubing or an equivalent inert material such as Teflon or glass.

2.2.2 Heated Filter Box – The sample system must have a heated filter box that is directly connected to the heated probe. The heated filter box must be maintained at 250 ± 25°F. The filter housing and connections may be made of stainless steel or an equivalent material, and the filter may be Teflon or an equivalent material. A thermocouple must be connected near or within the filter housing to record the filter housing or filter temperature. If two impinger trains are connected to one sample probe and heated filter box, the location at which the sample gas splits must be within the heated zone of the filter box. This filter box configuration would have an outlet connection for each impinger train.

2.2.3 Sample Line – An unheated Teflon line should be used to convey the sample from the back of the heated filter box to the first impinger. Care should be taken to avoid any condensation within the filter box, including insulating the connections at the heated box/unheated Teflon line junction.

2.2.4 Impingers – The sample line must be connected to three or more chilled impingers in series in an ice or ice/water bath. The impingers should have regular tapered stems or equivalent. All impinger train connectors should be glass and/or Teflon. The impinger size is not specified by this method, allowing midget impingers to large impingers. A condenser may be used prior to the first impinger, but all liquid and rinse from the condenser must be composited with the impinger liquid sample. Additionally, an impinger containing silica gel or another drying agent may be used after the three BHA impingers. This impinger and its contents do not have to be evaluated for capture of the compounds of interest.

2.2.5 Sample Flow Rate and Impinger Solution Volume – The ratio of sample gas flow through the impingers to the initial BHA solution volume (both expressed as milliliters) must be between 200:1 to 4000:1 (e.g., 30,000 mL of sample gas through the three impingers containing a total of 75 mL of BHA solution = 400:1). Note that this is a very wide ratio range. At the upper ratios, sampling companies should conduct calculations to evaluate the ability of the BHA solution to derivitize the aldehydes expected from the source (BHA capacity calculations). A general 'rule of thumb' is that no more than 10% of the capacity of the derivitizing solution should be used. However, since this is a self-validating method, sampling companies may exceed the 'rule of thumb' at their own risk. Sampling companies should conduct train spikes, before going into the field, to demonstrate that the sampling train can operate effectively at the upper ratios with the highest level of emissions expected in the field.

NCASI's work with this method has been conducted using three small impingers containing 75 mL of BHA solution and operating at a sampling rate of 500 mL/minute for one hour.

2.2.6 By-pass Valve – A by-pass valve may be located downstream of the flow rate control device (e.g. critical orifice) to alleviate the need to turn off the sample pump during off-line periods such as during leak checks or standby periods.

2.2.7 Variable Area Flow Meter – A flow meter should be placed in line after the impingers for a flow check during sampling.

2.2.8 Flow Control Device – A calibrated critical orifice or equivalent device should be used to maintain a steady flow rate through the collection train. Sample flow rate may be established by the use of a critical orifice and pre- and post-flow measurements. Also, the total sample flow may be established by a dry gas meter.

2.2.9 Vacuum Gauges – To provide a visual verification during a sample run that the flow through the critical orifice remains critical, two vacuum gauges should be placed on each side of the critical orifice capable of reading 25 inches of mercury gauge (in. Hg).

2.2.10 Vacuum Pump – The critical orifice must be followed by a pump or other device to pull the sample gas through the impingers. The pump or device must be capable of providing a vacuum of about 18 inches of mercury and must be able to maintain critical conditions at the orifice (a difference in pressure of about 15 inches of mercury). Other equivalent systems to insure steady-state flow through the impingers may be used, but these systems **must** be described in the report along with a discussion of their ability to maintain steady-state flow.

2.2.11 Thermometer – A calibrated thermometer is used to measure the ambient temperature.

2.2.12 Barometer – A calibrated barometer is used to measure atmospheric pressure.

2.2.13 Sample Bottles – Samples must be stored in glass bottles with Teflon-backed lids or equivalent lids. Plastic or other non-glass sample bottles cannot be used.

2.2.14 Laboratory Glassware and Supplies

2.2.14.1 Separatory funnels

2.2.14.2 Autosampler vials capable of holding 2 mL

2.2.14.3 Volumetric flasks

2.2.14.4 Volumetric pipets

2.2.14.5 Syringes

2.2.15 Analytical Equipment – Equipment in this section (all of Section 2.2.15) should be used unless equivalency is established. Records of equivalency must be maintained. Although detectors other than NPD could be used for detection of oximes in hexane, it is strongly suggested that laboratories use an NPD and mandatory that an equivalency test be conducted for any other detector used. Records of such an equivalency test must be maintained. Deviations from the use of a NPD must be recorded in the test report.

2.2.15.1 [AQU] GC System - GC analytical system with a purged packed injection port. A split/splitless injection port may be used if equivalency is established, but the MML and SSMML for methanol and phenol must be considered (see appendix).

2.2.15.2 [AQU] Guard Column - 10 m x 0.53 mm deactivated fused silica capillary column.

2.2.15.3 [AQU] Column – 60 meter or longer x 0.53 mm x 3 µm, 6% cyanopropylphenyl, 94% dimethylpolysiloxane bonded phase (624 phase) fused

silica capillary column (e.g., J&W Scientific DB-624, Hewlett Packard HP-624). Other columns may be used if equivalency is demonstrated.

2.2.15.4 [AQU] GC Detector - Flame ionization detector with appropriate data system.

2.2.15.5 [HEX] GC System - GC analytical system with split/splitless injection port.

2.2.15.6 [HEX] Guard Column - 10 m x 0.53 mm deactivated fused silica capillary column.

2.2.15.7 [HEX] Column - 30 m x 0.25 mm x 0.25 µm film RTX-200 fused silica capillary column (Restek or equivalent) or other column shown to be capable of resolving the analytes of interest.

2.2.15.8 [HEX] GC Detector – Nitrogen phosphorus detector (NPD) with appropriate data acquisition system.

2.3 Reagents

2.3.1 Chemical Quality - Reagent grade compounds or the highest purity available must be used.

2.3.2 DI Water - Deionized water quality is verified in the [AQU] GC/FID blanks.

2.3.3 [AQU] Primary Internal Standard – Cyclohexanol [108-93-0] or 2,2,2-trifluoroethanol [75-89-8].

2.3.4 [HEX] Primary Internal Standard –Nitrobenzene [98-95-3].

2.3.5 [HEX] Surrogate Standard – Methoxypropanone [5878-19-3] may be used as a surrogate standard.

2.3.6 Hexane - Hexane must be used to rinse the impingers in the field and extract the samples in the laboratory. Hexane should be reagent grade or better. Alternate extraction solvents may be used only after equivalency has been established.

2.3.7 Isopropanol and Methylene Chloride – Isopropanol and methylene chloride are used to wash the impingers and separatory funnels between samples. Isopropanol removes left over water and methylene chloride removes the isopropanol and any residual hexane and allows rapid drying. Reagent grade or better methylene chloride and isopropanol should be used. Equivalent, less toxic, substitutes for methylene chloride may be used but hexane and isopropanol must be soluble in the substitute solvent.

2.3.8 o-Benzylhydroxylamine – o-Benzylhydroxylamine is purchased as o-benzylhydroxylamine hydrochloride (BHA-HCl). This chemical should be reagent

grade or better. o-Benzylhydroxylamine (BHA) sampling solutions are made by dissolving 30 grams of BHA-HCl in a liter of DI water. (Note that the solubility is about 40 to 50 grams per liter at lab temperatures). Care should be taken to prevent ambient sources of aldehyde from reacting with the BHA solution. Keep the solution sealed and refrigerated.

A liter aqueous solution containing 30 grams of BHA is 188 millimolar. At a sampling ratio of 200:1 (see Section 2.2.5) this solution has a capacity to sample a gas stream of about 22,500 ppmvd of formaldehyde (assuming formaldehyde is the only aldehyde or ketone in the gas stream). For a ratio of 1000:1 the capacity is reduced to about 4,500 ppmvd of formaldehyde. This system should not be operated at levels approaching full capacity. A "rule of thumb" is no more than 10% of capacity. Since the method is a self-validating method, sampling companies may operate at conditions exceeding the 'rule of thumb' at their own risk.

2.3.9 [AQU] Primary Aqueous Internal Standard – Cyclohexanol [108-93-0], 2,2,2-trifluoroethanol [75-89-8], or an equivalent compound can be used as the internal standard.

2.3.9.1 [AQU] Cyclohexanol Internal Standard Solution – Prepare the aqueous [AQU] internal standard primary spiking stock solution by adding 3.12 mL cyclohexanol to a tared 100 mL ground glass stoppered volumetric flask filled to approximately 90 mL with DI water, taking care to inject the cyclohexanol directly into the water. Weigh the flask after the addition of the cyclohexanol and record the weight to the nearest 0.1 mg. Fill the flask to 100 mL with DI water. Assuming 100% compound purity, this will result in a nominal 30,000 mg/L [AQU] internal standard primary spiking stock solution. Compute the exact concentration (mg/L) using the weight gain and actual purity. The solution can be stored at room temperature for up to 6 months.

2.3.9.2 [AQU] 2,2,2-Trifluoroethanol Internal Standard Solution – Prepare the aqueous [AQU] internal standard primary spiking stock solution by adding 2872 µL of 2,2,2-trifluoroethanol to a tared 100 mL ground glass stoppered volumetric flask filled to approximately 90 mL with DI water, taking care to inject the 2,2,2-trifluoroethanol directly into the water. Weigh the flask after the addition of the 2,2,2-trifluoroethanol and record the weight to the nearest 0.1 mg. Fill the flask to 100 mL with DI water. Assuming 100% compound purity, this should result in a nominal 40,000 mg/L [AQU] internal standard primary spiking stock solution. Compute the exact concentration (mg/L) using the weight gain and actual compound purity. This solution must be stored in a refrigerator and held no longer than 6 months.

2.3.10 [HEX] Hexane Internal Standard Solution – Nitrobenzene [98-95-3] or an equivalent compound can be used as the internal standard.

2.3.10.1 [HEX] Preparation of the Hexane Internal Standard – Prepare the hexane based [HEX] internal standard primary spiking stock solution by

adding 1672 μL of pure nitrobenzene to a tared 100 mL ground glass stoppered volumetric flask filled to approximately 90 mL with hexane, taking care to inject the nitrobenzene directly into the hexane. Weigh the flask after the addition of the nitrobenzene and record the weight to the nearest 0.1 mg. Fill the flask to 100 mL with hexane. Assuming 100% compound purity, this should result in a nominal 20,000 mg/L [HEX] internal standard primary spiking stock solution. Compute the exact concentration (mg/L) using the weight gain and actual purity. This solution must be stored in a refrigerator and held no longer than 12 months.

2.3.11 [AQU] Alcohol Primary Stock Solution – Fill a 100 mL ground glass stoppered volumetric flask to approximately 90 mL with DI water. Tare the flask after the addition of the water. Using a syringe or equivalent device, add 126 μL of methanol, taking care to inject the methanol directly into the water. Weigh and record the weight gain to the nearest 0.1 mg. Add 100 mg phenol. Weigh and record the weight gain to the nearest 0.1 mg. Fill flask to the mark. Assuming 100% purity, this will result in a nominal 1,000 mg/L methanol and 1,000 mg/L phenol primary stock solution. Use the weight gain and the compound purity to compute the exact compound concentrations. An alternative would be to purchase a primary stock solution from a chemical reference supply company. The primary stock solution must be stored in the refrigerator and must be re-prepared monthly. The storage time of sealed or nitrogen blanketed standard solutions has not been evaluated at this time. Longer storage time may be allowed in cases where data are provided that supports it.

2.3.11.1 Alcohol Calibration and Matrix Spike Solutions – Prepare calibration standard solutions by dilution of the calibration primary stock solution using syringes or volumetric pipettes to measure the required aliquots of primary standard. The required dilutions are shown below. Prepare matrix spike solutions by calculating the concentration of analytes desired and diluting the primary stock solution.

μL of Stock Solution to Add to 10 mL Volumetric Flask	Resulting Methanol and Phenol Concentration, (mg/L)
1,000	100
500	50
250	25
100	10
50	5
10	1
4	0.4

2.3.12 Aldehyde Primary Stock Solution – Fill a 100 mL ground glass stoppered volumetric flask to approximately 90 mL with DI water. Tare the flask after the addition of the water. After each addition of analyte, weigh and record the weight gain to the nearest 0.1 mg. Using a syringe or equivalent device, add 127 µL of acetaldehyde, taking care to inject the acetaldehyde directly into the water. In a like manner, add 119 µL acrolein, 250 µL formalin, and 126 µL of propionaldehyde. Once all the analytes have been added, fill the flask to the mark. Assuming 100% compound purity and exactly 37% formaldehyde in the formalin, this will result in a nominal 1,000 mg/L acetaldehyde, 1,000 mg/L acrolein, 1,000 mg/L formaldehyde, and 1,000 mg/L propionaldehyde. Use the measured weight gains and actual compound purity to compute the exact analyte concentrations.

Note that acetaldehyde and propionaldehyde are extremely volatile and degrade as compounds over time. Acrolein, while less volatile, degrades as a neat compound and in aqueous solutions. A chilled (freezer temperature) gas-tight syringe should be used to deliver the neat compounds to the volumetric flask. Acrolein and acetaldehyde are also best kept in a freezer and measured at freezing temperatures. The syringe and neat compounds should be approximately the same temperature. New neat compounds or standards for acetaldehyde, acrolein, and propionaldehyde should be obtained when the second source standard requirement is not met using freshly prepared standards. An alternative would be to purchase a primary stock solution from a chemical reference supply company. The formalin solution should be checked to verify the actual formaldehyde concentration. Also, the formalin solution contains methanol at approximately 12% for stability and solubility purposes. This quantity of methanol should be considered for any instance in which the aldehyde and alcohol standards or spike solutions are mixed.

The aldehyde primary stock solution must be stored in the refrigerator and must be re-prepared monthly. The solution may need more frequent preparation for acrolein. The storage time of sealed or nitrogen blanketed standard solutions has not been evaluated at this time. Longer storage time may be allowed in cases where data are provided that supports it.

2.3.12.1 Aldehyde Calibration and Matrix Spike Solutions – Prepare calibration standard solutions by dilution of the calibration primary stock solution using syringes to measure the required aliquots of primary standard. The required dilutions are shown below. Prepare matrix spike solutions by calculating the concentration of analytes desired and diluting the primary stock solution.

µL of Stock Solution to Add to 10 mL Volumetric Flask	Resulting Formaldehyde, Acetaldehyde, Acrolein, and Propionaldehyde Concentration (mg/L)
1,000	100
500	50
250	25
100	10
50	5
10	1
5	0.5

2.4 Quality Assurance Procedures and Requirements – Laboratory and Field Testing

2.4.1 Laboratory Quality Assurance Procedures and Requirements

2.4.1.1 GC Maintenance

2.4.1.1.1 [AQU] [HEX] Injector Maintenance – The septum and injection liner should be replaced when necessary. If this is not done, retention time shifts and peak broadening can occur.

2.4.1.2 GC Performance and Quality Assurance Requirements – This section provides quality assurance (QA) procedures that must be conducted by the laboratories unless otherwise specified. The results of these procedures must be compared to the QA criteria and clearly reported. Sufficient data must be presented such that the QA results and calculations are transparent.

2.4.1.2.1 [AQU] [HEX] Laboratory Blank Sample – One method blank must be prepared per analytical batch to demonstrate that all materials are interference-free, and must be analyzed prior to further analyses. The concentration of the analytes in the blank should be below 0.5 mg/L for the [HEX] samples and below 0.4 mg/L for the [AQU] samples. Blank samples must include the appropriate internal standard.

2.4.1.2.2 [AQU] [HEX] GC Calibration Verification Standard – The calibration verification standard shall be the mid-range calibration standard. This calibration check must be performed prior to analysis of the sample batch, after every 10 source samples analyzed, and at the end of the sample batch. A calibration check is conducted to verify that the GC system is operating within acceptable parameters. The concentrations of the

analytes should be within ±15% of the expected concentrations. Additionally, the response (peak area) of the verification standard should be within 30% of the peak area of the mid-range calibration standard and the peak area of the internal standard should be within 30% of the mean peak areas of all calibration standards. For example, if a 50 mg/L mid level standard for methanol had a peak area of 60,000 and the cyclohexanol internal standard mean peak area was 30,000, the calibration verification standard should have an analytical value between 42.5 and 57.5 mg/L, a methanol peak area between 42,000 and 78,000 and a cyclohexanol peak area between 21,000 and 39,000.

If the criteria are not met, the GC system may require maintenance. If routine maintenance does not correct the problem, a new standard prepared from a fresh calibration stock solution should be run. If this still fails, the instrument will need to be recalibrated.

2.4.1.2.3 [AQU] [HEX] Laboratory Duplicates – One laboratory duplicate of a source sample must be analyzed. Additional laboratory duplicates must be analyzed for every 10 source samples analyzed. Duplicates are a replicate sample analysis of the same source sample. The percent difference of the duplicate concentrations should be within 20%. Percent difference is calculated as the difference between the two samples divided by the average of the two samples.

2.4.1.2.4 [AQU] [HEX] Matrix Spike Recovery (optional) – A matrix spike may be prepared for each batch of samples. Using the mean concentration determined by the replicate analyses or the level determined from a single measurement, determine the spiking level which will give 0.5 to 10 times the sample concentration. If the sample does not have detectable levels of analytes, spike the sample at approximately five times the lowest calibration level of the instrument. Spike the sample with the determined amount of the calibration standard/matrix spike solution and analyze the sample in the normal manner.

Calculate the percent recovery using Equation 2.1.

Equation 2.1

$$R = \left(\frac{C_S - C_N}{C_T} \right) \times 100$$

Where:

R = percent recovery of matrix spike
C_S = measured concentration of spiked sample
C_N = measured concentration of native sample
C_T = theoretical concentration of spike

2.4.1.2.5 [AQU][HEX] Second Source or Reference Standard – Analysis of a second source or reference standard is required for each analyte for each batch of samples. The reference standard should be approximately the same concentration as the calibration verification standard. The percent recovery of the second source standard should be 70 to 130%. If it is not, the lab should prepare a new standard or perform instrument maintenance. If necessary, recalibrate the instrument.

In the case of aldehyde or ketone oximes, a second source standard may be unavailable. If unavailable, a second source standard may be made in the lab from aldehydes or ketones purchased from a source other than the one from which the calibration standards, or calibration materials, were purchased.

2.4.2 Field Testing Quality Assurance Procedures – This section provides quality assurance (QA) procedures that must be conducted. The results of all these procedures must be compared to the criteria and clearly reported in the test report. Sufficient data must be provided such that the QA results and calculations are transparent.

Users of this method are required to implement the field testing quality assurance procedures in this section. Quality assurance measures are conducted prior to, during, and/or after field testing to provide a means of evaluating the quality of sampling conducted. Note that this method also requires laboratory quality assurance procedures as covered in the above Section 2.4.1.

The field quality assurance procedures for this method require: (1) a field blank, (2) a duplicate sample run, (3) a run spike(s), (4) a train spike, and (5) the associated field spikes for each sampling event at each sample location (defined in Section 1.4). These field quality assurance procedures are defined in this section and criteria are specified where applicable. Further, this method establishes criteria for the level or relative magnitude of the spikes, termed “equivalent spiking level,” as defined in Section 2.4.2.1.

The field quality assurance procedures are somewhat complicated and need to be planned well in advance of arriving at the facility to conduct testing. As indicated in the introduction to this method, it is strongly suggested that two qualification train spike runs be conducted in the sampling company’s office or laboratory prior to any

field work. Furthermore, laboratory trials of the duplicate and run spikes should be conducted prior to actual testing to acclimate the sampling crew(s) to the requirements of this method.

2.4.2.1 Equivalent Spiking Levels – All spikes introduced into the sample trains, either as a train spike (Section 2.4.2.6) or run spike (Section 2.4.2.5), have an "equivalent spiking level." This is defined as the compound concentration that would result if the spike were present in a dry standard gas (air) of the same volume as the sample gas volume of the spiked sample trains as shown in Equation 2.2. For example, assume a spiked sample train operates at a dry standard flow rate of 500 mL per minute for one hour (30 liters, total) and a 1 mL spike is introduced that contains 100 mg/L (µg/mL) of methanol. 100 µg of methanol in 30 liters of gas yields an equivalent spiking level of 2.50 ppmvd of methanol. This is a theoretical, calculated concentration in air - not a measured concentration.

Equation 2.2

$$ESL_{ppmvd} = \frac{(\mu g\ Field\ Spike)(24.04)}{(L\ Sample Vol_{spiked\ train})(Cmpd.MW)}$$

Where:

ESL = Equivalent Spiking Level
µg Field Spike = µg of Compound in Field Spike
L Sample $Volume_{spiked\ train}$ = Liters of Sample Volume for Spiked Train
Cmpd. MW = Compound Molecular Weight

Ideally, the spike solution used for single run spikes would yield an equivalent spiking level that matches the source concentration for each compound. This, of course, is impossible. But, efforts should be made to match the equivalent spiking level to the source gas concentration. This method sets criteria for equivalent spiking levels for single run spikes and bracketed run spikes. Labs and/or sampling companies should estimate the source concentrations for every compound to be sampled at every source, and a spike solution should be formulated for each source that provides equivalent spiking levels near the source concentrations. Equivalent spiking levels that are very small relative to the source concentration make it very difficult to obtain good spike recoveries. Equivalent spiking levels that are very large relative to the source concentration make it easy to obtain a good spike recovery but do not necessarily demonstrate sampling proficiency. For this reason, NCASI has established criteria for equivalent spiking levels for this method. This method also allows bracketed spikes intended to help the user for cases in which the source concentration cannot be closely estimated.

The verification of an equivalent spiking level used for a particular sample event can only be accomplished after the run spike results have been compiled. For a run spike, the results provided by the non-spiked (or normal) impinger train will determine the *actual* source gas concentration for a targeted compound. The equivalent spiking level will be calculated using the results from analysis of the field spike and the gas sample volume of the spiked sample train. (The mass of compound in the field spike, determined from lab analysis, is used as the spiked mass for calculation of the equivalent spiking level.)

To check whether an equivalent spiking level meets the method criteria for a **single run spike**, select the appropriate concentration range in the left column of Table 2.1, then determine the maximum equivalent spiking level allowed for that concentration range as indicated in the right column of the table. The equivalent spiking level for a single run spike compound must be within the specified limits.

For **bracketed run spikes** the equivalent spiking level criteria are provided in Table 2.2. Bracketed run spikes are discussed in Section 2.4.2.5.3.2.

Table 2.1 Single Run Spike Criteria for Equivalent Spiking Levels

If the *actual* source gas concentration of a targeted compound is…..	Then the equivalent spiking level for that targeted compound must be at or greater than the sample system minimum measurement level and….
…less than 0.5 ppmvd	….. no more than 2 ppmvd.
…between 0.5 to 1.5 ppmvd	….. no more than 6 ppmvd.
…is greater than 1.5 ppmvd	….. no more than four times the source concentration.

Table 2.2 Bracketed Run Spike Criteria for Equivalent Spiking Levels

Spiking Level	Criterion
Low Equivalent Spiking Level	Should be less than the source gas concentration. Must be no more than 5 times the actual source gas concentration, in order to be used in the spike recovery calculation
High Equivalent Spiking Level	Must be less than or equal to 10 times the actual source gas concentration, in order to be used in the spike recovery calculation

2.4.2.2 **Field Blank** – There must be at least one field blank per facility or

mill tested. The field blank is simply a sample bottle containing the BHA sampling solution. This bottle is taken out to the field, labeled, opened, hexane is added, and then it is handled along with the other sample bottles. The field blank must be extracted and analyzed along with the other samples collected by this method and the results reported in the source sampling report. NCASI recommends that one field blank be prepared per day so that more than one blank is available for analysis.

2.4.2.3 Duplicate Sample Run or Duplicate - One duplicate sample run must be conducted per sampling event at each sampling location (see Section 1.4.6 – a "location" may include more than one emission point). A common sampling configuration used to conduct a duplicate sample run will be to connect two separate impinger trains to a single probe and filter box. Two complete sampling trains may also be used. Alternative configurations for conducting a duplicate sample run can be used if the duplicate sample run criteria are met.

2.4.2.3.1 Notes Regarding Duplicate Trains – (1) Leak checks of duplicate trains are a common source of field error. Make sure that the impinger trains are isolated prior to leak checks. (2) Both impinger trains for a duplicate sample run should start and end the sample run at approximately the same time. (3) The results from duplicate sample trains must be reported as an average according to Section 2.4.2.3.2.

2.4.2.3.2 Reporting Results from Duplicate Sample Trains – The results from the two sample trains are averaged and reported. If either or both sampling trains are below the SSMML, the results should be reported according to the applicable regulation or as required by the applicable regulatory authority. The sampling report should include the individual results from the two trains in the report's QA/QC section.

2.4.2.3.3 Calculation of Percent Difference for a Duplicate Sample Run – Calculate the difference between the source gas concentration obtained from the two sample trains and divide by the average concentration as shown below. Note that the masses of the compounds collected in the two trains are not compared.

$$\%\,difference = Abs\left|\frac{Train1_{ppmvd} - Train2_{ppmvd}}{Average\left(Train1_{ppmvd}, Train2_{ppmvd}\right)}\right|$$

The percent difference is not calculated for cases in which the

compound concentration from one or both impinger trains is below the SSMML.

2.4.2.3.4 Duplicate Difference Criteria – Calculate the source gas concentration for each of the targeted compounds from the duplicate sample trains and determine the applicable duplicate difference criteria shown in Table 2.3. Clearly report the percent difference and compare it to the applicable criteria for each compound and for each sample event. Sufficient data must be presented such that the calculations are transparent.

Table 2.3 Duplicate Criteria

If the average source gas concentration for the duplicate sample run is….	Then the duplicate difference should be…...
…less than 0.5 ppmvd	…..equal to or less than 50%
…between 0.5 to 1.5 ppmvd	….equal to or less than 40%
…greater than 1.5 ppmvd	….equal to or less than 30%

2.4.2.4 Field Spike – Prepare one field spike for each run spike and train spike. The field spike is important because the mass collected in a spiked impinger train will be compared against the mass in the field spike for spike recovery purposes.

A field spike must be collected during or immediately after a run spike or a train spike. To collect a field spike, select an unused sample bottle containing BHA sampling solution and record the bottle ID and weight information on the field sheet used for the spiked QA sample run (or equivalent). Inject the same spike volume used for the run spike into the field spike sample bottle. Seal the container and allow it to sit at ambient temperature for 15 minutes or place in an ice chest or refrigerator for one hour. Add hexane to the sample bottle in an amount equivalent to the amount of hexane used for the impinger rinse of the spiked train (Section 2.5.2). Store and handle this sample with the other samples for analysis.

2.4.2.5 Run Spike – The run spike quality assurance requirement can be met by conducting either (1) a single run spike or (2) a bracketed run spike for each sampling event. For the run spike, a spike solution is introduced into one of the two impinger trains (referred to as the spiked train) to determine if the spiked mass can be recovered. The solution spiked into the sample train must meet the equivalent spiking level criteria (Section 2.4.2.1). Run spike recovery criteria are provided in Table 2.4.

Table 2.4 Spike Recovery Criteria

If the Actual Source Concentration is…..	Spike Recovery Range…..
…less than 0.5 ppmvd	…should be between 50 and 150%
…between 0.5 to 1.5 ppmvd	…should be between 60 and 140%
…greater than 1.5 ppmvd	…should be between 70 and 130%

A common sampling configuration used to conduct a run spike will be to connect two separate impinger trains to a single probe/filter box. Two complete sampling trains may also be used. Alternative configurations for conducting a run spike can be used if the spike recovery criteria can be met.

Note that for the run spike, the figure in the appendix shows that the spiked train is equipped with a spiking tee at the inlet to the first impinger. Alternatively, the spiking solution can be introduced into the impinger prior to beginning the run (but before the leak check). Note, however, that relatively slow introduction of the spiking solution during the sample run more closely emulates sampling conditions and may increase the chances of a successful spike recovery. NCASI recommends slow introduction of the spike solution by syringe through a tee and septa during the first 10 to 30 minutes of the run spike.

2.4.2.5.1 Notes Regarding Run Spikes – (1) Single run spikes must meet the equivalent spiking level criteria in Table 2.1. (2) The criteria for bracketed run spikes are more complicated (Table 2.2 and Section 2.4.2.5.3.2). (3) Each run spike must have an associated field spike (Section 2.4.2.4). (4) The spiked and non-spiked (referred to as "normal") sample trains and associated samples should be separately labeled and named. (5) Like duplicates, trains must be isolated during leak checks (Section 2.5.8.1). (6) Run spikes evaluate both accuracy and precision and, therefore, are typically more difficult than train spikes and duplicates. (7) The source gas concentration for a run spike will be based on the result obtained from the normal (non-spiked) impinger sample train.

2.4.2.5.2 Spike Recovery Calculation – The percent recovery calculation for the run spike has three basic steps. (1) The compound concentration obtained from the normal train is subtracted from the compound concentration obtained from the spiked train. (2) The resulting concentration difference is then multiplied by the gas sample volume of the spiked sample train (with appropriate conversion factors) to obtain the mass of the spike that was recovered. (3) The mass recovered is divided by the mass spiked and expressed as a percent recovery as shown in Equation 2.3.

Equation 2.3

$$Net\ Mass\ Recovered_{[i]} = \left(Concentration_{spiked\ train[i]} - Concentration_{normal\ train[i]}\right)$$
$$\times Sample\ Volume_{spiked\ train\ std[i]}\ x\ Conversion\ Factors$$

$$Spike\ Recovery_{[i]} = \frac{net\ mass\ recovered_{spiked\ train[i]}}{mass_{field\ spike[i]}}$$

For example, assume the normal sample train and spiked sample train have methanol concentrations of 2.5 and 5.5 ppmvd, respectively. Also, assume the spiked train had a dry standard sample volume of 30 liters and that 100 µg of methanol was spiked into the spiked train ($mass_{field\ spike}$) as determined from the field spike. The concentration difference between the two trains is 3.0 ppmvd. Multiplying the 3 ppmvd value by 30 liters and applying appropriate conversion factors yields a mass $recovered_{spiked\ train}$ of 120 µg of methanol. The final spike recovery is 120/100 * 100 = 120%. Note that the mass in the normal train cannot be subtracted from the mass of the spiked train (in the first step) because the two sample trains do not typically have the same sample volumes.

An alternative, simple, but perhaps less intuitive, means of calculating the spike recovery is shown in Equation 2.4.

Equation 2.4

$$Spike\ Recovery_{[i]} = \frac{\left(Concentration_{spiked\ train_{[i]}} - Concentration_{normal\ train_{[i]}}\right)}{ESL_{[i]}}$$

Where:

ESL = Equivalent Spiking Level (Section 2.4.2.1)

A spike recovery is not calculated for a targeted compound if the *actual* source gas concentration for that compound is measured below the SSMML in the normal impinger train.

2.4.2.5.3 Spike Recovery Criteria – This method provides two options for run spikes: (i) the single run spike and (ii) the bracketed run spike. The spike recovery result from either of these procedures should be compared to the criteria in Table 2.4. The

spike recovery results must be compared to the criteria and clearly reported. Sufficient data must be presented such that the results and calculations are transparent.

2.4.2.5.3.1 Single Run Spike – If a single run spike is conducted, the spike must meet the equivalent spiking level criteria provided in Table 2.1 and the spike recovery should meet the criteria in Table 2.4. The single run spike should be conducted when the user is familiar with the source and expected analyte concentrations. If the user cannot estimate the analyte concentrations of the source gas, bracketed run spikes are recommended.

2.4.2.5.3.2 Bracketed Run Spikes – This section provides rules for calculating the spike recovery from bracketed run spikes. The bracketed run spike is used when the concentration of the source gas at a source type is variable or not easily estimated. For this option, two run spikes will be required for each sample event.

A low level run spike should be conducted at a low equivalent spiking level anticipated to be *below* the *expected* source gas concentration but above SSMML for the targeted compound.

The high level run spike should be conducted at a high equivalent spiking level anticipated to be *above* the *expected* source gas concentration, but no more than 10 times the source gas concentration.

The following **rules** must be used for calculating the spike recovery for the bracketed run spike option:

Rule 1. If the low equivalent spiking level is determined to be greater than 5 times the *actual* source gas concentration and the high equivalent spiking level is less than or equal to 10 times the *actual* source gas concentration for a targeted compound, then the *high* level run spike is used in determining the spike recovery.

Rule 2. If the low equivalent spiking level is equal to or less than 5 times the actual source gas concentration, and the high equivalent spiking level is greater than 10 times the *actual* source gas concentration for a targeted

compound, then the *low* level run spike is used in determining the spike recovery.

Rule 3. If the low equivalent spiking level is less than or equal to 5 times the source concentration and the high equivalent spiking level is less than or equal to 10 times the *actual* source concentration for a targeted compound, then calculate the following four parameters:

(3a) The spike recovery of the low level run spike.

(3b) The percent difference in the low spike equivalent spiking level and the actual source gas concentration as shown in Equation 2.5.

Equation 2.5

$$LSPD = \frac{|LESL - C_A|}{C_A} x100$$

Where:

LSPD = low spike percent difference (absolute value)
LESL = low equivalent spiking level
C_A = actual source gas concentration

(3c) The spike recovery of the high level run spike.

(3d) The percent difference in the high spike equivalent spiking level and the actual source gas concentration as shown in Equation 2.6.

Equation 2.6

$$HSPD = \frac{|HESL - C_A|}{C_A} x100$$

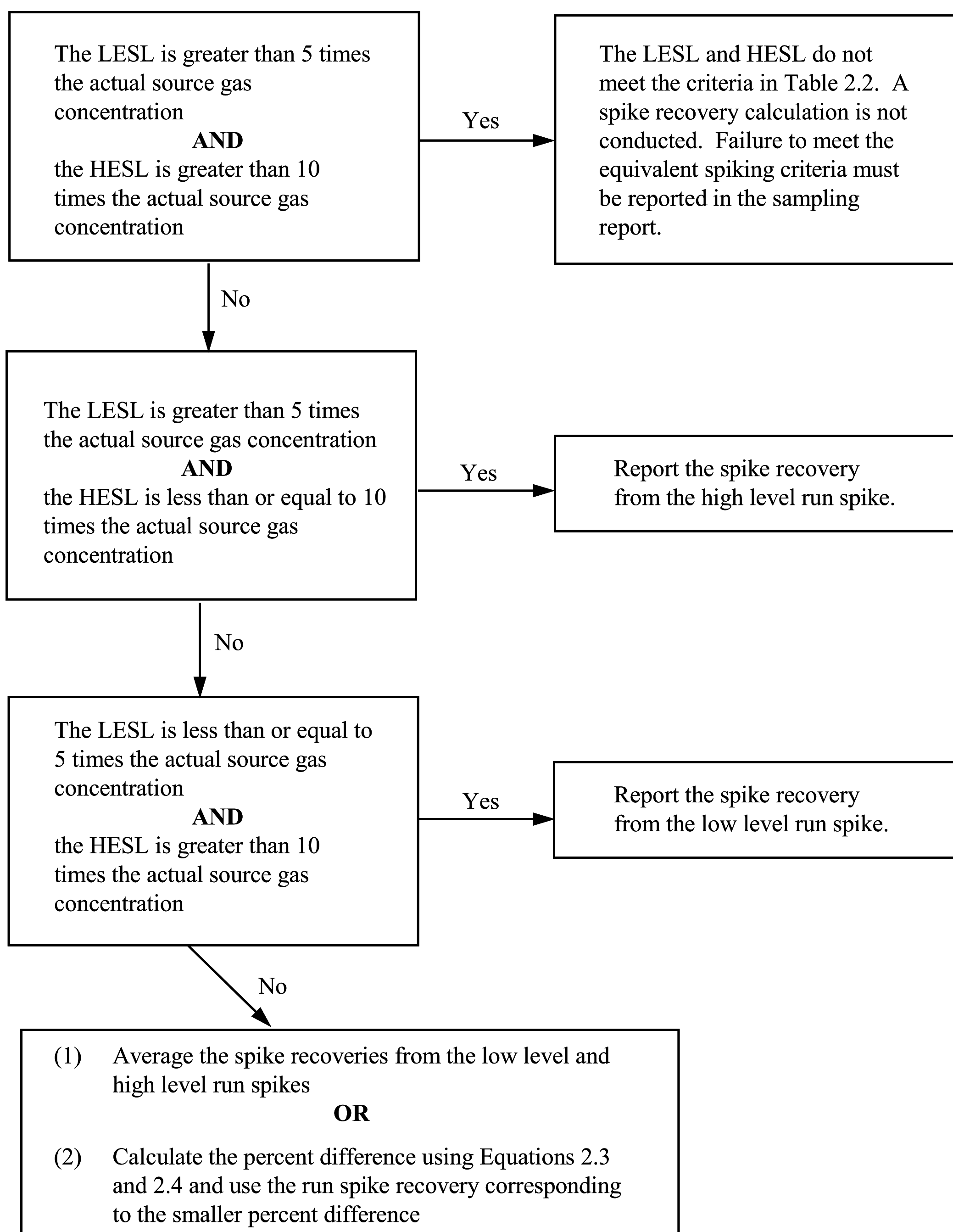
Where:

HSPD = high spike percent difference (absolute value)
HESL = high equivalent spiking level
C_A = actual source gas concentration

The spike recovery for **Rule 3** is based on the following two options: (i) the average of the spike recoveries determined in 3(a) and 3(c) above **OR** (ii) the spike recovery corresponding to the smallest percent difference determined in 3(b) and 3(d) above. The user may pick the option that provides the better spike recovery value. If the average spike recovery option is used, the actual source gas concentration, for the purposes of evaluating the spike recovery criteria (Table 2.4), will be the average of the two normal sample trains.

Rule 4. If the low equivalent spiking level is determined to be more than 5 times the actual source gas concentration and the high equivalent spiking level is greater than 10 times the actual source gas concentration, the equivalent spiking levels do not meet the criteria in Table 2.2. In this case, a spike recovery calculation should not be conducted and a spike recovery should not be reported. The report, however, must state that the sampling company failed to meet the equivalent spiking level criteria.

Figure 2.1 provides a flow diagram intended to help the user understand the bracketed spike recovery rules. Additionally, the appendix contains a worksheet and example calculation.



HESL – high equivalent spiking level
LESL – low equivalent spiking level

Figure 2.1 Bracketed Spike Recovery Rules

2.4.2.5.3.3 Example for a Bracketed Run Spike – A three run set on a source consisted of a duplicate, a high run spike, and a low run spike. The *normal* sample train from both spiked sample runs provided a source gas concentration of 10 ppmvd of methanol (considered the *actual* methanol concentration).

The low equivalent spiking level for the low run spike was 4 ppmvd. The spike recovery for the low run spike was 65%. Since 4 ppmvd is less than 5 times the actual source gas concentration, the low spike percent difference was calculated to be:

$$\frac{|4-10|}{10}\times 100 = 60\%$$

The high equivalent spiking level was 30 ppmvd for the high run spike. The spike recovery for the high run spike was 90%. Since 30 ppmvd is less than 10 times the *actual* source gas concentration, the high spike percent difference was calculated to be:

$$\frac{|30-10|}{10}\times 100 = 200\%$$

The bracketed run spike recovery for the source in this example could be based on either the (i) average of the low and high spike recoveries (77.5%) or (ii) the spiked sample train with the lower percent difference, which provided a spike recovery of 60%. Assuming the sampling company chooses to use the 77.5% spike recovery, this value is assessed against the criteria in Table 2.4 and the sample set is shown to meet the spike recovery criteria.

2.4.2.6 Train Spike – The primary purpose of the train spike is to evaluate the entire sampling train's sampling accuracy. (Note that the run spikes, which are spiked in the first impinger, do not evaluate the potential for compound loss in the probe and filter box.)

One train spike must be conducted for each mill visit. This QA procedure can be conducted prior to source testing, while in the field, or after source testing.

However, this procedure must be conducted within 7 days of the first or last day of the mill sampling or mill visit.

Each compound evaluated by the train spike must be spiked at an equivalent spiking level above the detection limits but no more than 5 ppmvd.

The train spike will be conducted using only one collection train attached to the heated probe and filter box as shown in the appendix. This collection train will be operated outside or independent of the source(s) tested. The spike is injected into the probe tip of the collection train.

If desired, the train spike can be configured using two impinger trains operating in parallel behind a single heated probe and filter box. Note that the spike recovery for each impinger train is expected to be half that of a single impinger train, so spike volumes or concentrations may need to be adjusted for this configuration.

2.4.2.6.1 Train Spike Notes – (1) Care must be taken to prevent introduction of any ambient organic contaminants during this procedure. Charcoal sorbent tubes placed at the probe tip to treat the ambient air entering the measurement system will minimize bias due to contamination. (2) Care should also be taken to inject the spike solution far enough into the heated probe to ensure complete volatilization of the aqueous spike. (3) The spike should be introduced over a 10 to 30 minute time period because a single quick injection may cause poor spike recovery. (4) The train spike must be operated for the same time period (usually one hour) and sample flow rate that is expected to be used during source sampling.

2.4.2.6.2 Train Spike Recovery - The spike recovery is determined by dividing the mass collected in the spiked train by the mass measured in the associated field spike. The spike recovery is reported as a percent.

$$\text{Spike Recovery}_{[i]} = \frac{\text{mass}_{\text{spiked train}[i]}}{\text{mass}_{\text{field spike}[i]}}$$

2.4.2.6.3 Train Spike Criteria - The spike recovery criteria for the train spike is 70% to 130%. These criteria are not concentration dependent but the equivalent spiking level must be less than 5 ppmvd.

2.5 Procedure

It is imperative that all users of this method first thoroughly read the entire method prior to executing any field testing. An understanding of both the required reagents (Section 2.3) and the quality assurance procedures (Section 2.4) is necessary to execute this method. The following procedures are written primarily for a sampling system much like the one used for NCASI Method CI/WP-98.01 but an attempt has been made to allow substantial flexibility. The following procedures will need to be altered for other sample trains. The user should, however, comply in some manner with the intent of the following procedures.

2.5.1 Preparation of the BHA Sample Bottles – Determine the volume of aqueous BHA sampling solution required for each sample run (Sections 2.3.8 and 2.2.5). Select a sample bottle that has sufficient capacity to accommodate the BHA solution volume plus rinse and condensate that will be collected during sampling. Record the sample ID and tare weight (sample bottle with cap and label) for each sample bottle. Add the required BHA solution to each sample bottle and record the pre-sample weight of each bottle. Alternative procedures for measuring or tracking the volumes of the [AQU] and [HEX] samples may be used; however, the final volumes must be accurate.

2.5.2 Preparation of Hexane Rinse Bottles – This method requires a rinse of the impingers with hexane after sample collection. The hexane used in the rinse will also be used for the first of the three extractions. The sampling company may want to prepare an additional set of bottles containing known quantities of hexane for the impinger rinses. Alternative procedures for measuring or tracking the volumes of the [AQU] and [HEX] samples may be used; however, the final volumes must be accurate.

Since this method allows for different impinger sizes, the volume of hexane rinse is not specified. The amount of hexane to be used in the rinse must conform to the following rules:

1. A minimum of one milliliter of hexane must be used for every 12 mL of BHA solution initially used in the impingers.

2. The amount of hexane rinse used should be approximately one-third of the total amount of hexane used for extraction of the sample (Section 2.5.11).

After determining the volume of hexane rinse required for a representative sample run, select a container that has sufficient capacity to accommodate this volume of hexane or three times this volume if the bottle is to be re-used for the lab sample. Record the ID and tare weight (bottle with cap and label) for each bottle. Add the required volume of hexane to each sample bottle and record the new weight of each bottle. Alternative procedures are allowed, but the volume of hexane used in the rinse must be tracked and recorded.

2.5.3 Field Data Sampling Sheet – Each sample run must have a field sheet that documents pertinent information concerned with field testing this method. (An example is provided in the appendix.)

2.5.4 Preparation of the Spike Solution – The aqueous spike solution will consist of the appropriate concentration of each targeted compound in DI water. The spike solution should result in 'equivalent spiking levels' (Section 2.4.2.1) that meet the criteria in Tables 2.1 and 2.2.

2.5.4.1 Verification and Handling of Spiking Solution – The spiking solution and spike addition procedures may be the most common sources of spike recovery failure. NCASI suggests that all spiking solutions be analyzed and quantified for verification after formulation on the same instrument(s) that will analyze the samples (if possible). This should be done before the spikes are taken into the field to address any gross differences in the formulas (theoretical values) and measured values. Similarly, it is strongly recommended that some of the spiking solution should be returned to the lab after the field trip and again analyzed. This will provide information on degradation of the spike solution during the field trip. The spike solution must be kept on ice or refrigerated from the time of formulation until all sampling and analysis are complete.

For convenience, 2 mL GC vials with no headspace can be used to transport and store the spike solutions. If the GC vials are used, then the laboratory should retain one (or more) vials for an analysis record of each unique spike solution formulated. Furthermore, one GC vial for each unique spike solution should be retained from the batch of spikes sent to the field for the analysis record.

One milliliter is a convenient spike volume if GC vials are used. A syringe needle inserted through the vial septum will allow air to enter the vial during extraction of the spike with a separate needle and syringe.

2.5.5 Selection of the Equivalent Spiking Level – Criteria are established for the equivalent spiking level in Sections 2.4.2.1 and 2.4.2.5.3.2, thus it is important that an appropriate equivalent spike level for a particular source type or sample location is chosen. Run spike criteria are established for "single run spikes" and "bracketed run spikes." The criteria are more lenient for bracketed run spikes, but two run spikes must be conducted rather than one.

2.5.6 Preparation of Collection Train – The probe and filter housing must be cleaned with DI water or alternative cleaners and the filter replaced prior to testing each new source type or sample location. All unheated sample lines must be cleaned by rinsing thoroughly with DI water. The impingers must be cleaned according to Section 2.5.10.7. If an empty impinger or other vessel is to be used as a condenser prior to the first BHA impinger, then rinse the condenser with DI water. Replace the

silica gel or drying impinger at the end of the impinger train as necessary if applicable. Select one pre-weighed BHA sampling solution bottle for each impinger train for the sample run. Record the bottle ID and weight data on the field sheet. Place approximately one-third of the BHA sampling solution in each of the three impingers. An empty impinger may be placed prior to the three BHA impingers to condense the bulk of the moisture when testing high moisture sources. Furthermore, a silica gel or drying impinger may be used following the three BHA impingers.

2.5.7 Initial Leak Check (optional) – It is recommended that the sample probe and filter assembly be leak checked when the collection train is first assembled or after the filter is changed and before the system is brought up to operating temperature for the sample run.

2.5.8 Heated Probe/Impinger Train Leak Check – A leak check procedure must be conducted when all of the heated components have reached operating temperature (250°F ± 25°F). The leak check must include all of the components from the probe tip to the by-pass valve for the sample pump. A vacuum of at least 15 inches of mercury should be exerted on the system. A drop in vacuum of 1.0 inch of mercury over a two minute period indicates a leak that must be repaired. Results of the leak check must be recorded on the sample run field sheet.
***Caution:** Release the vacuum on the sample train at the probe tip.

Alternative leak check procedures may be used. If Method 5 type systems are used, the Method 5 leak check procedure may be used. For larger impinger trains with dry gas meters, a leak check conducted at the maximum vacuum (during the test run) must show a leak to be less than 4% of the sample rate during the test. Results of the leak check must be provided in the report.

2.5.8.1 Dual Impinger Train Leak Check Procedure – For systems using one heated probe and filter with two parallel impinger trains, care must be taken to isolate the two impinger trains during leak checks. If this is not done and there is a leak in the system, the impinger contents from one impinger train may be transferred through the filter housing to the other impinger train. Should this occur, the impinger contents for both impinger trains and the filter should be discarded and the sampling system reconstructed.

Two valves installed at the back of the heated filter box may be used to isolate the sample trains during leak checks. Alternative configurations can also be used but the sampling company must demonstrate that both impinger trains and the probe/filter box meet the leak check criterion.

2.5.8.2 Leak Check Troubleshooting – The presence of bubbles in the first impinger indicates a leak located between the probe and the first impinger. A leak between the impingers or behind the impingers will be indicated by aqueous solution being drawn up one of the impinger stems (flow direction is backwards through the system).

2.5.8.3 Post Leak Check – When an impinger train has passed the leak check, release the vacuum ***slowly*** at the probe tip to ensure that the aqueous solution remains evenly distributed between the impingers.

2.5.9 Sample Run Procedures – Prior to each sample run, verify that the probe and filter housing are both at operating temperature and all impingers are partially immersed in crushed ice and water.

2.5.9.1 Pre-Sample Run Flow Rate Measurement (single impinger train) – The required flow rate will depend on the size of the impingers and the amount of BHA solution used as specified in Section 2.2.5. The sample flow rate readings are obtained at the probe tip with the measurement system operated outside the source. The average of five flow rate readings will represent the pre-sample flow rate. Pre- and post-sample run flow rates are averaged for the sample run flow rate. Record the ambient temperature and pressure within the vicinity of the probe tip at the time of the measurement.

The measurement system should be operated only long enough to record the five flow rate measurements. First, turn the by-pass valve for the sample pump to “ambient” and turn the sample pump on, then switch the by-pass valve to “sample” in order to draw ambient air in at the probe tip. Obtain the required flow rate measurements and then return the by-pass valve back to “ambient.” Keep the sample pump on for the remainder of the sample run.

If dry gas meters are used to determine sample volume, readings of ‘delta H’ across the orifice or an equivalent parameter must be reported to demonstrate relatively steady-state sample flow during the sample run.

2.5.9.2 Pre-Sample Run Flow Rate Measurement (dual impinger trains) – At the conclusion of a successful leak check for dual impinger trains, obtain the sample flow rate for both impinger trains independently. After the flow rates for the individual impinger trains are measured the combined sample flow rate from both trains is measured. The total sample flow rate should be within 10% of the sum of the independently measured trains.

If dry gas meters are used with each sample train to determine sample volume, readings of ‘delta H’ across the orifice or an equivalent parameter must be reported to demonstrate relatively steady-state sample flow during the sample run.

2.5.9.3 Pre-Sample Run Stack Flow Measurement – Verify that the source to be tested is operating at a reasonably steady state condition. Obtain the flow rate of the source gas at the stack test port using appropriate stack measurement methods. Other source gas parameters required must include stack gas temperature, moisture content, static pressure, and percent O_2 and CO_2.

2.5.9.4 Non-Isokinetic Sampling Single Point – Insert probe into the test port so that the probe tip is aligned perpendicular to source gas flow and situated at the sample extraction point. Check that the operating temperature of the probe and filter housing has not changed due to probe placement.

2.5.9.5 Start Sample Run – Start the sample run by switching the by-pass valves for the impinger sample pump(s) to “sample.” Record the start time and observed sample flow rate through the impingers. This method does not specify a sample run time, but the run should be a minimum of 45 minutes. One hour runs are recommended. Three hour runs at reduced sample flow rates are reasonable for lumber kilns and other sources that have extended batch cycle times.

2.5.9.6 Verify Operating Parameters – At various intervals during the sample run, record the impinger flow rate observed, and vacuum gauge readings for the two gauges.

2.5.9.7 End Sample Run – At the end of the sample run, switch the sample pump by-pass valve for the impinger train(s) to “ambient.” Record the time for the end of the sample run. Remove the probe from the stack test port to obtain the post-sample run flow rate.

2.5.9.8 Post-Sample Run Stack Flow Measurement – Obtain the flow rate of the source gas at the stack test port using appropriate stack measurement methods. Other source gas parameters required must include stack gas temperature, moisture content, static pressure, and percent O_2 and CO_2.

2.5.9.9 Post-Sample Run Flow Rate Measurement (single impinger train) – The sample flow rate readings are obtained at the probe tip with the measurement system operated outside the source. The average of five flow rate readings will represent the post-sample flow rate. Record the ambient temperature and pressure within the vicinity of the probe tip at the time of the measurement.

The measurement system should be operated only long enough to record the five flow rate measurements. Switch the by-pass valve for the sample pump to “sample” in order to draw ambient air in at the probe tip. Obtain the required flow rate measurements and then return the by-pass valve back to

"ambient." Keep the sample pump on in order to collect the sample line DI rinse.

2.5.9.10 Post-Sample Run Flow Rate Measurement (dual impinger trains) – At the end of the sample run, both impinger trains are attached to the heated filter housing and therefore the post-sample run flow rate can be measured at the probe tip. Switch the by-pass valves for both pumps to "sample" and record five flow rate measurements, then turn both by-pass valves back to "ambient." The average of these five readings will represent the post-sample run flow rate.

Next, obtain the independent flow rates for each impinger train. Verify that the sum of the independently measured flow rates for the two sample trains is within 10% of the total flow rate of the system.

2.5.9.11 Measurement System Sample Flow Rate Check – Verify that the difference between pre- and post-sample run flow rate measurements is within 20% (not applicable to sample systems with dry gas meters).

If the difference is greater than 20% for a given sample run, then examine the collection train and determine if the sample run is valid. A post-sample run leak check may be conducted in order to examine flow rate differences, but care is required to avoid loss of sample.

2.5.10 Sample Recovery Procedure

2.5.10.1 Rinse Sample Line – The sample line between the outlet of the filter housing and the first impinger must be rinsed with DI water. To accomplish this, disconnect the sample line at the heated filter box, turn the by-pass valve to "sample," and rinse the sample line with a small amount of DI water (approximately 5 mL for midget impingers). The rinse will be drawn into the first impinger (or the condenser if used).

2.5.10.2 Aqueous Sample Collection and Impinger Rinse – Verify that the ID of the original BHA sample bottle is documented correctly on the field sampling sheet for the impinger train and sample run type being processed. Transfer the BHA solution in the impingers to the original sample bottle. Rinse the three impingers with small amounts of DI water and add the rinse aliquots to the original sample bottle. If a condenser was used, empty the condensate into the BHA sample bottle along with the condenser's DI rinse.

Any loss of sample during the sample recovery and DI rinse must be estimated and that lost volume recorded on the field sheet and discussed in the sampling report. Care should also be taken to avoid contamination from airborne particles (e.g., MDF fiber) during sample recovery and DI rinse.

2.5.10.3 Hexane Impinger Rinse – Select a prepared hexane rinse bottle (Section 2.5.2) and record on the field sheet the bottle's ID and tare, pre-, and post-weights. If alternative means of tracking the hexane volume are used, record the appropriate information.

The aldehyde oximes formed by the reaction of the aldehydes with BHA are insoluble or slightly soluble in water. These oximes form an emulsion and also will float on the water surface and adhere to the impinger walls. To quantitatively capture the oximes, the impingers should be rinsed (washed) well with hexane. Begin the hexane rinse procedure by pouring the entire contents of the of hexane bottle into the third impinger. Wash the third impinger well. Transfer the hexane solution from the third impinger to the second impinger and wash the second impinger in the same manner. Repeat the process for the first impinger. The hexane rinse from the first impinger is then added to the BHA sample bottle. This rinse is used in the lab for the first extraction. Any spillage that occurs during this washing procedure must be estimated and recorded on the field sheet and discussed in the sampling report. Alternative procedures for measuring and tracking the aqueous sample volume and hexane volume are allowed. For example, the aqueous impinger catch and rinse may be measured or weighed in the field prior to the hexane impinger rinse.

If a condenser is used prior to the BHA impingers, the condenser is not rinsed with hexane, but is rinsed with DI water.

2.5.10.4 Post-Sample Weight – Obtain the post-sample weight of the bottle (this may be done in the laboratory) that will represent the weight of the bottle, the BHA aqueous sample, and the hexane rinse. Subtraction of the hexane rinse weight (mass) will provide the volume of aqueous sample that is needed to quantify methanol and phenol. This volume will be difficult to determine accurately if the weight (mass) of hexane in the sample is unknown. Note that hexane and water have different densities.

2.5.10.5 Sample Storage in the Field – The sample bottles must be stored at the test site on ice or in a refrigerator set at approximately 4°C. If the water samples are required to be shipped to the laboratory for analysis, pack the sample bottles in ice. **Be careful with frozen packs - they can freeze the water and cause breakage of sample bottles.** Also note that VOA vial type caps (with septa) can rupture if shipped by air. Solid caps with Teflon seals are suggested. Note that the samples contain hexane, and proper shipping procedures should be followed.

2.5.10.6 Sample Preservation – The samples should be refrigerated or remain on ice until processed.

2.5.10.7 Cleaning Impingers – After sample collection, all of the impingers must be cleaned. If the impingers are to be used again for subsequent testing, they must be cleaned in the field using isopropanol and methylene chloride or equivalent substitutes. The isopropanol is used first to remove any water or hexane remaining in the impingers. The methylene chloride provides a final wash and dries relatively rapidly so the impingers can be reused. Isopropanol and methylene chloride washes are not part of the sample and do not need to be analyzed. These materials should be disposed of properly. If the impingers are not reused during field testing, they should be cleaned using appropriate cleaning techniques for laboratory glassware prior to reuse.

2.5.10.8 Sample Storage in the Laboratory – All samples must be stored on ice or in a refrigerator (4°C) until analysis**.**

2.5.10.9 Timetable for Oxime Extraction and Sample Analysis – Extraction of the oximes must occur within 21 days of field sampling. The hexane extracting solution must be analyzed within 35 days of field sampling, and the aqueous fraction must be analyzed within 21 days of field sampling. If equivalency is demonstrated longer hold times can be utilized.

2.5.11 Sample Extraction Procedure

2.5.11.1 Sample Extraction and Separation of the Aqueous [AQU] and Hexane [HEX] Fractions

2.5.11.1.1 Sample Condition - The field samples should arrive at the laboratory in an ice chest or other container with ice or equivalent. The temperature of the samples should be between 0 and 10 degrees C. The samples should not be frozen. If the samples are not cold upon arrival at the lab, the test report must report the lack of proper shipping and the temperature of the samples upon arrival at the lab.

2.5.11.1.2 Sample Bottle Weight – Each sample bottle should contain the hexane rinse and associated aqueous sample solution. If the sample bottle containing all the sample has not been weighed, the bottles should be wiped dry and weighed, and the weight recorded. This step is necessary to quantify the methanol and phenol and insure that the full sample has been received.

2.5.11.1.3 Sample Extraction – After weighing the sample bottle, but before opening, shake the bottle vigorously for approximately 30 seconds. Pour the entire contents of the sample bottle into a properly sized separatory funnel. Cap and save the empty sample bottle. The hexane delivered with the sample will be used as the

first one-third of the total hexane volume used in the sample extractions. The total hexane volume used for the three extractions should be a minimum of 25% of the initial BHA solution volume (v/v). Shake the separatory funnel for 30 seconds and allow the hexane and water to separate. Drain the water fraction into a clean, labeled container. It is better to drain a little hexane into the water than to leave a little water in the hexane. Drain the hexane into the empty hexane container used in the field or a new tared container. Pour the water fraction back into the separatory funnel. Take the second-third of the hexane to be used in the extraction and pour it into the now-empty sample bottle. Shake vigorously for 20 seconds. Transfer this hexane solution to the separatory funnel. Shake and separate the fractions as before. Repeat for the third extraction, but the hexane used in this extraction will be "fresh" or "clean." All hexane fractions may be composited. The hexane and aqueous fractions are stored until analysis in separate labeled containers. The extracted (washed) aqueous sample contains methanol, phenol, and perhaps other non-hexane-extractable, polar compounds. The hexane solution contains the aldehyde oximes, perhaps ketone oximes, and other extractables.

The separatory funnels and other glassware should be cleaned between samples. An acetone rinse followed by a methylene chloride rinse and oven drying is sufficient. Other standard lab glassware cleaning practices are also acceptable. Care should be taken to avoid contamination with alcohols, ketones, or aldehydes. If acetone is an analyte, an equivalent solvent may be substituted.

2.5.12 [AQU] Aqueous Sample Lab Procedure

2.5.12.1 [AQU] Aqueous Sample Analysis – Prior to analysis, thoroughly review all calibration information (Section 2.6), all laboratory quality assurance procedures (Section 2.4), and make sure that all calibration standards, solutions, and reference standards are available or have been prepared (Section 2.3).

2.5.12.2 [AQU] GC/FID Procedure – Transfer an aliquot (2.0 mL) of the aqueous sample to an autosampler vial. Add 10 µL of the internal standard primary spike solution (30,000 mg/L cyclohexanol or 40,000 mg/L 2,2,2-trifluoroethanol) to each of the autosampler vials. (Other procedures that provide a standardized, equivalent internal standard concentration may also be used). Perform the analysis by direct aqueous injection into the GC/FID. If the concentration of an analyte is more than 10% above the calibrated range, the sample should be diluted and reanalyzed to measure the analyte concentration.

2.5.12.3 [AQU] GC/FID Operating Conditions – Table 2.7 in Section 2.8 provides GC/FID operating conditions. These conditions must be followed unless equivalency is demonstrated. Note that forest products industry exhausts contain large numbers of organic compounds, and the potential for coelution is substantial. Cryogenic conditions, the specified column, and other parameters have been developed to avoid co-elution of common forest products compounds. Elimination of cryogenic conditions or substitution of columns must not be done unless equivalency is established.

2.5.13 [HEX] Hexane Sample Lab Procedure – Prior to analysis, thoroughly review all calibration information (Section 2.6), all laboratory quality assurance procedures (Section 2.4), and make sure that all calibration standards, solutions, and reference standards are available or have been prepared (Section 2.3).

2.5.13.1 [HEX] GC/NPD Analysis – Transfer an aliquot (2.0 mL) of the hexane sample to an autosampler vial. Add 10 µL of the internal standard primary stock solution (20,000 mg/L nitrobenzene or equivalent compound and concentration) to each of the autosampler vials. (Other procedures that provide a standardized, equivalent internal standard concentration may also be used). Perform the analysis by direct injection into the GC/NPD. If the concentration of an analyte is more than 10% above the calibrated range, the sample should be diluted and reanalyzed to measure the analyte concentration.

2.5.13.2 [HEX] GC/NPD Operating Conditions – Table 2.8 in Section 2.8 provides GC/NPD Operating Conditions. These conditions must be followed unless equivalency is demonstrated. Few nitrogen or phosphorous containing organic compounds are present in forest products industry exhausts, therefore little potential for co-elution exists with an NPD detector. Typically the NPD chromatograms are very clean in the oxime region.

2.6 Calibration

2.6.1 Calibration and Standardization

2.6.1.1 [AQU] GC/FID Analyses

2.6.1.1.1 Notes – Assemble the GC/FID and establish the operating conditions outlined in Table 2.7. Once the GC/FID system is optimized for analytical separation and sensitivity, the same operating conditions must be used to analyze all samples, blanks, calibration standards, and quality assurance samples. Note for split/splitless injection ports constant injections of aqueous samples can cause water to build up in the system. This will cause the retention times to shift and the peaks to broaden. It is recommended that a bake-out of the system be performed after approximately 50 injections. This should consist of heating the injector to 250°C, the oven to 250°C, and the detector to 350°C for several hours.

2.6.1.1.2 Retention Times – Determine the retention times of the analytes by taking 2.0 mL of the mid-range calibration solution and adding 10 µL of the internal standard solution. This will result in concentrations of 150 mg/L of cyclohexanol or 2,2,2-trifluoroethanol in the autosampler vial. Inject 1.0 µL of this solution and determine the relative retention times of the analytes to the internal standard using Equation 2.7.

Equation 2.7

$$RRT_Z = \left[\frac{Rt_Z}{Rt_{IS}} \right]$$

Where:

RRT_Z = relative retention time of compound Z
Rt_Z = retention time of compound Z
Rt_{IS} = retention time of internal standard (cyclohexanol or 2,2,2-triflouroethanol)

2.6.1.2 [HEX] GC/NPD Analyses

2.6.1.2.1 [HEX] Extraction – All [HEX] samples to be analyzed by GC/NPD must be extracted from the aqueous impinger solution into hexane prior to analysis. This procedure is presented in Section 2.5.11. Extraction is necessary to remove the interference due to unreacted BHA and to quantitatively capture the oximes.

2.6.1.2.2 [HEX] Notes – Assemble the GC/NPD and establish the operating conditions outlined in Table 2.8. Once the GC/NPD system is optimized for analytical separation and sensitivity, the same operating conditions must be used to analyze all samples, blanks, calibration standards, and quality assurance samples.

2.6.1.2.3 [HEX] Retention Times – Determine the retention times of the analytes by taking 2.0 mL of the mid-range calibration solution and adding 10 µL of the internal standard solution. This will result in concentrations of 100 mg/L of nitrobenzene in the autosampler vial. Inject 1.0 µL of this solution and determine the relative retention times of the analytes to the internal standard using Equation 2.7.

2.6.1.3 [AQU] [HEX] 7 Point Calibration Curve - Prepare a seven-point calibration curve for each of the analytes by taking 2.0 mL of each calibration solution and adding the appropriate internal standard (Sections 2.5.12.2 and 2.5.13.1). The lower limit calibration standard must be 0.5 mg/L for the [HEX] samples and 0.4 mg/L for the [AQU] samples. The upper limit of the calibration standards should be 100 mg/L. Use of an internal standard for calibration is required. The calibration curve may be split into two curves, one for low concentration samples and one for the remainder. This may be done at the discretion of the analyst. It is strongly suggested that the analyst evaluate the need for splitting the curve relative to low and high sample concentrations.

2.6.1.4 [AQU] [HEX] Relative Response Factor - Calculate the relative response factor (RRF_A) for each analyte using Equation 2.8. If the relative standard deviation (RSD) of the average RRF_A is less than 15%, the calibration is acceptable. The average RRF_A can be used in all subsequent calculations. If the calibration does not pass the criteria, the calibration curve solutions must be reanalyzed and reevaluated. It may be necessary to perform instrument maintenance prior to reanalysis. If reanalysis also fails to produce a linear curve, new calibration standards must be prepared and analyzed.

Equation 2.8

$$RRF_Z = \left[\frac{A_Z}{A_{IS}} \times \frac{C_{IS}}{C_Z} \right]$$

Where:

RRF_Z = relative response factor of compound Z
A_Z = area of compound Z peak
A_{IS} = area of internal standard peak
C_Z = concentration of Compound Z injected
C_{IS} = concentration of internal standard injected

2.6.1.5 [AQU] [HEX] Calibration Verification Standard - Analyze and calculate the concentration of the mid-range calibration standard daily, prior to each sample set, using Equation 2.9. Calculate the percent recovery of the standard using Equation 2.10 to verify the calibration. In-house percent recovery control limits must be determined and are not to exceed ±15%. If the limits are exceeded, either prepare a new standard or perform instrument maintenance. If necessary, recalibrate the instrument.

Equation 2.9

$$C_Z = \left[\frac{A_Z \times C_{IS}}{A_{IS} \times RRF_Z} \right]$$

Where:

C_Z = concentration of compound Z in sample (mg/L)
A_Z = area of the compound Z peak in the sample
C_{IS} = concentration of the internal standard (mg/L)
A_{IS} = area of the internal standard peak
RRF_Z = relative response factor of compound Z

Equation 2.10

$$R = \left[\frac{C_M}{C_E} \times 100 \right]$$

Where:

R = percent recovery
C_M = concentration of analyte measured
C_E = concentration of analyte expected

2.6.1.6 [HEX] Aldehyde Calibration Standards – At this point in time the aldehyde oximes are not readily available commercially in small calibration grade quantities. Manufactured standard solutions may be available through a few suppliers. At this time, labs will (1) have to synthesize (manufacture) the oximes and prepare standard solutions from the synthesized neat oximes or (2) prepare or purchase standard solutions of aldehydes (and ketones) and derivitize these standards with a BHA solution. Instructions for synthesizing the oximes are provided in the appendix.

2.6.1.6.1 [HEX] Quantifying and Expressing Oxime Standards –The results from the chromatograms could be expressed as mg/L of aldehyde or mg/L of aldehyde oxime. Either method is acceptable, but all users will need to understand the basis or means of expressing the results. The least confusing way may be to develop the calibration curves based on the amount of aldehyde stoichiometric equivalent. For example, an addition of 3.386 grams of acetaldehyde oxime to one liter of hexane would provide an acetaldehyde oxime concentration of 3,386 mg/L but would provide an acetaldehyde stoichiometric equivalent concentration of 1000 mg/L. Labs should be clear about the reporting basis for their GC results.

2.6.1.7 [HEX] Stock Solution Made from Neat Oximes – If neat aldehyde or ketone oximes are manufactured or purchased, the calibration standards may be manufactured from the neat oximes using hexane as a solvent. Table 2.5 provides information for making a 1000 mg/L aldehyde stoichiometric equivalent stock solution for selected aldehydes.

Table 2.5 Standards from Oximes

Aldehyde	Aldehyde Molecular Weight	Oxime Molecular Weight	Milligrams of Oxime to Add to 100 mL of Hexane
Formaldehyde	30.05	135.15	450
Acetaldehyde	44.05	149.15	339
Acrolein	56.06	161.16	287
Propionaldehyde	58.08	163.18	281

2.6.1.7.1 [HEX] Oxime Calibration and Matrix Spike Solutions – Prepare calibration standard solutions by dilution of the stock solution made from neat oximes using syringes to measure the required aliquots of primary standard. Table 2.6 shows the required dilutions. Prepare matrix spike solutions by calculating the concentration of analytes desired and diluting the primary stock solution.

Table 2.6 Primary Stock Solution Dilutions

µL of Stock Solution to Add to 10 mL Volumetric Flask	Resulting Formaldehyde, Acetaldehyde, Acrolein, and Propionaldehyde Aldehyde Stoichiometric Equivalent Concentration (mg/L)
1,000	100
500	50
250	25
100	10
50	5
10	1
5	0.5

2.6.1.8 [HEX] Calibration Standards Made from Neat Aldehydes and Formalin – As an alternative to making or purchasing neat oximes, labs may prepare calibration standards from formalin and neat aldehydes. The neat aldehydes and formalin will be added to a BHA sampling solution (Section

2.3.8) where the oximes will be formed. Alternatively, purchased standard aldehyde solutions may be used. The oximes will be extracted from the solution with hexane providing a stock solution that can be diluted to provide standards.

Fill a 250 mL ground glass stoppered volumetric flask to approximately 240 mL with BHA sampling solution. Tare the flask. After the addition of each analyte, weigh and record the weight gain to the nearest 0.1 mg. Using a syringe or equivalent device, add 127 µL of acetaldehyde, taking care to inject the acetaldehyde directly into the water. In a like manner, add 119 µL acrolein, 250 µL formalin, and 126 µL of propionaldehyde. Once all the analytes have been added, fill the flask to the mark with BHA sampling solution. Allow to stand for 15 minutes at lab temperature or for one hour refrigerated. Shake the 250 mL volumetric flask and pour the contents into a properly sized separatory funnel for extraction. Add 40 mL of hexane to the 250 mL volumetric flask, cap, shake and then pour the hexane into the separatory funnel. Shake the separatory funnel for 30 seconds and allow the hexane and BHA solution to separate. Drain the BHA solution into a clean container. (It is better to drain a little hexane into the aqueous solution than to than to leave a little water in the separatory funnel.) Drain the hexane into a 100 mL volumetric flask and cap with a ground glass stopper. Pour the aqueous BHA solution back into the separatory funnel and add 30 mL of hexane. Shake and separate the fractions as before. Repeat with a third hexane extraction using 30 mL of hexane. After the third hexane fraction has been added to the 100 mL volumetric flask, use additional hexane to fill to the mark. Assuming 100% derivitization, 100% compound purity and exactly 37% formaldehyde in the formalin, this will result in individual oxime concentrations that are the stoichiometric equivalent of 1,000 mg/L of the corresponding aldehydes. Use the measured weight gains and actual compound purity to compute the exact analyte concentrations. This stock solution can be diluted as shown in Table 2.6 to provide standards.

2.6.1.9 Calibration Curve Checks – Section 2.4.1.2.2 requires a calibration check using a calibration verification standard. Section 2.4.1.2.5 requires a check by a second source or reference standard.

2.6.1.10 [HEX] [AQU] Calibration Frequency – It is critical that gas chromatography conditions remain stable. Calibration frequency will depend on the lab's practices, ability to control the chromatography conditions, and/or the ability to meet the calibration check standard criteria.

For this method calibration verification standards (Section 2.4.1.2.2) and a second source or reference standard (Section 2.4.1.2.5) are run at the beginning of each sample batch as a check on the calibration curve. The calibration verification standard must be evaluated for both compound concentration and response (peak area). The criteria are provided in Section

2.4.1.2.2. The calibration verification standard must be run prior to the sample batch, after every 10 source samples, and at the end of the sample batch. Each time it is run, the peak area and compound concentration must be evaluated relative to the QA criteria. Additionally, the peak area of the internal standard must be evaluated relative to the mean peak areas from the calibration curve. A 'new' calibration curve or recalibration is required if any of the calibration QA criteria are not met.

2.7 Calculations

2.7.1 GC Data Analysis

2.7.1.1 [AQU] [HEX] Relative Retention Time – The analytes are identified by comparison of their retention time relative to the internal standard established in the calibration to the relative retention time in the samples. The sample component relative retention time (RRT) should fall within ±0.01 RRT units of the RRT of the standard component.

2.7.1.2 [AQU] [HEX] Sample Concentration – Calculate the sample concentration, using the internal standard response factors established in Section 2.6.1.4, according to Equation 2.11. Use a dilution factor of 1 if no dilution is made and choose the proper correction factor based on the internal standard and hardware configuration used. Use a correction factor of 1 if no significant correction factor is found.

Equation 2.11

$$C_Z = \left[\frac{A_Z \times C_{IS} \times DF}{A_{IS} \times RRF_Z} \right]$$

Where:

C_Z = concentration of compound Z in sample (mg/L)
A_Z = area of the compound Z peak in the sample
C_{IS} = concentration of the internal standard (mg/L)
A_{IS} = area of the internal standard peak
RRF_Z = relative response factor of compound Z
DF = dilution factor

2.7.1.3 [AQU] [HEX] Dilution – If samples cannot be analyzed without dilution, the minimum measurement level (MML) must be adjusted to reflect the lowest dilution factor used by multiplying the MML by the dilution factor.

2.7.1.4 [HEX] Peak Summing – Some peak summing will be necessary as a result of the [HEX] GC/NPD analyses. Due to chemical structure, acetaldehyde oxime, acrolein oxime, methoxypropanone oxime, and propionaldehyde oxime each have two peaks. The main peak in each case is designated as A, and the lesser peak as B.

2.7.1.5 [AQU] [HEX] Data Review – The data are reviewed for accuracy of the identification, GC difficulties, interferences, and bias. Any difficulties are to be corrected prior to reporting analytical results.

2.7.1.6 [AQU] [HEX] Chromatogram Review – All the chromatograms are manually reviewed to confirm internal standard and analyte identification as well as the integrated areas. As part of this review, the analyst assesses whether or not the concentration is within the calibration range of the instrument. The analyst should determine whether dilution of the samples is required. Another tool that can be utilized to identify the analyte peaks is to overlay the sample chromatogram with the standard chromatogram.

2.7.1.7 [AQU] [HEX] Internal Standard Review – The internal standard area counts should be reviewed and added to a control chart. The in-house determined control limits should not exceed ±20% of the mean.

2.7.1.8 [HEX] Surrogates – If a surrogate standard is used, the surrogate standard concentration should be reviewed and added to a control chart. The in-house determined control limits should not exceed ±30% of the mean. Low recovery of the surrogate standard generally indicates that insufficient BHA solution was used to form the oximes. Should this be seen, the sample, or a dilution of the sample, must be re-extracted using larger quantities of BHA complexing solution.

2.7.1.9 [AQU] [HEX] Replicate Inconsistencies – Any inconsistencies between replicate analyses must be resolved (i.e., if an analyte is detected in one replicate and not the other) and attempts made to determine the reason for the inconsistencies.

2.7.1.10 [AQU] [HEX] Reporting – Generate a report that includes the internal standard recovery (based on area counts) and calculated concentration of the analytes.

2.7.1.11 [AQU] [HEX] Reporting of MML – Where analytes are not detected or are detected below the lowest calibration standard, report the MML.

2.7.1.12 [AQU] [HEX] Significant Figures – Report results in mg/L to no more than three significant figures.

2.7.1.13 [AQU] [HEX] QA Reporting – Report all blanks, duplicates or replicates, matrix spike recoveries, and the results of calibration verification standards and second source standards for each analytical batch of samples.

2.8 Tables, Diagrams, Flowcharts, and Validation Data

Table 2.7 GC/FID Operating Conditions for Aqueous [AQU] Analysis

Injection:	Purged Packed Injection Port
Purge Flow Rate:	Approx. 40 mL/min
Purge Time:	0.25 min
Injector Temperature:	110°C
Injection Volume:	1 μL
Injection Liner Size:	2 mm id
Syringe Rinse:	10 rinses with VOC free DI water
FID Detector Temperature:	275°C
H_2 Flow Rate:	Approx. 50 mL/min
Air Flow Rate:	Approx. 500 mL/min
Makeup Gas:	Nitrogen or Helium
Makeup Gas Flow Rate:	Approx. 25 mL/min
Carrier Gas:	Helium
Carrier Gas Flow Rate:	constant pressure mode to give 6 mL/min at room temperature, or use constant flow mode at 6 mL/min
Column:	J&W DB-624, 60 meters or longer x 0.53 mm id x 3 micron fused silica capillary column with 10 m deactivated fused silica guard column
Cryogenics:	On
Temperature Program °C:	
Initial:	5°C for 1 min
Ramp 1:	6°C/min to 90°C for 0 minutes
Ramp 2:	40°C/min to 150°C for 7 minutes
Ramp 3:	70°C/min to 250°C for 4 minutes
Retention Time Order:	Acetaldehyde, Methanol, Propionaldehyde, 2,2,2-Trifluoroethanol, Methyl Ethyl Ketone, Cyclohexanol
Cyclohexanol Retention Time:	22.081 min
Relative Retention Time:	Acetaldehyde - 0.336; Methyl Mercaptan - 0.356; Methanol - 0.367; Ethanol - 0.458; Propionaldehyde - 0.487; Acetone - 0.499; Dimethyl sulfide - 0.503; 2,2,2-Trifluoroethanol - 0.608; MEK - 0.672

Table 2.8 GC/NPD Operating Conditions for Hexane [HEX] Analysis

Injection:	Split (Split, 10:1, split flow 13.9 mL/min, total flow 22.9 mL/min)
Injector Temperature:	200°C
Injection Volume:	2.0 µL
Injection Liner Size:	4 mm id with glass wool packing
Syringe Rinse:	4 rinses with hexane
NPD Detector Temperature:	280°C
H_2 Flow Rate:	3 mL/min
Air Flow Rate:	60 mL/min
Carrier Gas:	Helium
Carrier Gas Flow Rate:	1.4 mL/min
Column:	RTX-200, 30 m x 0.25 mm id x 0.25 micron film capillary column with 10 m deactivated fused silica guard column
Cryogenics:	Off
Temperature Program °C:	
Initial:	55°C for 2 min
Ramp 1:	2°C/min to 105°C for 0 minutes
Ramp 2:	25°C/min to 280°C for 2 minutes
Retention Time Order:	Formaldehyde, Acetaldehyde B, Acetaldehyde A, Nitrobenzene, Acetone, Propionaldehyde A, Acrolein A, Propionaldehyde B, Acrolein B, MEK, Methoxy-propanone A, Methoxypropanone B
Nitrobenzene Retention Time:	14.700 min
Relative Retention Time:	Formaldehyde – 0.545 Acetaldehyde B – 0.853 Acetaldehyde A – 0.876 Nitrobenzene – 1.00 Acetone – 1.068 Propionaldehyde A – 1.123 Acrolein A – 1.148 Propionaldehyde B – 1.160 Acrolein B – 1.220 MEK - 1.317 Methoxypropanone A – 1.683 Methoxypropanone B – 1.704

Appendix

APPENDIX

Summary of Quality Assurance Procedures A1

Quality Assurance Configurations A2

Sampling Train Diagram A3

Example Calculation of Sample System Minimum Measurement Level (SSMML)
Based on a 0.4 mg/L Analytical Minimum Measurement Level (MML) for the GC/FID
(Aqueous Analysis) and 0.5 mg/L for the GC/NPD (Hexane Analysis) A4

Example Field Sheet – NCASI Method ISS/FP-A105.01 .... A5

Oxime Synthesis Procedure A6

Bracketed Spike Recovery Example A7

Bracketed Spike Recovery Worksheet A8

SUMMARY OF QUALITY ASSURANCE PROCEDURES

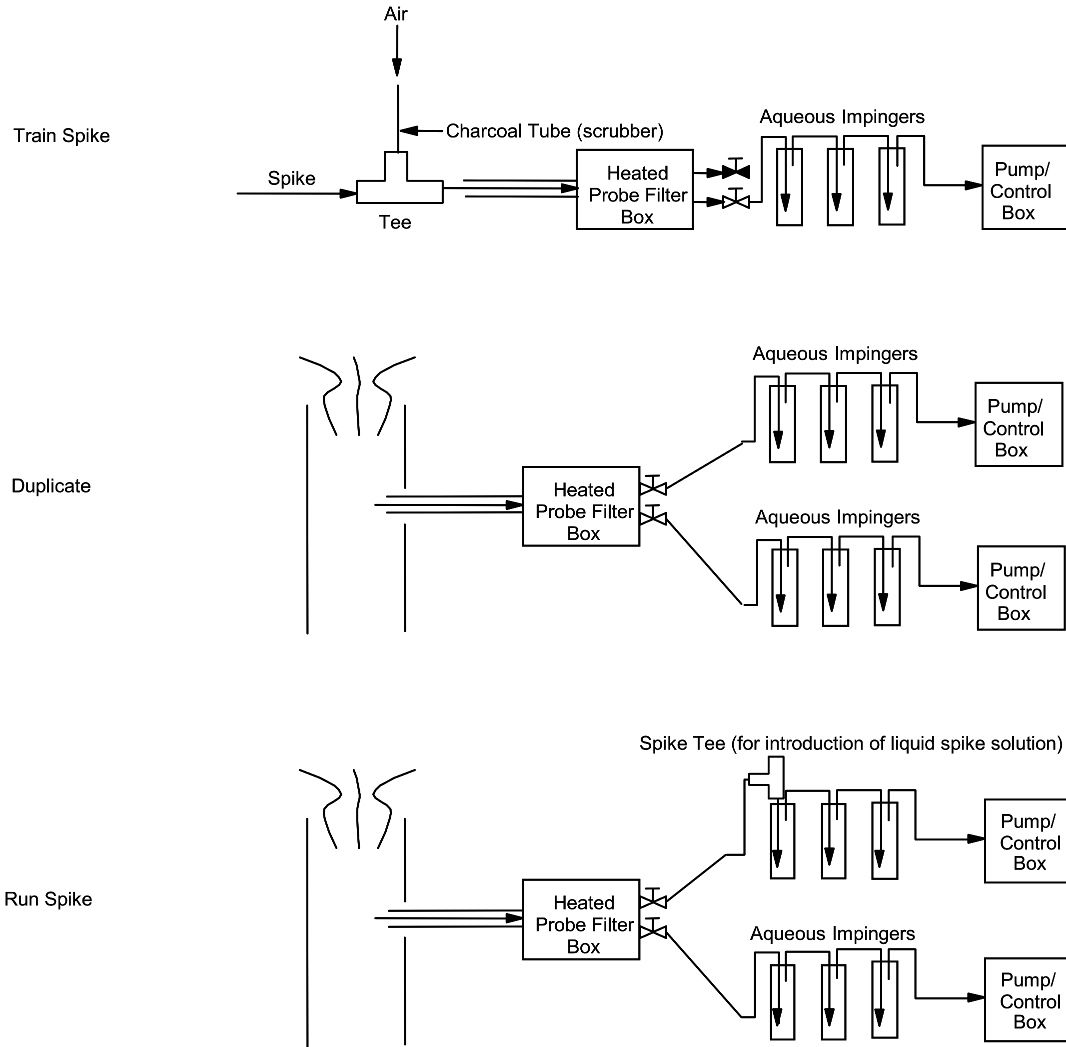
Field Quality Assurance Procedures

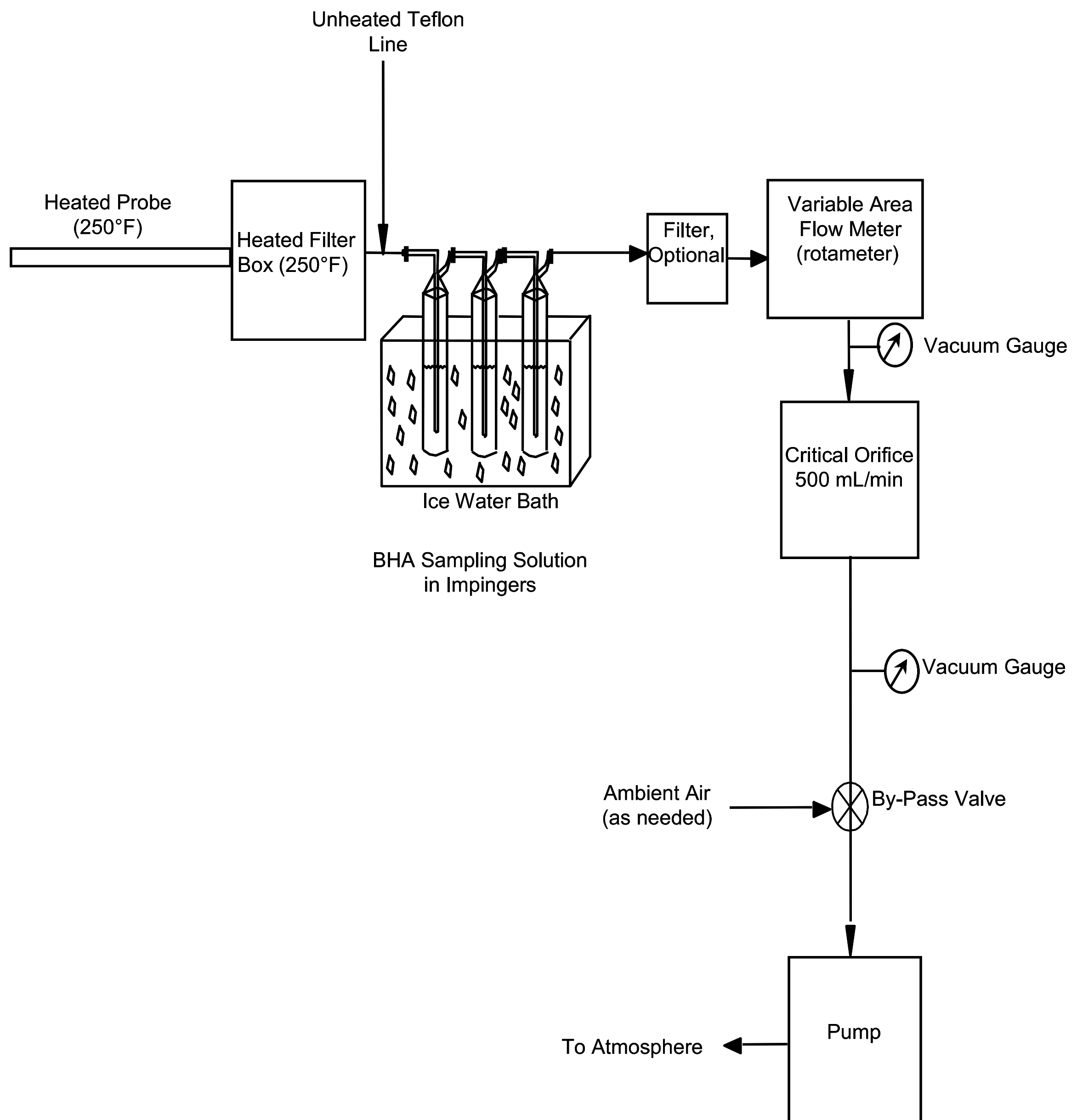
Procedure	Method Section	Criteria
Field Blank	2.4.2.2	None
Duplicate Sample Run	2.4.2.3	Table 2.3
Run Spike	2.4.2.5	Table 2.4
Train Spike	2.4.2.6	Section 2.4.2.6.3
Equivalent Spiking Level	2.4.2.1	Tables 2.1 and 2.2
Field Spike	2.4.2.4	None
Leak Check	2.5.8	Section 2.5.8
Sample Flow Check	2.5.9.1, 2.5.9.2, 2.5.9.9 and 2.5.9.10	Sections 2.5.9.11, 2.5.9.10, and 2.5.9.2

Laboratory Quality Assurance Procedures

Procedure	Method Section	Criteria
Lab Blank	2.4.1.2.1	Section 2.4.1.2.1
Calibration Verification Standard	2.4.1.2.2 and	Section 2.4.1.2.2
Laboratory Duplicates	2.4.1.2.3	Section 2.4.1.2.3
Matrix Spike Recovery (optional)	2.4.1.2.4	None
Second Source or Reference Standard	2.4.1.2.5	Section 2.4.1.2.5
Relative Response Factor	2.6.1.4	Section 2.6.1.4
Calibration Verification Standard	2.6.1.5	Section 2.6.1.5
Calibration Frequency	2.6.1.10	Section 2.6.1.10
Internal Standard Review	2.7.1.7	Section 2.7.1.7
Surrogates (optional)	2.7.1.8	Section 2.7.1.8

Quality Assurance Configurations





Sampling Train for NCASI Method ISS/FP-A105.01

EXAMPLE CALCULATION OF SAMPLE SYSTEM MINIMUM MEASUREMENT LEVEL (SSMML) BASED ON A 0.4 MG/L ANALYTICAL MINIMUM MEASUREMENT LEVEL (MML) FOR THE GC/FID (AQUEOUS ANALYSIS) AND 0.5 MG/L FOR THE GC/NPD (HEXANE ANALYSIS)

Assume:

(1) Sampling rate = 500 dry standard milliliters per minute for 60 minutes = 30 liters total.
(2) Three impingers with 25 mL each of BHA solution, plus 10 mL aqueous rinse, plus 5 mL of moisture from source (condensate) = 75+10+5 = 90 mL of aqueous impinger sample.
(3) Total hexane used in impinger rinse and extraction procedure = 30 mL.

Example Aldehydes SSMMLs

[(0.5 mg/L aldehyde) X (30 mL hexane) X (1000 µg per mg)] / (1000 mL per liter) = 15 µg of aldehyde. For the four aldehydes, 15 µg of aldehyde in 30 liters of gas sample volume yields the following concentrations in the air sample:

acetaldehyde	0.27 ppmvd
acrolein	0.21 ppmvd
formaldehyde	0.40 ppmvd
propionaldehyde	0.21 ppmvd

Example Methanol and Phenol SSMMLs

[(0.4 mg/L alcohol) X (90 mL aqueous sample) X (1000 µg per mg)] / (1000 mL per liter) = 36 µg of alcohol. For the two alcohols, 36 µg of alcohol in 30 liters of gas sample volume yields the following concentrations in the air sample:

methanol	0.90 ppmvd
phenol	0.31 ppmvd

Note that the sample system minimum measurement levels (SSMMLs) will vary according to the aqueous BHA solution volume, sample gas volume, and, for the aldehydes, the amount of hexane used in the extraction (alcohols are not affected by the hexane extraction). The above example is based on a sample flow to initial impinger ratio of 30,000 mL to 75 mL or 400:1. The method allows ratios from 200:1 to 4000:1. If lower methanol detection limit is desired, the BHA solution volume can be reduced or the flow rate through the impingers increased. Alternatively, the laboratory could double the aqueous injection volume (GC/FID) but, in this case, the lab **must** use a purged packed splitless inlet because of the volume of water. Doubling the injection volume would decrease the SSMML by 50%. Note that very high moisture sources will add water (condensate) to the impingers and increase the detection limits for the alcohols.

EXAMPLE FIELD SHEET
NCASI METHOD ISS/FP-A105.01

Mill Name: ______________________ City: __________
State: __________
Source Name: ______________________
Description of Location Sampled (include description of all control devices, quenches, air inlets, etc.):

____

____

Run Number: _____ Start Time: _________ Date: ________
Stop Time: _________

Measurement System Leak Check

Time: __________ Initial Measurement (in. Hg): __________
Time: __________ Final Measurement (in. Hg): __________
Leak Check Criteria - Must not lose more than 1 inch of Hg (vacuum) in 2 minutes. Meet Criteria? Yes No

Measurement System Flow Rates

Average 5 flow measurements below for Pre-Sample Flow (SF) = _______________

1.	2.	3.	4.	5.

Average 5 flow measurements below for Post-Sample Flow (SF) = _______________

1.	2.	3.	4.	5.

Average Sample Flow Rate [ ] (indicate units)

Temperature Measurements

Ambient Temperature at Start of Run:	_________	Time Recorded:	________
Ambient Temperature at End of Run:	_________	Time Recorded:	________
Temperature Heated Probe at Start of Run:	_________	Time Recorded:	________
Temperature Heated Probe at End of Run:	_________	Time Recorded:	________
Temperature Heated Filter at Start of Run:	_________	Time Recorded:	________
Temperature Heated Filter at End of Run:	_________	Time Recorded:	________

Rotameter Readings		Quality Assurance Measures		
Time: __________	Flow: ________			
Time: __________	Flow: ________	Train Spike Conducted?	Yes	No
Time: __________	Flow: ________	Duplicate Conducted?	Yes	No
Time: __________	Flow: ________	Run Spike Conducted?	Yes	No
Time: __________	Flow: ________	Field Blank Made?	Yes	No
Time: __________	Flow: ________	Field Spike Made?	Yes	No

Notes

Field Sampling Data Sheet

OXIME SYNTHESIS PROCEDURE

General steps in making aldehyde-oxime oils:

1. For each aldehyde-oxime to be synthesized, add 5 grams of BHA-HCl to about 100 mL of water in a 150 mL beaker. (Scale up or down as needed.) Completely dissolve the BHA.

2. 5 grams of BHA-HCl is 0.0314 moles or 31.35 millimoles (5/159.6 = 0.0627). The stoichiometric amount of aldehyde for each 100 mL flask is:

   formaldehyde (not formalin) - 0.94 grams
   acetaldehyde - 1.38 grams
   propionaldehyde - 1.81 grams
   acrolein - 1.75 grams
   methoxypropanone - 2.76 grams

   Since residual aldehydes are undesirable, values less than the stoichiometric amount should be added. At the following amounts of aldehyde the theoretical yield of the aldehyde-oxime oil is provided.

Table in mL of Aldehyde

Compound	Amount Aldehyde Added (mL)	Theoretical Aldehyde-Oxime Oil Yield (g)
formalin	2.0	3.13
acetaldehyde	0.75	2.01
propionaldehyde	1.0	2.28
acrolein	1.0	2.42
methoxypropanone	2.0	4.20

3. While constantly stirring, add aldehyde to the BHA solution in the beaker using a syringe with a long needle. Add the aldehyde slowly and below the solution surface. A white, finely divided material will form initially. It is best to place this mixture in a separatory funnel overnight. The aldehyde-oxime oil will separate from the aqueous phase and can be removed with a Pasteur pipette or manipulated into a small vial with a minimum of aqueous phase retention.

4. Freeze the vial containing the oil. (The oil will remain liquid, but ice crystals will form if water is present.) Place a glass wool filter in a small funnel. Place the stem of the funnel in a small empty vial, and place this assembly in a beaker to hold the funnel vertical. Place this assembly in the freezer.

5. After freezing, quickly filter the oil through the glass wool filter. Freeze the vial a second time. If ice crystals are seen, the filtering procedure should be conducted until no ice crystals are visible.

6. Synthesized oximes should be kept in a refrigerator.

Example: Bracketed Spike Recovery

compound	acrolein	acetaldehyde	formaldehyde	methanol	propionaldehyde	phenol
molecular weight	56.06	44.05	30.05	32.04	58.08	94.11
Low Level Run Spike (Low Level Spiked Sample Train)						
normal sample train sample volume (L)	30	30	30	30	30	30
spiked sample train sample volume (L)	33	33	33	33	33	33
concentration in normal train (ppmvd)	1.1	2.1	3.5	12.4	BDL	1.1
concentration in spiked train (ppmvd)	2.1	2.4	6.1	13.2	0.7	9
normal train (ug)	77.0	115.4	131.3	495.8	BDL	129.2
spiked train (ug)	161.6	145.1	251.6	580.6	55.8	1162.7
field spike (ug)	70	800	118	487	41	1200
Equivalent Spiking Level (ESL) (ppmvd)	0.91	13.23	2.86	11.07	0.51	9.29
ESL, % of actual source gas concentration	83%	630%	82%	89%	not calculated, normal train BDL	844%
Does ESL meet criteria?	yes	no	yes	yes	not calculated, normal train BDL	no
percent difference	17%	not calculated, ESL criteria not met	18%	11%	not calculated, normal train BDL	not calculated, ESL criteria not met
low spike recovery (%)	110%	not calculated, ESL criteria not met	91%	7%	not calculated, normal train BDL	not calculated, ESL criteria not met
High Level Run Spike (High Level Spiked Sample Train)						
normal sample train sample volume (L)	29	29	29	29	29	29
spiked sample train sample volume (L)	30	30	30	30	30	30
concentration in normal train (ppmvd)	1.3	1.9	4.1	13.2	0.5	BDL
concentration in spiked train (ppmvd)	13.6	15.3	34.3	100	20.4	9
normal train (ug)	87.9	101.0	148.6	510.2	35.0	BDL
spiked train (ug)	951.4	841.1	1286.3	3998.3	1478.6	1057.0
field spike (ug)	1050	800	118	4000	470	1200
Equivalent Spiking Level (ESL) (ppmvd)	15.01	14.55	3.15	100.04	6.48	10.22
ESL, % of actual source gas concentration	1155%	766%	77%	758%	1297%	not calculated, normal train BDL
Does ESL meet criteria?	no	yes	yes	yes	no	not calculated, normal train BDL
percent difference	not calculated, ESL criteria not met	666%	23%	658%	not calculated, ESL criteria not met	not calculated, normal train BDL
high spike recovery (%)	not calculated, ESL criteria not met	92%	960%	87%	not calculated, ESL criteria not met	not calculated, normal train BDL
Bracketed spike recovery	110%	92%	91%	7%	not calculated, low spike BDL, high spike did not meet ESL criteria	not calculated, high spike BDL, low spike did not meet ESL criteria
Alternate Value *			525%	47%		
Successful spike and recovery?	yes	yes	yes	no	no	no

* Section 2.4.2.5.3.2, Rule 3 allows the user to average spike recoveries or to use the spike with the smallest percent difference

WORKSHEET FOR DETERMINING THE SPIKE RECOVERY QA PROCEDURE FOR WP ISS-FP-A105.01

Step 1: Calculate Equivalent Spiking Levels

$$\text{ESL} = \text{mass}_{\text{field spike}} \div \text{MW} \times 24.055 \text{ L/gmol} \div \text{V}_{\text{run spike sample}}$$

	Mass, µg	MW, g/gmol	$V_{run\ spike\ sample}$, dsL
LESL			
HESL			

$$\text{LESL} = \frac{(\qquad \text{ug}) \times 24.055\text{L/gmol}}{(\qquad \text{g/gmol}) \times (\qquad \text{L})} = _______ \text{ ppmvd}$$

$$\text{HESL} = \frac{(\qquad \text{ug}) \times 24.055\text{L/gmol}}{(\qquad \text{g/gmol}) \times (\qquad \text{L})} = _______ \text{ ppmvd}$$

Step 2. Sample Train Results

Spike Level	ESL, ppmvd	Normal Train (C_A), ppmvd	5 x C_A Ppmvd	10 x C_A ppmvd	Spike Train, (C_{ST})ppmvd
Low Bracket					
High Bracket					

Step 3. Spike Recovery Determination

- If using the bracketed run spike option, then the rules for the determining the spike recovery are:

Rule 1. Use this rule if both criteria are <u>YES</u>: (enter values)

Is LESL	>	5x$C_{A\ Low}$?	Yes/No
	>		

Is HESL	#	10x$C_{A\ High}$?	Yes/No
	#		

$$\text{If Yes, spike recovery} = \frac{[\text{C}_{\text{ST High}}(ppmvd) - \text{C}_{\text{A High}}(ppmvd)]}{\text{HESL}(ppmvd)} \times 100$$

$$= \frac{(\qquad \text{ppmvd -} \qquad \text{ppmvd})}{_______ \text{ ppmvd}} \times 100 = _________ \%$$

Rule 2. Use this rule if both criteria are <u>YES</u>: (enter values)

Is LESL	#	$5xC_{A\ Low}$?	Yes/No
	#		

Is HESL	>	$10xC_{A\ High}$?	Yes/No
	>		

$$\text{If Yes, spike recovery} = \frac{[C_{ST\ Low}(ppmvd) - C_{A\ Low}(ppmvd)]}{\text{LESL}(ppmvd)} \times 100$$

$$= \frac{(\qquad \text{ppmvd} - \qquad \text{ppmvd})}{_____\ \text{ppmvd}} \times 100 = _________\%$$

Rule 3. Use this rule if both criteria are <u>YES</u>: (enter values)

Is LESL	#	$5xC_{A\ Low}$?	Yes/No
	#		

Is HESL	#	$10xC_{A\ High}$?	Yes/No
	#		

$$\text{(3a) LESL Spike Recovery} = \frac{[C_{ST\ Low}(ppmvd) - C_{A\ Low}(ppmvd)]}{\text{LESL}(ppmvd)} \times 100$$

$$= \frac{(\qquad \text{ppmvd} - \qquad \text{ppmvd})}{______\ \text{ppmvd}} \times 100 = ______\%$$

$$\text{(3b) Low Spike \%difference} = \text{ABS}\left|\frac{\text{LESL(ppmvd)} - C_{A\ Low}\text{(ppmvd)}}{C_{A\ Low}\ \text{(ppmvd)}}\right| \times 100$$

$$= \text{ABS}\left|\frac{\qquad - \qquad}{\qquad}\right| \times 100 =$$

$$\text{(3c) ESL}_{High}\text{ Spike Recovery} = \frac{[C_{ST\ High}(ppmvd) - C_{A\ High}(ppmvd)]}{\text{HESL}(ppmvd)} \times 100$$

$$= \frac{(\qquad \text{ppmvd} - \qquad \text{ppmvd})}{______\ \text{ppmvd}} \times 100 = _______\%$$

$$\text{(3b) High Spike \%difference} = \text{ABS}\left|\frac{\text{HESL(ppmvd)} - C_{A\ High}\text{(ppmvd)}}{C_{A\ High}\ \text{(ppmvd)}}\right| \times 100$$

$$= \text{ABS}\left|\frac{\qquad - \qquad}{\qquad}\right| \times 100 =$$

Choices for Rule #3 Spike Recovery:

Choice 1: Use average of LESL Spike Recovery (3a) and HESL Spike Recovery (3c)

$$= \frac{\left[(high)\qquad\% + (low)\qquad\%\right]}{2} = _______\%$$

Choice 2: Use the ESL with the smallest *spike %difference* to calculate the spike recovery,

Which ESL Spike %difference is smaller? (circle one)

LESL Spike %difference (Step 3.3b) or HESL Spike %difference (Step 3.3d) ?

Then use (H or L)ESL Spike Recovery result from Step 3.3a or 3c = _______%

Which choice is going to be used? (circle on)

Choice #1 or Choice #2

Selected Spike Recovery from Choice # _____ for Step 3 = _________%

Rule 4.

Is LESL	>	$5xC_{A\ Low}$?	Yes/No
	>		

Is HESL	>	$10xC_{A\ High}$?	Yes/No
	>		

If the answer to both is "YES," then ESLs do not meet the criteria and spike recovery should not be calculated and reported. Report, instead, that the spike equivalent levels did not meet the Bracketed Spike Run Criteria.

State of California
Air Resources Board

Method 501

Determination of Size Distribution of
Particulate Matter from Stationary Sources

Adopted: March 23,1988
Amended: September 12, 1990

Method 501

Determination of Size Distribution of

Particulate Matter Emissions from Stationary Sources

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METHOD 501
DETERMINATION OF SIZE DISTRIBUTION OF
PARTICULATE MATTER EMISSIONS FROM STATIONARY SOURCES

1 PRINCIPLE AND APPLICABILITY

Skilled operators are needed for proper operation of cascade impactors, the subsequent analysis of the sample, and presentation of the data. As the skill, experience, and judgment of the user are important factors in the successful application of this method, any deviations from recommendations should be reported.

1.1 PRINCIPLE

Particulate matter is withdrawn isokinetically from the source and segregated by size in a cascade impactor at the sampling point exhaust conditions of temperature, pressure, etc. Cascade impactors use the principle of inertial separation to size segregate particle samples from a particle laden gas stream. The mass of each size fraction is determined gravimetrically.

1.2 APPLICABILITY

This method is applicable in ducted source sampling environments with a particulate mass concentration range of 0.005 to 50 grains per cubic foot, a pressure range of –5 to +20 inches water gauge, a temperature range of 32 to 840°F and a velocity range of 10 to 100 feet per second.[1]

DETERMINATION OF PM_{10} EMISSIONS FROM STATIONARY SOURCES

Any rule or regulation which refers to this test method for the purposes of determining PM_{10} emissions should specify the procedures by which such emissions are defined. PM_{10} is defined for ambient sampling, but for source sampling, carefully detailed sampling and analytical procedures should be referenced and the results defined as PM_{10}.

The recommended procedure is to determine a mass fraction of PM_{10} by ARB Method 501 while conducting a total PM mass emissions test using ARB Method 5. Then the mass fraction (of those particles with aerodynamic diameters equal to or less than ten microns) multiplied by the total emissions is defined as the PM_{10} emissions. Any rule or regulation so written should specify whether or not the impinger catch from Method 5 should be included in the calculation.

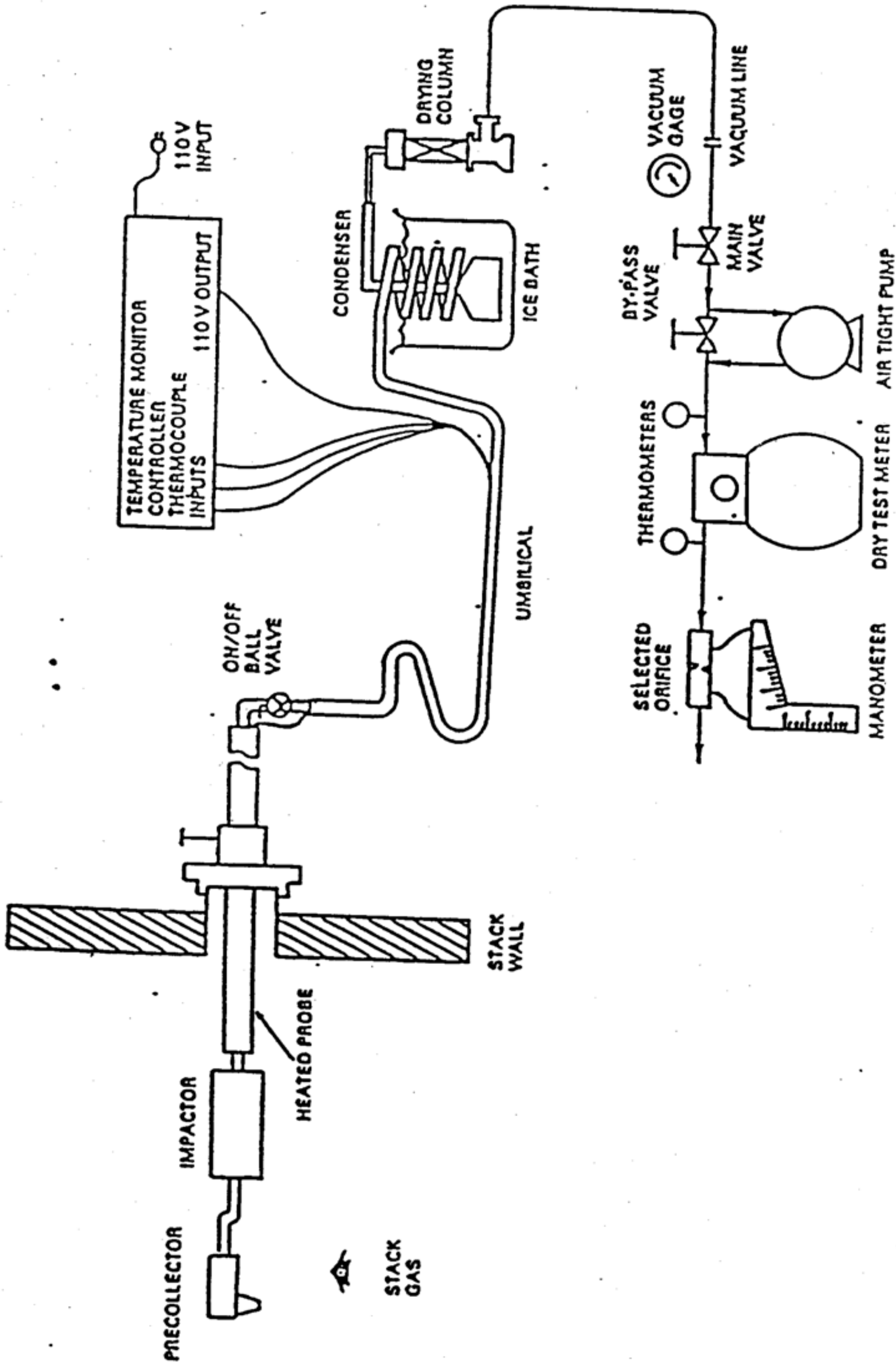
Figure 1 on page 3 of this method shows a sampling train employing the minimum apparatus necessary for the determination of a PM_{10} mass fraction using a cascade impactor. After the construction of a particle size distribution curve following the

[1] Much of the text of this method was taken from the “Procedures Manual for the Recommended ARB Particle Size Distribution Method (Cascade Impactors),” hereafter referred to as “Manual.”

impactor manufacturer's instructions, the PM_{10} mass fraction should be taken as the mass fraction of particles with aerodynamic diameters less than ten microns.

Figure 2 on page 4 is EPA's schematic diagram of a constant sampling rate (CSR) sampling train. The reference for Figure 2 is EPA's Method 201A—Determination of PM_{10} Emissions (Constant Sampling Rate Procedure), published in the Federal Register/Volume 54 No.107/Tuesday, June 6, 1989/Proposed Rules/pages 24235-24247. This sampling train allows the PM_{10} mass emissions determination from only one train, but does not allow consistent comparisons with a Method 5 database which includes condensable particulate mass. If this is not an important issue, then the CSR alternative may be used.

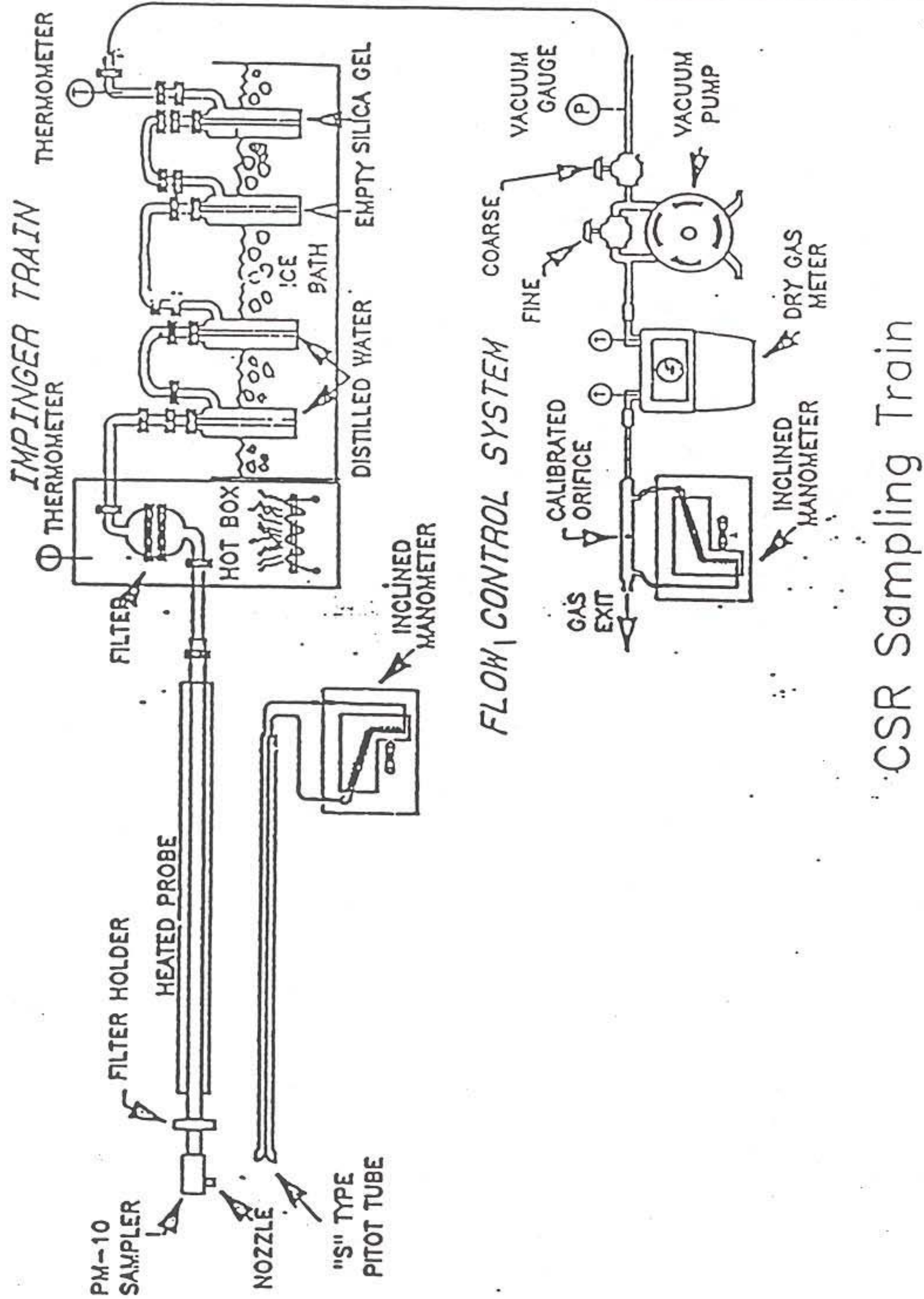
Figure 1



Cascade Impactor particulate sampling train for noncondensible particulate (modified EPA Method 5 Train).

Figure 2

24240 Federal Register / Vol. 54, No. 107 / Tuesday, June 6, 1989 / Proposed Rules



2 APPARATUS

The following paragraphs describe the apparatus used with cascade impactors.

2.1 A schematic of the sampling train is shown in Figure 1. The right angle precollector and cascade impactor are mounted on the modified probe of a standard Method 5 sampling train. The pitot head normally used on a standard Method 5 sampling train is not used with impactors. The flow metering orifice on the dry gas meter may need to be changed to an appropriate size for the desired impactor flow rate. Since the impactor is operated in-situ, the filter/oven section of the Method 5 train is not used. This is analogous to using Method 5 sampling equipment to run Method 17 Emission Tests. The reader is referred to U. S. E. P. A. Publication APTD-0581 (Construction Details of Isokinetic Source-Sampling Equipment) (Martin, 1971) for a more detailed equipment description. All in-situ components should be constructed of stainless steel for purposes of temperature tolerance, ruggedness, and resistance to corrosive flue gases. High temperature heating tapes permit the same probe to be used in hot side as well as cold side sampling situations. Method 5 sampling trains are available from numerous commercial vendors. The following paragraphs describe the various components of the sampling train.

NOTE: The condenser in Figure 1 should be removed and replaced by a Method 5 type impinger train as shown in Figure 2 if condensible emissions are to be included in the PM_{10} mass fraction determination. A determination of total PM_{10} emissions (including condensible emissions) should have condensible emissions (impinger catches) included in both the Method 5 and Method 501 determinations on which it is based.

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2.1.1 RIGHT ANGLE PRECOLLECTOR

In most situations the use of a right angle precollector is essential. The precollector serves to (1) turn the sample stream through a 90° angle and (2) help prevent overloading of first impactor stage. If the port arrangement distribution of the sample stream does not cause over loading problems with the first impactor stage, then the precollector is not necessary.

The curved nozzles (90° Bend and Buttonhook) used with Methods 5 and 17 are unacceptable for use with particle sizing devices because of high particulate losses in the nozzle. At moderate to high duct velocities it is quite possible for such a nozzle to have a 50% collection efficiency diameter, D_{50}, smaller than the D_{50}'s of the later stages (See Section 4.3.1.2, Nozzle Choice Flowrate and Impactor Stages).

If the capacity of the upper stage needs to be increased to permit collection of weighable quantities at the lower stages, the precollector provides a means of accomplishing this.

The right angle precollector is separate from the impactor and as such can be attached to almost any impactor which is operable at a compatible flow rate. The Zoltec Brink Model C cascade impactor has a built-in cyclone that serves as a right angle precollector to this low flow rate sampler. The Brink is designed for inlet sampling situations.

2.1.2 NOZZLES

When attached to the right angle precollector, the nozzle should not inhibit entry through a four inch diameter port. However, if the impactor can be rotated into flow it may not be necessary to use a precollector. As discussed earlier, the curved nozzles (90° Bend and Buttonhook) used with Methods 5 and 17 are unacceptable for use with particle sizing devices because of high particulate losses in the nozzle. The nozzles should have a sharp leading edge. The inside of the nozzle should have an even taper from the inlet diameter to a correct exit diameter for the particular precollector. It is important that all nozzles have the same exit diameter since this is one of the critical dimensions in the aerodynamic performance of the precollector (inlet jet diameter).

A range of nozzle sizes is needed for isokinetic sampling. The recommended range is from 1/8 to ½ inch (3.2 to 12.7 mm) diameter in increments of 1/16 inch (1.6 mm). For inlet sampling with a low flow rate impactor, it may be necessary to use smaller increments in nozzle diameter. Problems with nozzle pluggage establish a minimum diameter of about 0.0550 inches (1.4 mm, wire guage drill size No. 54). Note that a 1400 um particle will plug this nozzle. Nozzles should be calibrated as described in Section 5, Calibration. Emergency field repairs can be made using a sharp round tapered metal tool such as an awl or a scribe. Care should be taken to avoid flaring the thin metal edges of the nozzle when performing the emergency repair. Repaired

nozzles must be so noted in equipment log books and recalibrated before use. A dial caliper (0.001 inch) as described in Section 5.2 should be on hand for this calibration.

2.1.3 CASCADE IMPACTOR

Appendix B of the Manual and Section 8 of this method give a list of current commercially available cascade impactors suitable for use as in-situ stack samplers (An acceptable impactor is one which produces acceptable results per the quality assurance and control criteria in Section 7.) Operation of one of the suitable impactors shall be in substantial conformance with the manufacturer's operating instructions. All of these impactors are designed with an internal filter holder. The calibration of the impactor type used must have been verified as described in Section 5.9, Impactor Stage Constants, for the configuration to be used (choice of substrate material and stages used). The Pollution Control Systems (University of Washington) Mark V Cascade Impactor together with an accessory right angle precollector and nozzle set (EPA/SoRI design) will meet the performance criteria of this test method in proper operation. Other impactors may be acceptable, as mentioned above; the examples given in this method are all for this manufacturer as a matter of consistency, not endorsement. The Mark V impactor is of an in-line design permitting the user to choose the appropriate stages for a given sampling situation (inlet), outlet, stack velocity, temperature, etc). The right angle precollector's connecting tube serves as a single jet first stage (zero stage) for the impactor and uses a solid disk-shaped collection substrate rather than the donut-shaped collection substrates used with the multi-jet stages. The impactor design requires that the solid disk must be used to direct the airflow to the subsequent multi-jet stages. Up to ten of these multi-jet stages may be selected as described from the twelve multi-jet stages furnished with the Mark V (i.e. there are two extra jet plates). Spacers may be used to permit operation with fewer than eleven stages. The preferred configuration is to use the single jet inlet followed by six multi-jet stages with one disk-shaped collection plate, seven donut-shaped collection plates respectively and two filters. The second filter serves as a quality control check. The extra donut-shaped collection plate is loaded with the selected substrate material and inserted upside down directly behind the collection plate of the last stage. This extra substrate is out of the gas flow path and thus never subjected to particulate matter. It serves as a quality control blank for the individual run and quantifies handling losses, balance changes, flue gas interaction, etc. Spacers may be used in the Mark V shell or a shorter Mark III shell may be used to make the impactor lighter and easier to traverse in and out of small ports with long probes. Viton-o-rings and Teflon inserts (at the filter) are normally used with this impactor. For high temperature applications metal o-rings and Kapton inserts may be substituted for the Viton and Teflon.

A filter holder and filter are needed to perform the blank impactor run described in Section 4.3.2. The filter is attached to the impactor inlet in place of the precollector and prevents particulate from entering the impactor, thus providing a quantitative measure of substrate flue gas interactions. Method 17, Section 2.1.2 describes a suitable filter. Nozzles are not required. Filter sizes commonly used are 47 mm or 63 mm.

2.1.4 SAMPLING PROBE AND UMBILICAL LINES

A pitot tube may be used as part of the sampling train if desired but is not required. Velocity profile information is obtained prior to the sampling run by performing a velocity traverse using Method 2. The sampling flow rate, nozzle, and sampling points are selected based on this velocity traverse.

The sampling probe and umbilical lines are the same as those for a Method 5 train. The internal tubing of the probe should be stainless steel. The probe should be heated. The probe length should be sufficient to reach all traverse points.

2.1.5 CONDENSER

The impinger system described in Method 5 shall be used.

2.1.6 METERING SYSTEM

The metering system is the same as that for a Method 5 Sampling Train with the exception that in sampling situations requiring low impactor flow rates it may be necessary to use a smaller orifice that the standard 0.180 inch ID orifice. Construction of such smaller orifices is the same as for the standard Method 5 orifice except that a smaller diameter (e.g. 0.130, 0.093, and 0.059 in. i.d.) is used to obtain a higher pressure drop reading for the lower flows. These orifices should be calibrated as described in Section 5.4.

2.1.7 GAS DENSITY DEVICES

Temperature sensor and pressure guages, are described in Sections 2.3 and 2.4 of Method 2, and gas analysis equipment is described in Method 3. Data from Method 100, where applicable, may also be used.

2.1.8 BAROMETER

A mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg) may be used. In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which should be the absolute barometric pressure, not corrected to sea level) shall be requested and an adjustment for evaluation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase.

2.2 ANALYTICAL EQUIPMENT

2.2.1 SUBSTRATE PREPARATION

See Section 4.2.2

2.2.2 SAMPLE RECOVERY

Various items are used in the sample recovery process. A polyethylene wash bottle may be used to washdown the nozzle with acetone after cleaning the exterior and dry brushing the larger particles onto the precollector substrate with a small camel hair or nylon bristle brush. Note that acetone should not be stored in polyethylene bottles for longer than one month. A clean nozzle brush is used with the acetone washdown. The nozzle brush should have nylon bristles, a stainless steel wire handle and may be properly sized for the probe nozzle. For small nozzles, ultrasonic cleaning may be used. If the probe wash is to be evaporated on site, glass sample storage containers will not be needed. If post-test evaporation is to be done in the laboratory (where a vented hood is available) the wash should be stored in properly labeled glass sample bottles. These bottles should be chemically resistant, borosilicate glass, 500 mL or 1000 mL, with screw cap liners. The liners should be either be rubber-backed Teflon or constructed so as to be leak-free and resistant to chemical attack by acetone. The acetone rinse is then carefully evaporated in a preweighed aluminum evaporation dish placed on a hot plate. Use extreme care as acetone is highly flammable and has a low flash point. A ring stand and funnel are helpful during washdown.

A graduated cylinder (rugged plastic is recommended) is used to measure the volume of water removed during the sample run by the ice bath condenser or impingers. The cylinders should not have graduations larger than 2 mL. This will permit determinations to the nearest 1 mL. The condensers are followed by silica gel drying columns. Gravimetric determinations of water uptake by the silica gel may be made using a lab balance capable of weighing to the nearest ½ g or less. The conversion factor 1 g H_2O = 1 mL H_2O is then used to obtain moisture volumes.

Petri dishes (plastic is recommended) are used to protect the substrates. Each petri dish should be clearly labeled with the substrate identification number. Prior to the initial pre-run weighings and the post-run weighings the petri dishes are placed in airtight desiccators (plastic food storage containers work well) containing silica gel.

2.2.3 ANALYSIS

2.2.3.1 BALANCES

Various analytical equipment is needed for the on-site laboratory where the impactors are loaded and unloaded and the substrates are weighed. The most important of these items is the analytical balance. Accurate weighing of the particulate matter collected on the impactor substrates requires a balance having a sensitivity of 0.01 mg or better.

Several electrobalances marketed have the insensitivity to vibration required for field use, as well as weighing chambers and pans large enough to accommodate flat unfolded substrates. Some may require modification if abnormally large substrates are to be weighed. Various items are used with the analytical balance. These include tare weights, Class S standard calibration weights, smooth tweezers for handling the calibration weights, tweezers for handling the substrates, control weights, thread strips, special large sample pans, and tape for bundling petri dishes with substrates from the same run.

If at all possible, the substrates should be weighed in the on-site laboratory rather than being transporting back to the home laboratory for weighing. The collected particulate matter will be lying on an open substrate and distances can easily cause some material to be spilled over to the petri dish. Because the weight changes are so small (less than 15 mg per stage) any losses during transport can represent a large percentage of the total weight change.

2.2.3.2 OTHER ANALYTICAL EQUIPMENT

Other on-site lab items include plastic desiccators with silica gel, a triple beam lab balance for determining silica gel drying column weight gains, 50 g Class P calibration weight for this balance, and equipment for leak checking samplers before sending them to the sampling location. High temperature fiberglass tape and permanent markers should be used to label the loaded sampler with its run number and substrate set identifier. Data is recorded on the run sheet bearing these numbers and all pre-run calculations are attached to this sheet. A hygrometer and thermometer are used to determine the relative humidity in the on-site laboratory. A portable barometer may be located in the lab and elevation connections used to obtain the pressure at sampling sites. This barometer can be carried into the control room and checked against the control room barometer (provided it reads room pressure and not the pressure at some point in the process).

In order to calculate stage D_{50}s on a Stokes diameter basis, one must determine the average particle density (gm/cm^3). This value is determined from helium pycnometer measurements on screened hopper samples. The hopper ash is screened with a No. 60 Sieve (ASTM E 11 sieve Designation, 250 um openings) to remove rust, agglomerates, etc., which would not have been captured by the control device but may be found in hopper samples. This type of testing is performed by numerous commercial testing laboratories.

Calibration procedures are described in Section 5. Laboratory calibration equipment used includes a wet test meter for calibration of the dry gas meter and orifice and a reference dry gas meter to determine when recalibration (by wet test meter) is required. Other calibration equipment may be used either pre-test in the lab or on-site. These include a precision glass thermometer with ice water bath and hot plate for thermocouple/controller calibration, dial calipers as listed above for nozzle calibrations, mercury barometer, standard pitot or reference pitot, slant tube manometer for

magnehelic differential pressure meters, and Class S calibration weights for the analytical balance.

3 REAGENTS AND CONSUMABLES

Various reagents are used in connection with cascade impactor sampling. These include substrate materials and filters as well as any chemical used to prepare them, desiccants, water, ice, acetone and stopcock grease. The water is used for priming the condensers and the ice for chilling the condensers in an ice bath. If Method 5 glassware is used in place of the condenser and drying column, acetone-insoluble, heat-stable silicone grease (stopcock grease) may be needed to form an airtight seal at the ground ball and socket joints. Alternate designs which eliminate the ball and socket joints do not require the stopcock grease. Indicating type silica gel (6 to 16 mesh) may be used as a desiccant in the drying column and desiccators. Previously used silica gel may be rejuvenated by heating at 175°C (350°) for two hours. A change in color indicates that the desiccant has been depleted. Acetone is used for washing down the nozzles, etc. The wash is evaporated and weighed to determine the total amount of particulate present. Consequently the acetone should be reagent grade with no more than 0.0001% residue. Acetone should only be stored in glass bottles (or temporarily in polyethylene bottles) since metal containers can greatly increase the residue content. Acetone blanks are run prior to the field test and only acetone with low blank values (0.001%) may be used.

The filters and substrate material used depend on the sampling situations and the type of impactor to be used. High temperatures can prohibit the use of grease inserts. High flue gas sulfur levels can cause significant weight changes in the filter due to reactions with the flue gas constituents. For these reasons blank impactor runs are required as described in Section 4.3.2. In most cases only four to ten impactor runs will be made during a field test. When this is the case one can arrive on site with sufficient quantities of two or more types of substrates so that if a blank run shows unacceptable weight changes with, for example, greased substrates, preweighed quartz would be on hand for use. If numerous runs are to be performed and it is impractical to have prewashed substrates or multiple types, blanks should be run during the pretest site survey to select the substrate material to be used. Acid washing of fiberglass substrates to minimize reactions with SO_2 is described in Section 4.2.2.3 along with a detailed discussion of substrate options. Any filters used should be certified as 99.95% efficient on 3.0 um dioctyl phthalate smoke particles. This filter test is described in ASTM Standard Method D2986-71. Test data from the supplier's quality control program are sufficient for this purpose.

4 PROCEDURES

4.1 PRE-TEST LABORATORY PREPARATION

Pre-test laboratory preparations include equipment maintenance, equipment calibration, and substrate preparation and weighing.

4.1.1 EQUIPMENT MAINTENANCE

The right angle precollector and impactor do not require any special maintenance other than simple cleaning and ultrasonic cleaning of the impactor jet plates (to prevent any buildups that could change the hole sizes). All internal parts must be spotlessly clean before a run so that any particulate on the substrates can accurately be attributed to the stack gases. From time to time it may be necessary to use a lapping compound between threaded surfaces to repair rough threads and prevent gauling. Some impactors have silver plating on their threads to prevent gualing. Silver plating is highly recommended for temperatures above 425°F. The threads should be loose and smooth, not tight or rough. Teflon tape may be used to prevent gauling when the temperature is less than 425°F. It should be noted that some liquid base thread lubricants can contaminate the substrates and should be avoided. When needed, use them sparingly. The blank impactor run should reveal problems of this type. When nozzles are damaged they usually require repair by a machine shop. Frequently, this requires being bored out to a larger diameter.

The sampling train is a standard Method 5 train and is to be maintained as described in Method 5.

4.1.2 SUBSTRATE MATERIALS AND PREPARATION.

Cascade impactors use lightweight inserts for the collection plate below each jet stage. These inserts must be lightweight to permit the detection of very small weight changes (0 to 15 mg) and must hold the captured particulate matter in place. As discussed in Section 3 (Deviations from Theory) particle bounce can present problems. Some aerosols are wet and sticky and can be satisfactorily collected with bare metal inserts, but such is not generally the case. Hence, most aerosols require the use of something to absorb the particle momentum and keep particles from bouncing to surfaces where they don't belong. Various substrate material options are available for this purpose. Certain impactor designs, however, exclude or make it difficult to use some of these options. The main options are bare metal, greased metal, polypropylene coated metal, fiberglass, and quartz. Bare metal is restricted to sticky aerosols that do not exhibit bounce problems.

4.1.2.1 COATED METAL FOIL

Greased metal foils are generally the preferred substrate choices, except at higher temperatures. Felix, et al ii, (1977) tested 19 different greases for possible use at typical stack temperatures. Many were found to be unstable at stack temperatures. Some hardened and others flowed too freely. Only one was found to be sufficiently stable at 177°C (350°F), Apiezon H. This particular brand of grease is commonly used in gas chromatography (GC) and is available through several laboratory supply vendors. The manufacturer is James G. Biddle Co., Plymouth Meeting, PA 19462. The company offers a second version formulated for temperatures near ambient, Apiezon L (L for low temperature and H for high temperature). Apiezon H was found to be too hard a

coating at lower temperatures (125°C) but the L formulation worked well at some sources at these temperatures.

Other greases or polymers have been used successfully under conditions of flue gas composition and temperature which are hostile to Apiezon H. Specifically, low-molecular-weight amorphous polypropylenes have been found to perform well with little weight change in gases containing high levels of sulfur oxides. Unpublished results of research by J. D. McCain at Southern Research Institute showed that Hercules AFAX 800 and 500 (HL1) amorophous polypropylenes have suitable viscosities to be used, respectively, at ambient and stack (up to 165°C) temperatures. Another compound which has been found not to degrade at stack temperatures up to 230°C is Exxon 065 butyl rubber. An additional benefit of these polymers is that they contain sufficient low levels of trace metals to be used as collection surfaces for samples intended for elemental analysis by such techniques as neutron activation analysis (NAA).

It is probable that other greases or compounds may perform as well as those mentioned above for particular conditions. In general, any material is suitable if it has the consistency of a tacky fluid at the sampling temperature and if it does not show a significant change in weight or other physical properties due to interaction with the hot flue gases.

The greases are normally applied as suspensions or solutions of 10-20% grease in a solvent. Toluene is a suitable solvent for Apiezon H and L. Cyclohexane has been used for the polypropylene and butyl rubber polymers. The mixture is placed on the cut foil substrate with a brush medicine dropper, or sprayed onto the foil with an airbrush. Approximately the same amount of coating (same number of drops) should be applied to each substrate. This can be very significant in situations where a flue gas interaction is occurring. The reproducibility of any weight changes is discussed in Section 4.7.17, but different amounts of coating on different substrates can prevent weight change from being uniform. The coated foil is baked at 150°C (300°F) for 1 to 2 hours and then dried 12-14 hours over silica gel in a desiccator at ambient temperature prior to weighing. It is important to avoid an excess of grease. Too much grease, or one with too low a viscosity, causes “blow off” problems—the physical removal, spreading, or creep, of the grease off the impactor stage. The dry greased surface of the substrate should be tacky, but not slippery, with a film of thickness equal to or greater than the diameter of the particles which are to be captured. Typically, the amount of grease on a suitably coated substrate will be about 10 to 25 milligrams.

4.1.2.2 FIBER MATS

Glass or quartz fiber mats are used routinely in some commercial impactors and in all impactors for sampling at temperatures above the limits of greases. In addition to providing a light-weight impaction surface, such fiber mats reduce reentrainment due to particle bounce. Fibrous substrates have different collection characteristics from those of flat surfaces, so calibrations performed with fiber mats must be used for reduction of data taken with fiber mat substrates.

Glass fiber mats and in some instances, quartz mats, cut to the required shape, can usually be obtained from the impactor manufacturer. Mats of other fibers can usually be cut to shape upon request to the manufacturer. In particular, quartz fiber mats may be preferable for substrates for use at higher temperatures or where sulfur oxides are a problem as mentioned below. The quartz mats must be handled carefully to avoid loss of fibers.

In hot gases containing sulfur oxides, glass fiber mats often exhibit anomalous gains in weight due to reaction with sulfur oxides and the formation of sulfates. After extensive laboratory and field experiments on a number of glass fiber mats (Felix, et al., 1977; Cushing, 1978; Peters and Adams, 1978), the only mats that have to date been found suitable for use as impactor substrates are Whatman 934AH (former Reeve Angel 934AH) and Schleicher and Schuell No. 30. Both are available from Whatman, Inc., 9 Brideswell Place, Clifton, NJ 07014. When these materials are treated with sulfuric acid by the procedure outlined below, gains in weight caused by reaction with flue gas constituents can be kept acceptably low. Glass fiber backup filters exhibit the same behavior and should be treated in the same manner.

In the studies mentioned above, quartz fibers were found to have negligible weight changes in the presence of sulfur oxides, but most pure quartz fiber mats were also found to be too fragile for use as substrates. Since the time of these studies, Pallflex 2500 QAST quartz fiber filters have been introduced. While still more fragile than glass fiber mats, these quartz mats have proven to be sufficiently strong for use as substrates for several impactors. As appears general for quartz fiber materials, 2500 QAST mats were found to exhibit low blank weight gains at stack conditions, even without the acid washing treatments recommended below for glass fiber mats.

4.1.2.3 ACID WASHING FIBER MATS

1. The mats should be submerged in a 1:1 mixture (by volume) of distilled water and reagent-grade concentrated sulfuric acid at 100-115°C (210-240°F). Maintain the mixture at this temperature for 2 hours. This operation should be conducted in a fume hood using clean glassware and a temperature controlled laboratory hot plate. If the fiber mats need to be weighted down to keep them submerged in the acid bath, Teflon disks may be placed on the top and bottom of the stack and a glass or Teflon weight placed on top of this disk.

2. After removing the mats from the acid bath, they should be allowed to cool to room temperature and then be placed in a bath of distilled water and rinsed continuously with a water flow of 10-20 mL/min. until the pH value of the rinse water, after a few minutes in contact with the mats, is nearly the same as that of distilled water. The importance of thorough washing <u>cannot</u> be over-emphasized.

3. After rinsing in the distilled water, the mats should be rinsed in reagent-grade 2-propanol (isopropanol, isopropyl alcohol) by submerging them for several minutes. Repeat this step four or five times using fresh 2-propanol each time.
4. Allow the mats to drain and dry. After they are dry enough to handle, spread them out in a clean place to dry.

5. When the mats are dry to the touch, they should be baked in a laboratory oven at 100°C (212°F) for about 2 hours, to vaporize residual water and alcohol, then raise the oven temperature to 370°C (700°F) for 3 hours. This vaporizes any residual sulfuric acid. The mats may become discolored unless the water and alcohol are driven off prior to vaporizing sulfuric acid.

6. To verify that the acid has been removed, one can tear two mats into small pieces, immerse them in about 50 mL of distilled water, stir the water for about 10 minutes and measure the pH with a meter. If the pH is significantly lower than that of the distilled water, the remaining mats may be baked at 370°C (700°F) for several additional hours to remove any residual acid. The 370°C (700°F) temperature is necessary because of the high boiling point of sulfuric acid, 340°C (640°F).

4.1.2.4 ON-SITE MAT CONDITIONING

Even after being washed with sulfuric acid, glass fiber mats have still shown anomalously high gains in weight in some process streams, particularly those at extremely high temperatures and those containing relatively large concentrations of sulfur oxides. If blank runs with acid-washed substrates reveal problems, they can be minimized by conditioning the glass fiber mats in the process gas stream prior to use. Place the mats, loosely packed, in a suitable container preceded by a filter; insert the container into the gas stream, and draw filtered flue gas through the container for 6-24 hours before the initial desiccation and weighing. Blanks should be run with these in-situ conditioned and washed glass fiber mats. These will be used to verify the magnitude and reproducibility of any remaining weight changes.

4.1.3 BACKUP FILTERS

Backup filters are used on all impactors to collect the material that passes the last impactor stage. Binderless glass fiber filter mats are normally used for this purpose in all impactors, although the shape and size of the filter varies according to the impactor design.

Glass fiber backup filters have the same reactivity problems as glass fiber impaction substrates and may also require acid washing or conditioning. Quartz fiber filters should not require this treatment, and are available in many standard sizes. At temperatures below 150°C, Teflon fiber or membrane on fiber filters have also been found to perform well. Teflon inserts (washers) may be used to prevent the filter from sticking to the metal surfaces and a foil pouch is used to prevent the loss of particulate

collected on the fiber. In high temperature situations where Teflon is unacceptable, Kapton inserts may be substituted. A second filter is frequently used as a quality assurance check.

4.1.4 WEIGHT RECORDS

A normal part of the pre-test laboratory preparations is to both prepare the substrates to be used during the test and then obtain their dry prerun weights. This weighing function may be performed on-site if desired but is generally performed before hand so that the on-site time can be more effectively utilized. Calibration procedures and control weights are used to insure that no errors are introduced by moving the weighing laboratory between weighings (pre and post). The post-run desiccation and weighing should be done on-site to avoid particulate losses from occurring during transport back to the home laboratory.

4.2 ON-SITE PROCEDURES

The following paragraphs describe the procedures that must be performed on-site in order to characterize particle size distribution of a stationary source using cascade impactors. Some of the functions may be performed during a pre-test site visit and some may be performed prior to the test in the home laboratory rather than on-site.

4.2.1 PRELIMINARY PREPARATION

Manual, Table C-1 (Preliminary Survey for Particulate Sizing) and Table C-2 (Safety Checklist) list preliminary information that is needed prior to any field test. In situations where a pre-test site survey is performed, most of this information would be obtained at that time. The normal situation would not require that a pre-test site survey be conducted since most testing would be performed with a small 2 or 3 person crew at a familiar site. Most of the information in Table C-1 and Table C-2 could be obtained through dialogue with plant personnel and examination of previous compliance test reports. Any information not yet obtained should be gathered immediately upon arrival at the test site. Most of the missing information will be obtained during the initial inspection of the sampling site.

4.2.1.1 TRAVERSING PROTOCOL

In order to obtain a representative measurement one must obtain samples at representative points across the duct (stack) at isokinetic rates. In the case of conventional total particulate testing (e.g., Methods 5 and 17), this is accomplished by dividing the duct into a large number of equal area segments (per Method 1) and obtaining an isokinetic sample at the centroid of each of these areas. Isokinetic sampling is achieved by selecting a nozzle which is appropriate for the combination of the nominal flow rate at which the sampler is intended to operate and the average duct velocity. Compensation for duct velocity variations is then achieved by adjusting the sampling rate. This procedure cannot be used with the inertial particle classifiers

specified in this method because changes in sampling rates result in shifts in the characteristic diameter(s) of the size fractions.

With a fixed flow rate sampler the following procedure is recommended: establish anisokinetic limits and divide the sample plane (Method 1 Traverse points) into multiple regions such that all points within a given region nay be sampled at a fixed flowrate with a single nozzle and satisfy the anisokinetic limits. Separate runs are then performed for each region. The runs are averaged using a weighting proportional to the total volumetric flow of each region, this average synthesizes a complete traverse. Method 1 procedures are used to define the complete traverse and Method 2 procedures are used to determine the velocity at each point.

The recommended isokinetic error limit for the above procedure is that each point sampled by an impactor should have a point velocity that is within +20% of the impactor inlet velocity. Each of the traverse points which would be used in a standard Method 5 run should be sampled; thus if the ratio of the minimum velocity to the maximum velocity is greater than 1.5, multiple impactor runs are required. In this case, two or more regions would be selected such that for each region the velocity at every point within the region satisfies the 20% requirement.

Thus for any point i within a given region, the velocity at that point (i_i) meets the criteria $.8V < i_i < 1.2v$ where V is the sampling velocity into the impactor nozzle (fixed by the choice of the Nozzle Diameter and Impactor Flow Rate).

The following is a suggested technique for selecting the regions and respective sampling velocities when more than one region is required (i.e., $i_{max}/i_{min} > 1.5$):

Order the point velocities from the lowest (i_{min}) to the highest (i_{max}) then determine the 20% limits associated with each of the regions as follows:

For Region A:

$$i_{min} = i_{Amin} = 0.8\ v_A$$

$$\text{thus} \quad v_A = 1.25\ i_{min}$$

$$\text{and} \quad i_{Amax} < 1.2\ v_A$$

For Region B

$$i_{max} = i_{Bmax} = 1.2\ v_B$$

$$\text{thus:} \quad v_B = 0.833\ i_{max}$$

$$i_{Bmin} > 0.8\ v_B$$

If $i_{Amax} < i_{Bmin}$ it may be necessary to assign a third Region (Region C) since there are some point velocities which are not covered by Regions A and B. It should be noted that it is very possible to have a skewed velocity distribution where there are two tight groupings of low velocity points and high velocity points such that although i_{Amax} is less than i_{Bmin}, all the points are either less than i_{Amax} (Region A) or greater than i_{Bmin} (Region B). If there are points that lie between these two limits

$$i_{Amax} < i_{i} < i_{Bmin}$$

then a third region, Region C, (or possibly more than one additional region) would be required. Denote these points as i_{i} and repeat our previous approach as follows:

For Region C:

$$i'_{min} = i_{Cmin} = 0.8\ v_C$$

$$\text{thus} \quad v_C = 1.25\ i'_{min}$$

$$\text{and} \quad i_{Cmax} < 1.2\ v_C$$

If there are still some points remaining which do not fall within Region C then additional Regions would be called for as follows:

$$i'_{max} = i_{Dmax} = 1.2\ v_D$$

$$\text{thus} \quad v_D = 0.833\ i'_{max}$$

$$i_{Dmin} > 0.8\ v_D$$

In the unlikely event that additional points remained then yet more regions could be constructed by repeating the process above using "i" to designate all remaining points. Two regions will usually be sufficient. In some cases additional regions may be required. These cases would generally be situations where major flow obstructions existed close to the sampling ports.

If a 10% anisokinetic limit is desired rather than the 20% limit used above, then one may substitute $i_{min} = i_{Amin} = 0.9\ v_A$ and $i_{Amax} = 1.1\ v_A$, etc.

To be rigorous, one should adjust the dwell time at each point within a region so that the sample time at each point is velocity weighted and rounded to the nearest half minute. Although this is valid in that emissions factors are velocity dependent, the use of variable dwell times at each sample point can cause confusion on the part of the operator. As total emission rates are normally based on Method 5/17 Runs, which are isokinetic, the suggested procedure is that equal dwell times be used.

It should be noted that use of different nozzles with the same impactor flow rate will produce different sampling velocities (V). the actual sampling velocity will depend on the choice of nozzle diameter and impactor flow rate as velocity will depend on the choice of nozzle diameter and impactor flow rate as described in Section 4.2.1.6. It may be necessary to reassign points from one Region to another if it is not possible to obtain $V_{A'}$, etc. (as calculated above) in light the constraints of Section 4.2.1.6.

4.2.1.2 NOZZLE CHOICE, FLOW RATE, AND IMPACTOR STAGES

The general process is as follows: (1) measure/calculate the flue gas temperature, pressure, moisture, mean molecular weight, and required sampling velocity for a given traverse region then estimate the mass loading; (2) make an initial guess at the impactor flow rate that will give a reasonable sample time to collect weighable quantities on each stage; (3) select a nozzle and adjust the initial guess at the impactor flow rate so as to obtain the required sampling velocity for this traverse region; and (4) select stages that will give the desired stage cuts at this flow rate without resulting in particle bounce (VD_{50} product guidelines) or unacceptably low Reynold's numbers. The following paragraphs elaborate on these four steps. Steps 3 and 4 must be repeated for each of the traverse regions since different regions may require different flow rates, nozzles, and/or stage configurations. The following paragraphs illustrate the selection process for region A.

4.2.1.2.1 PRELIMINARY CALCULATIONS

Section 6 discusses the calculation of the flue gas temperature, pressure, moisture, mean molecular weight, and required sampling velocity for traverse region A. Plant personnel are generally able to provide approximate particulate concentration information (mass loading, gr/acf). If this information is not available, it may be necessary to run the in-stack filter to obtain a "good guess" at the particulate concentration so that t_{50mg} may be determined as described below.

4.2.1.2.2 TIME FOR 50 mg

An initial guess for the impactor flow rate is made by calculating the time to collect a total sample of 50 mg particulate (t_{50mg}). Equation 30 may be used to calculate this value for various flow rates or the nomogram shown in Figure 2 may be used to estimate t_{50mg} as described in Section 6.1.6.1. In this manner a flow rate may be found that will result in an acceptable run time as described in Section 6.1.6.1.

Note: It may be necessary to select a different flow rate and repeat steps 3 and 4 if the criteria of Step 4 are not satisfied.

4.2.1.2.3 NOZZLE CHOICE AND FLOW RATE

In Step 2 we determined the impactor flow rate which would produce an acceptable run time (t_{50mg}). We may now use Equation 32 to calculate the ideal nozzle diameter that would yield the required sampling velocity (V_A) for this traverse region when the sampler is operated at the flow rate determined in Step 2 above. From the set of available nozzles one would now select the real nozzle (D_{nA}) closest to this ideal size and use Equation 12 to calculate the corrected flow rate (Q_A) for this real nozzle. This flow rate is isokinetic to v_A, the mean velocity of Region A.

Figure 3, Nomograph for Selecting Nozzles for Isokinetic Sampling, is used to determine this corrected flow rate.

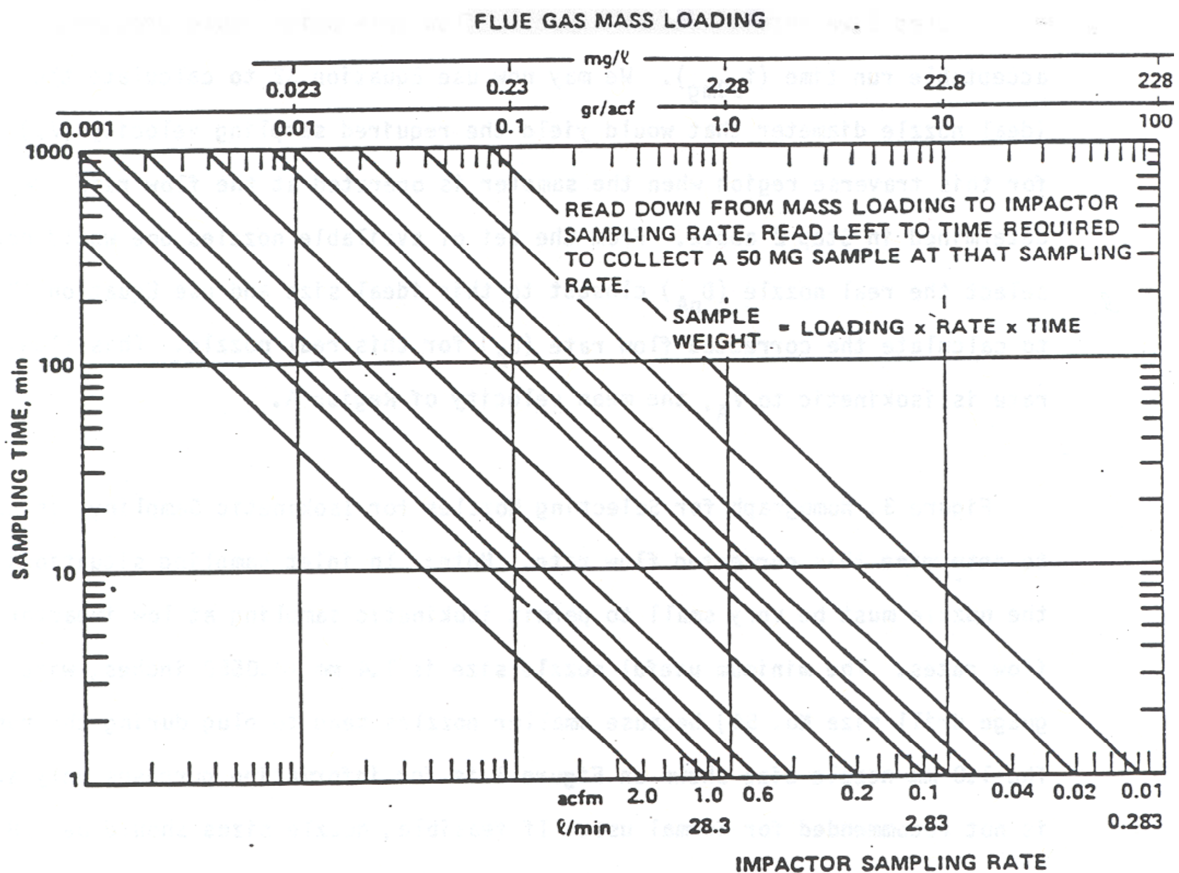
Note: In inlet sampling situations the nozzle must be very small to permit isokinetic sampling at low impactor flow rates. The minimum useful nozzle size is 1.4 mm (0.0550 inches, wire guage drill size No. 54) because smaller nozzles tend to plug during the run. The 1.0 mm nozzle size shown on Figure 3 is for information purposes only and is not recommended for normal use. If feasible, nozzle sizes should be 1/8 inch or larger.

4.2.1.2.4 STAGE CONFIGURATION

Using the corrected flow rate (Q_A) determined in Step 3, one would now select the stages which would give the desired size cuts without resulting in (1) particulate bounce or (2) unacceptably low Reynold’s numbers.

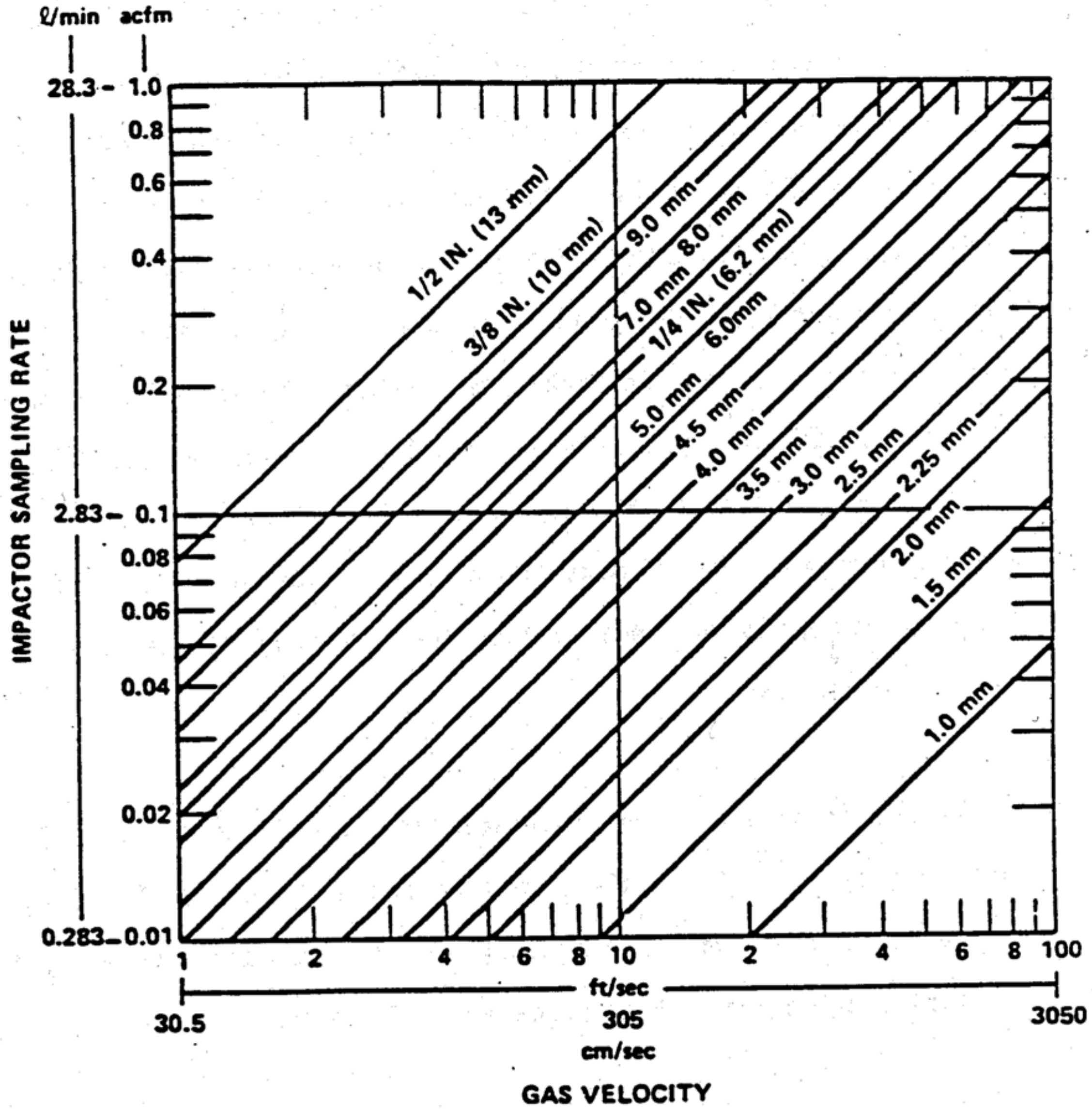
Note: It may be necessary to choose a different flow rate and repeat Step 3 if the criteria are not satisfied. If the design of the impactor used does not permit stages to be selected/deleted then one must continue to try different flow rates until one is found for which all the stages satisfy the two criteria given above. In such cases, one may be forced to compromise on either the desired stage cuts or to tolerate undesirably short or long run times. Data is suspect and may need to be rejected if any one of the stages are operated in a bounce mode or at very low Reynold’s numbers. the preferred impactor design is one that permits the selection of stages to optimize the configuration used.

FIGURE 2



Nomograph for determining sampling time (50 mg sample).

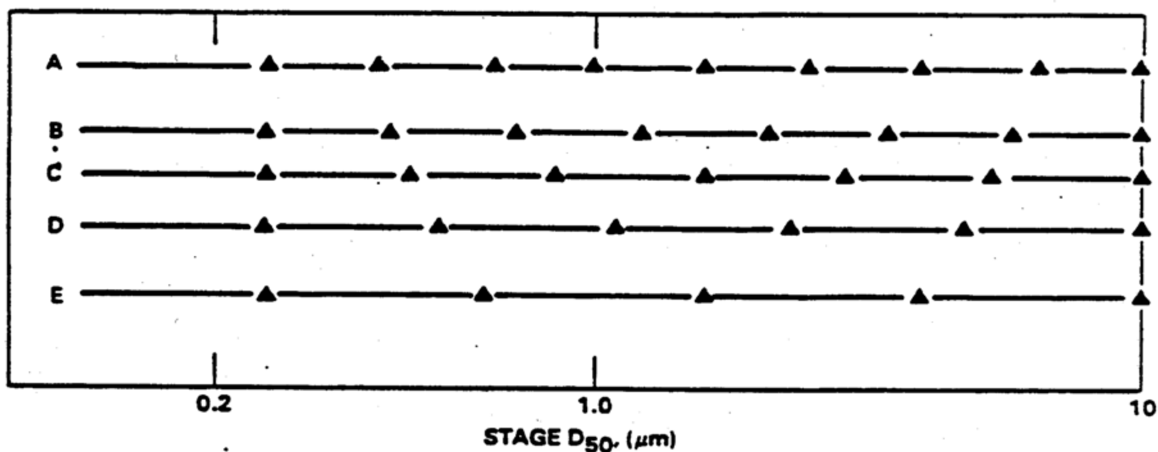
FIGURE 3



Nomograph for selecting nozzles for isokinetic sampling.

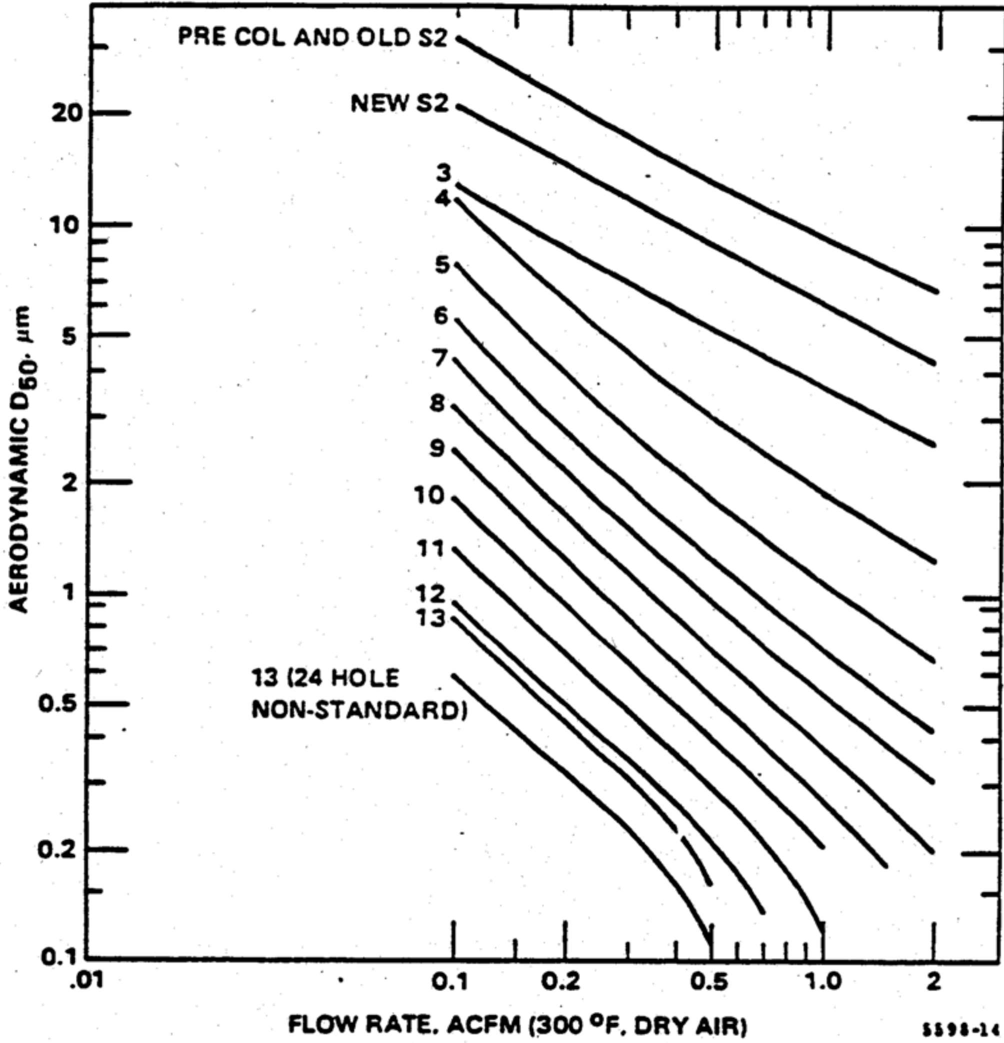
FIGURE 4

NUMBER OF CUTS		: 9	8	7	6	5
RATIO OF CUTS		: 1.585	1.694	1.849	2.089	2.518
CONSTANT Δlog D		: 0.200	0.229	0.267	0.320	0.401
PRECOLLECTOR D_{50} (μm)		:≥10	≥10	≥10	≥10	≥10
FIRST STAGE	D_{50}(μm) :	6.3	5.9	5.4	4.8	4.0
SECOND STAGE	D_{50}(μm) :	4.0	3.5	2.9	2.3	1.6
THIRD STAGE	D_{50}(μm) :	2.5	2.1	1.6	1.1	.63
FOURTH STAGE	D_{50}(μm) :	1.6	1.22	.85	.52	.25
FIFTH STAGE	D_{50}(μm) :	1.0	7.2	.46	.25	—
SIXTH STAGE	D_{50}(μm) :	.63	.42	.25	—	—
SEVENTH STAGE	D_{50}(μm) :	.40	.25	—	—	—
EIGHTH STAGE	D_{50}(μm) :	.25	—	—	—	—
PLOT DESIGNATION	:	A	B	C	D	E



Desired size cuts range of interest: 0.25 μm to 10 μm.

FIGURE 5



Pollution Control System Mark V Impactor stage cuts (at 300 °F, 29.00 Hg, dry air) for multiple flow rates.

The desired size range and resolution is 0.25 to 10 um with 5 to 8 cuts evenly spaced on a log scale (constant ratio of 2.52 to 1.69) as shown in Figure 4. Thus we want the precollector to cut at or above about 10 um and the last stage to cut at or below about 0.25 um.

It should be noted that any stages having a D_{50} comparable to or larger than the D_{50} of the precollector will have little if any particulate catch and these catches will have no significance as sizing data. If possible, such stages should not be used. For data analysis purposes, (if they must be included) the weights of the material collected on such stages should be combined with the catch of the first stage having a D_{50} smaller than that of the precollector; and the intermediate stages should be omitted in the D_{50} calculations, etc.

One must verify that each stage selected meets the two criteria given below for the specified flowrate (Q_A).

Note: "V" has been previously used to represent the stack gas velocity. In the following paragraphs, we are using "V_i" to represent the jet velocity for any one of the jets on impactor stage i.

The criteria are (1) VD_{50} product be less than a critical value, CV, to prevent bounce and scouring and (2) the jet Reynolds Number, Re be greater than 50. These two considerations compete against each other. For a given jet size as the flow rate is increased the D_{50} decreases, but the Re and the VD_{50} increase. As the velocity is decreased, one can stay below the VD_{50} limits but the run time increases and Re may approach values where the impactor calibration data ceases to be valid. The VD_{50} product guideline, CV, depends on the type of substrate material used, and has the following values: Bare Metal: 5 um-m/s, Fiberglass: 15 um-m/s, and Grease: 25 um-m/s. The desired Re value is greater than 100. It is possible to operate at lower values, but the desired range is at least 100. If a run results in Re values of 50 or less it should be considered suspect because the theory has not been proven in this regime. The other considerations in selecting a flow rate are the desired maximum and minimum D_{50}'s. The higher the flow rate the smaller the D_{50} for the same stage. This is illustrated for the Pollution Control Systems Mark V impactor (U of W) in Figure 5 for the stated conditions of temperature, and flue gas composition. Equations for calculating stage D_{50}'s are given in Section 6.1.19 and Computer Programs for performing these calculations are described in Manual, Appendix A.

4.2.1.6 RUN TIME

As mentioned above, Figure 2 is a nomograph for determining the sample time to collect 50 mg (t_{50mg}) of particulate given the Flue Gas Mass Loading and sample flow rate. The equations used to calculate run time are given in Section 6.1.6.1. Figure 2 should be used to make an initial guess at the run time for the initial impactor run. Adjustments for subsequent runs are then made after examining the substrates from the initial run.

To use Figure 2, one must make an initial guess at the flue gas mass loading (G_A, gr/acf) then read down to the appropriate impactor sampling rate curve (2 ACFM to 0.01 ACFM). Reading to the left from the intersection of the mass loading and sampling flow rate one will find the time required to collect a 50 mg total sample (sum of all the stage weights plus filter). The 50 mg total sample is a rule of thumb, the actual constraints are that no stage with the exception of the filter or precollector should collect more than 15 mg. At the outlet from a high efficiency control device, long run times may be unavoidable. Two hour outlet samples are desirable but six hour run times are common, and even longer runs are sometimes required. For inlet situations the concentration is typically very high and run times generally need to be very short to prevent overloading. The recommended minimum run time is 90 sec. If possible run times should be at least three minutes.

4.2.2 BLANK IMPACTOR RUN

After an initial selection is made of sampling flow rate, stage configuration and nozzle diameter, two impactors are assembled as described in configuration and nozzle diameter, two impactors are assembled as described in Section 2 with the selected components. These will be the blank run and initial run. For simplicity, both the blank run and the initial run are usually single point runs rather than following the traversing protocol. If large concentration gradients are expected, the initial run should traverse the entire area to be sampled.

After the selected orifice has been installed on the dry gas meter the initial setup leak check of the meter box back half should be performed as described in Section 4.3.4.4 (Leak Check Procedures). The initial check does not need to be repeated unless the meter box is moved or a different orifice is installed.

It has been shown that some substrate materials can change weight by simple exposure to particulate free stack gases. When such substrate-flue gas interactions occur, it is important to determine the magnitude and reproducibility of these extraneous

weight changes so that the true particulate loadings can be determined. The problem usually relates to sulfur oxides in the flue gas and the chemistry of a particular type of substrate material being used. When greased metal foils are used as substrates, temperature can also be a problem. Proper selection of substrate material and, in some cases in-situ conditioning of the material, can eliminate or minimize the problem. Section 4.2.2 gives guidance for the judicious selection of substrate materials for various sampling situations. As a quality control check the precollector is replaced by a filter holder containing one or more unweighed filters and attached to the inlet of a impactor loaded with prewighed substrates of the selected material (greased metal, fiberglass, etc.). This configuration is referred to as a “blank” impactor. This assembly is then inserted in the stack and, after warmup, stack gas is pulled through the impactor at approximately the same flow rate and for the same duration as a real run. The objective is to expose the substrates to flue gas under the same conditions as those of

the real runs. With the filter preceding the impactor, all the particulate should have been removed so that any weight changes can be ascribed to the flue-gas substrate interactions. The blank weight change for any given substrate should not exceed 0.25 mg or 10% of the stage catch of the most lightly loaded substrate in the real runs, whichever figure is smaller. The impactor filter blank weight change should not exceed 0.25 mg. Larger blank weight changes can be tolerated if they are reproducible. An average change of 1.5 mg which is reproducible to $\pm$0.1 mg is preferable to an average change of 0.1 mg with a range of $\pm$0.25 mg as corrections can be applied if the changes are reproducible. If these limits are exceeded, alternative substrate materials should be tested until one is found which does satisfy the above criteria.

If no substrate material appears to be satisfactory, one last technique is to use in-situ conditioning as discussed in Section 4.2.2.4. If in-situ conditioned substrates are used, a blank must still be run to verify that weight changes are acceptable.

It should be noted that the precollector substrate is not included in the blank run. If the same substrate coating material is used on the both the precollector substrate and the impactor collection plate substrates, the same correction factor may be used for both if approximately the same amount of coating material was applied to both surfaces. Frequently, the precollector catch is very large and the collection factor is less than 1% of the total catch. In cases where the catch is low and the correction factor is significant, one may choose to scale the correction factor to the relative amount of coating material used on the two different surfaces or to construct special hardware that would permit the precollector to be included in the blank run.

Some precollectors permit the optional use of a fiberglass (or quartz) insert. If such inserts are used and loadings are low it may be desirable to construct the special hardware mentioned above. If the filter is constructed of the same material, one can obtain an estimate of any weight change by scaling the filter correction factor. Where the change seems to be significant, one should use coated foil inserts in the precollector

rather than fiberglass inserts.

In situations where testing has been performed at similar sampling sites, experience will aid one in the substrate selection process. In other situations, one must run numerous blanks until an acceptable substrate material is found. Sometimes this is done during a pretest site or the crew may carry sufficient quantities of substrates of multiple kinds of material so that when the blank run shows a given material to be acceptable, testing can proceed without delay. If the test program is complex and involves a large number of people, it will usually pay to run blanks well beforehand to avoid lengthy delays should problems with substrates be found.

4.2.3 INITIAL IMPACTOR RUN

The initial impactor run is used to gather information that can be used to adjust the sampling time for the subsequent runs. The initial run itself is seldom useful as data,

often being run only half as long as the rest of the runs. For this reason, it is often referred to as an explatory run or “trash” run. It is usually a single point run rather than a full traverse and is normally run concurrently with the blank run. If the blank run indicates that a different substrate material must be used, it is at the discretion of the operator to run a second “trash” run concurrently with the second blank or run only the second blank. The normal case would be to assume the second choice of substrate material will prove to be acceptable and use the results of the initial run to adjust the run time so that this run (with) the new material) will provide acceptable data. If this second trash run is traversed and is deemed acceptable (examination shows that minimum/ maximum stage loadings were obtained, scouring and bounce did not occur, etc.) then it may be counted as acceptable data. Each successive run is adjusted based on information gained from the previous runs. For a run to be counted as data, it must satisfy all the criteria listed in Section 7.1.2.

4.3.4 SAMPLING RUNS

After making preliminary determinations and completing the blank impactor run and initial impactor run as described above, the individual sampling runs for data purposes may be made. The following paragraphs detail this process. Note: At this time all ports should have been opened, cleaned, and any needed port adapters installed.

4.3.4.1 PRELIMINARY CALCULATIONS

Once decisions have been made about stage configuration, nozzle selection, and sampling flow rate, it becomes necessary to calculate the target ΔH needed to obtain the desired sampling flow rate at the given set of stack conditions. This calculation is the same as that used for Method 5 sampling except that it is not necessary to generate the table of ΔH vs. P_{pto} used to maintain isokinetic sampling. Once the run is started, the flow rate is not changed. As explained earlier, changing the flow rate changes the stage $D_{50's.}$ For this reason, a constant ΔH setting is maintained throughout the entire run. The only flow adjustments made are those necessary to compensate for the filter loading. The traversing protocol described in Section 4.2.1.1 may be used to select a subset of the Method 1 traverse points such that the constant flow rate is always $\pm 20\%$ of isokinetic for each point sampled. Multiple runs may be needed (each at a different flow rate or with a different nozzle) in order to traverse the full stack.

4.2.4.2 IMPACTOR PREPARATION

Onsite laboratory preparation of the impactor includes loading the impactor with the selected jet plates and with preweighed, numbered substrates (same material as used with the blank impactor run), loading the precollector, attaching the calibrated nozzle, and attaching the precollector to the impactor, then leak testing the impactor/precollector combination. This leak test is optional because the mandatory QA postrun leak test will show if leaks have occurred and will either accept or reject the run as valid with respect to leaks. The purpose of this quality control laboratory leak test is to catch and correct any leaks (missing o-rings, loose fittings, etc.) before the run is

made. For this reason, a simple quick untimed procedure may be used. Once the impactor and precollector are loaded they are labled with the run code (run identification number) shown on the run sheet. All data related to this run are recorded on the run sheet with the exception of the weight records. The substrate weight records are maintained in a separate log book that never leaves the on-site laboratory. Section 4.2.4.5 outlines the instructions for preparing the run sheet (shown in Figures 6 and 7). The velocity traverses are recorded on Method 2 Velocity Traverse Forms and are maintained separately from the run sheets. The following paragraphs describe the procedures for loading the imapctor.

Before loading the substrates in the impactors, the impactor and precollector parts should be inspected to ensure that they are free of loose dirt, lubricants, or liquids. An ultrasonic cleaner is useful for removing contamination from small crevices (e.g. the inside of an Andersen impactor o-ring and the small jet holes of the last stages of the impactor). The jets of each impactor stage should be inspected by holding the plate between a light and the eye using a 10 x ocular. Metal gaskets should be checked for warpage or nicks and pliable gaskets checked for hardening, cracking, tears, slits, or imbedded dirt which could cause leaks. If there is any doubt about a gasket it should be replaced. The nozzle should be clean and the edges sharp and free of nicks.

During loading, handle the precollector, impactor, and nozzles with clean fingers and the substrates with tweezers or clean fingers by the edges. Make a final inspection of the substrates during loading. The substrates should have been inspected prior to the prerun weighings but this is a second check. If a substrate must be replaced, the replacement should be pulled from an “extra” set and the weight records and the run sheet annotated accordingly.

Where mating threads are both stainless steel, chrome, or silver plating of one or both mating surfaces will greatly reduce the potential for galling. Teflon thread sealent tape can be used on any threads that are not otherwise protected. Antiseize compounds should be used sparingly or not at all because of the possibility of contaminating the substrates.

After the nozzle, precollector, and impactor have been assembled they should be checked for leaks as mentioned above. Leaks at this point in the procedure can be easily found and corrected. Checking the pressure drop across the assembly for various flows of filtered air against predetermined values will indicate deviations from the norm resulting from both external and internal leaks and plugged jets.

When the impactor has been loaded and leak checked and the target H value calculated according to the traversing protocol, the sampler, run sheet, and preweighed drying column are ready to be carried to the sampling area. Section 4.2.4 provides a step-by-step guide to the preparation and operation of a sampling run. At this point, items L1 through L15 of Section 4.2.4.5.1 have been completed.

The following ecample illustrates the Pollution Control Systems (University of Washington) Mark III impactor which might be used. The case illustrated in Figures 8 and 9 is substrate set number I23 ("I" for impactor). The substrate set numbering code permits any set to be loaded into any impactor configuration (inlet or outlet). The designation of sampler hardware description and assignment is made on the run sheet, not in the substrate set coding.

FIGURE 6 *Run Sheet - Lab Side.*

LAB LOAD/UNLOAD SHEET FOR UNIVERSITY OF WASHINGTON IMPACTOR (SIX JET PLATES)

RUN CODE L1	PERSON UNLOADING IMPACTOR AND DATE UNLOADED U4
SUBSTRATE SET IDENTIFICATION NO. L2	NOTE YOUR OBSERVATIONS ON THE APPEARANCE OF EACH STAGE, SUBSTRATE, OR CYCLONE UPON DISASSEMBLY U5
PERSON LOADING IMPACTOR AND DATE LOADED L3	PRECUTTER I -P U5
• LOAD IMPACTOR • MARK SHELL AND PRECOLLECTOR WITH RUN CODE • LEAK TEST	STAGE ZERO (DISK) I -D U5
UNIVERSITY OF WASHINGTON MARK V IMPACTOR L4 SHELL ID NO. ____ JET PLATE SET ID NO. ____ STAGE CONFIGURATION ____ PRECOLLECTOR ID NO. ____ NOZZLE ID NO. ____ NOZZLE DIAMETER ____ (INCHES)	STAGE ONE (FIRST PLATE, NO. L5A) I -1 U5 STAGE TWO (SECOND PLATE, NO. ____) I -2 U5
LAB LEAK CHECK (60 SEC PRESSURE CHANGE) CHECK UNDER VACUUM (~ 8 IN. Hg). WITH PRECOLLECTOR: L6 INITIAL ____ (IN. Hg) FINAL ____ (IN. Hg) WITHOUT PRECOLLECTOR (ONLY IF LEAKS FOUND ABOVE) INITIAL ____ (IN. Hg) FINAL ____ (IN. Hg)	STAGE THREE (THIRD PLATE, NO. ____) I -3 U5
NOTES AND OBSERVATIONS U3	STAGE FOUR (FOURTH PLATE, NO. ____) I -4 U5 STAGE FIVE (FIFTH PLATE, NO ____) I -5 U5 STAGE SIX (SIXTH PLATE, NO. ____) I -6 U5 BLANK OR BEHIND DISK (CIRCLE ONE) I -BX U5 L5B BACK UP FILTER I -F U5

FIGURE 7 *Run Sheet - Run Side.*

L7
REAL BLANK

RUN CODE L8	DATE 1	DIFFERENTIAL STACK PRESSURE 2 (IN H_2O)
CONTROL BOX ID L9	START TIME 11	AMBIENT PRESSURE (LAB BAROMETER) 3 (IN Hg)
GAS METER ID L10	END TIME 28	AMBIENT TEMPERATURE 4 (F)
THE CALCULATED TARGET ΔH VALUES REQUIRES THE OPERATOR TO USE ORIFICE ID L11	SAMPLING DURATION (MIN) 12	—60 SEC LEAK TEST— PRE HOT A. 15 IN Hg W/SAMPLER 5 FT^3
SAMPLING ASSIGNMENT INLET, OUTLET, OTHER: L12	GAS METER-START (FT^3) 13	B. 5 IN Hg W/SAMPLER FT^3
	GAS METER-FINISH (FT^3) 29	C. 15 IN Hg W/O SAMPLER FT^3 POST HOT 30
TARGET ΔH L13	TOTAL VOLUME BY GAS METER (ACF) U6	NOTE: RELEASE VACUUM AT NOZZLE TO AVOID RUPTURING FILTER. PASS ≤0.02 FT^3 FOR A OR B OR C. VISUAL CHECK OF NOZZLE ☐

	RUN TIME (MIN)	PORT NO. TRAVERSE POINT	GAS METER READING	GAS METER TEMP. (F)	FLUE GAS TEMP. (F)	19	ORIFICE ΔH IN. H_2O	PUMP VACUUM (IN Hg)	PROBE TEMP. (F)
	Pre	15	16	17	18				20
1	14	21	22	23	24		25	26	27
2	↓	↓	↓	↓	↓	↓	↓	↓	↓
3									
4									
5									
6									
7									
8									
9									
10									
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19									
20									
21									
22									
23									
24									
25									
26									
27									
28									
29									
30									
	POST TEST CALCULATIONS								
	U7	TOTAL	U8						
		AVG.		U9	U10	U11	U12		

—WATER—

CONDENSER ID NO. 6

CONDENSER H_2O CATCH 31 (ml)

DRYING COLUMN WEIGHT CHANGE

ID NO. L14 INITIAL WT L15 (gm)

FINAL WT. U1 (gm)

(1 gm = 1 ml) H_2O GAIN U1 (ml)

TOTAL VOLUME H_2O U2 (ml)

NOTES AND OBSERVATIONS

32

7 SAMPLING LOCATION INLET OUTLET

IN THE SPACE BELOW GIVE THE UNIT, CHAMBER, DUCT PANTLEG, ETC. WHERE THE SAMPLER WAS RUN

PORT NUMBER(S)

SAMPLER ORIENTATION (CIRCLE ONE)

HORIZONTAL 8
TOP ENTRY VERTICAL
W/ TURN AROUND
W/O TURN AROUND
BOTTOM ENTRY VERTICAL
OTHER

OPERATORS

(1) 9 (2)

Figure 8

Example of a completed Run Sheet - Lab Side.

RUN CODE
SAMPLE CALC

SUBSTRATE SET IDENTIFICATION NO.
I 23

PERSON LOADING IMPACTOR AND DATE LOADED
SS D 4-20-84

✓ • LOAD IMPACTOR
✓ • MARK SHELL AND PRECOLLECTOR WITH RUN CODE
✓ • LEAK TEST

UNIVERSITY OF WASHINGTON MARK ~~IMPACTOR~~ MARK III
SHELL ID NO. III Z
JET PLATE SET ID NO. III Z
STAGE CONFIGURATION P,2,3,4,5,6,7,B,F,BF
PRECOLLECTOR ID NO. Z
NOZZLE ID NO. Z-3
NOZZLE DIAMETER 3/16 (0.188) (INCHES)

LAB LEAK CHECK (60 SEC PRESSURE CHANGE) CHECK UNDER VACUUM (~ 8 IN. Hg)

WITH PRECOLLECTOR:
INITIAL 7.8 (IN. Hg)
FINAL 6.0 (IN. Hg)

WITHOUT PRECOLLECTOR (ONLY IF LEAKS FOUND ABOVE)
INITIAL 7.8 (IN. Hg)
FINAL 7.8 (IN. Hg)

NOTES AND OBSERVATIONS

$\bar{v}$ = 50 fps

PRE

LEAK AT PRECOLLECTOR NOZZLE, SMALL

POST

BF STICKING TO F. COMBINE THESE WEIGHTS FOR DATA ENTRY. NOZZLE GOOD, NO NICKS.

PERSON UNLOADING IMPACTOR AND DATE UNLOADED
SSD 4-21-84

NOTE YOUR OBSERVATIONS ON THE APPEARANCE OF EACH STAGE, SUBSTRATE, OR CYCLONE UPON DISASSEMBLY

PRECUTTER
I P 23 GOOD LOADING, NO SIGN OF NOZZLE SCRAPINGS IN CATCH.

STAGE ZERO (DISK)
I D 23 LIGHT LOADING

STAGE ONE (FIRST PLATE, NO 2 (OLD))
I -1 23 GOOD PEAKS, NO INDICATION OF BOUNCE FROM SOLID DISK

STAGE TWO (SECOND PLATE, NO. 3)
I -2 23 GOOD PEAKS

STAGE THREE (THIRD PLATE, NO 4)
I -3 23 GP

STAGE FOUR (FOURTH PLATE, NO. 5)
I -4 23 GP

STAGE FIVE (FIFTH PLATE, NO 6)
I -5 23 GP

STAGE SIX (SIXTH PLATE, NO 7)
I -6 23 GP

(BLANK) OR BEHIND DISK (CIRCLE ONE)
I -BX 23

BACK UP FILTER
I -F 23 AND I 23 BF BLANK FILTER IS STICKING TO THE DIRTY FILTER. MUST COMBINE AND WEIGH AS ONE PACKAGE

Figure 9

Example of a completed Run Sheet - Run Side.

REAL (circled) BLANK

RUN CODE	SAMPLE CALC	DATE	4-20-84	DIFFERENTIAL STACK PRESSURE (IN H_2O)	$-\phi.3$
CONTROL BOX ID	RAC # 1	START TIME	0900	AMBIENT PRESSURE (LAB BAROMETER) (IN Hg)	29.60
GAS METER ID	RAC # 1	END TIME	1110	AMBIENT TEMPERATURE (F)	74
THE CALCULATED TARGET ΔH VALUES REQUIRES THE OPERATOR TO USE ORIFICE ID	12φ5	SAMPLING DURATION (MIN.)	120	—60 SEC LEAK TEST— PRE HOT A. 15 IN. Hg W/SAMPLER (FT^3)	.016
SAMPLING ASSIGNMENT INLET, OUTLET (circled), OTHER:		GAS METER-START (FT^3)	321.450	B. 5 IN. Hg W/SAMPLER (FT^3)	.007
		GAS METER-FINISH (FT^3)	361.640	C. 15 IN. Hg W/O SAMPLER —— FT^3 POST HOT	0.017
TARGET ΔH	0.44	TOTAL VOLUME BY GAS METER (ACF)	40.190	NOTE: RELEASE VACUUM AT NOZZLE TO AVOID RUPTURING FILTER. PASS ≤ 0.02 FT^3 FOR A OR B OR C. VISUAL CHECK OF NOZZLE ✓	OK

	RUN TIME (MIN)	PORT NO. TRAVERSE POINT	GAS METER READING	GAS METER TEMP (F)	FLUE GAS TEMP (F)		ORIFICE ΔH (IN. H_2O)	PUMP VACUUM (IN. Hg)	PROBE TEMP. (F)
	Pre	A1	321.450	72	300				310
1	5	A1	23.12	74	300		.44	2	
2	10	A2	24.80	74	301		.44		
3	15	A3	26.47	74	300		.44		
4	20	A4	28.15	74	301		.44		
5	25	A5	29.82	74	301		.44		
6	30	A6	31.50	74	301		.44	3.3	300
7			MOVE						
8	5	B1	33.17	74	298		.44		
9	10	B2	34.85	74	300		.44		
10	15	B3	36.52	74	300		.44		
11	20	B4	28.20	74	298		.44		
12	25	B5	39.87	74	302		.44		
13	30	B6	41.54	74	300		.44	4.5	305
14			MOVE						
15	5	C1	43.22	74	300		.44		
16	10	C2	44.89	74	300		.44		
17	15	C3	46.57	74	298		.44		
18	20	C4	48.24	74	299		.44		
19	25	C5	49.92	74	300		.44		
20	30	C6	51.59	74	301		.44	6.0	300
21			MOVE						
22	5	D1	53.27	74	299		.44		
23	10	D2	54.94	74	302		.44		
24	15	D3	56.62	74	300		.44		
25	20	D4	58.29	74	298		.44		
26	25	D5	59.97	74	301		.44		
27	30	D6	61.64	74	300		.44	7.2	305
28			END	RUN		361.640 AT	1110	hrs.	
29						120 MIN.	TOTAL SAMPLE TIME		
30									
	POST TEST CALCULATIONS:								
	120	TOTAL	40.190						
		AVG.		74	300		.44		

—WATER—

CONDENSER ID NO. RAC#1

CONDENSER H_2O CATCH 39 (ml)

DRYING COLUMN WEIGHT CHANGE

ID NO. E W/O HOSE INITIAL WT. T+478.0 (gm) FINAL WT. T+482.0 (gm)

(1 gm = 1 ml) H_2O GAIN 4.0 (ml)

TOTAL VOLUME H_2O 43.0 (ml)

NOTES AND OBSERVATIONS

$CO_2 = 0.22\%$ dry

$O_2 = 19.75\%$ dry

No PLANT UPSETS DURING RUN.

SAMPLING LOCATION

INLET OUTLET (circled)

IN THE SPACE BELOW GIVE THE UNIT, CHAMBER, DUCT PANTLEG, ETC. WHERE THE SAMPLER WAS RUN

UNIT 3 ESP OUTLET

PORT NUMBER(S)

ALL

A, B, C, D

SAMPLER ORIENTATION (CIRCLE ONE):

HORIZONTAL (circled)

TOP ENTRY VERTICAL

W/ TURN AROUND

W/O TURN AROUND

BOTTOM ENTRY VERTICAL

OTHER

OPERATORS

(1) JWR (2) SJG

DESCRIPTION	NUMBER ON PETRI DISH
Precollector	
Precollector Substrate Foil	I23P
Zero Stage (Impactor Inlet Throat)	
Collection Disk and Substrate (Solid Disk)	I23D
First Jet Plate (No. 2)	
Collection Disk and Substrate (Donut)	I23-1
Second Jet Plet (No. 3)	
Collection Disk and Subdtrate	I23-2
Third Jet Plate (No. 4)	
Collection Disk and Substrate	I23-3
Fourth Jet Plate (No. 5)	
Collection Disk and Substrate	I23-4
Fifth Jet Plate (No. 6)	
Collection Disk and Substrate	I23-5
Sixth Jet Plate (No. 7)	
Collection Disk and Substrate	I23-6
Blank Collection Disk (Inverted)* and Substrate	I23-BX
Teflon Insert Ring**	
Filter	I23F***
Teflon Insert Ring**	
Teflon Insert Ring (BF)**	
Blank Filter	I23BF***
Teflon Insert Ring (BF)**	
Support Screen	

Notes:

*The Extra Collection Stage can be used in either of two different locations. If this is an outlet run the extra collection stage is used as a blank. The blank is a collection stage (loaded with a number substrate) that has been inserted upside down (out of the flow) directly behind the collection plate of the last jet. It is referred to as a blank because it is not preceded by a jet stage and is oriented out of flow. It is intended to act as a check in weighing and for any flue gas-substrate interactions. It is treated the same as all the other substrates for conditioning and handling. Because of high loadings at an inlet sampling location, it may be placed directly beneath the solid disk which precedes the first multijet stage to catch any overload or blow-by from the zero stage (impactor inlet and solid disk). Usually at inlets the run time is so short and the flow rate so low that no problems are encountered from the gas-substrate interactions. Outlet loadings are typically low enough that zero stage overloading is not normally a problem, thus this collection substrate is used as a blank rather than a safety.

**Thin light weight Teflon may be cut in a donut shape and placed in front of and behind a filter to prevent the filter from sticking to the metal. The Teflon rings should be

weighed with their respective filters. Kapton plastic film can be used if the flue temperatures are too high for Teflon.

***The petri dish with the filter also contains the filter's pouch (aluminum foil envelope) and the Teflon inserts. All of these pieces are weighed as a package rather than separately. The envelope remains in the petri dish while the inserts and filter are loaded into the impactor. The purpose of the envelope is to prevent particles falling off the filter prior to and during the post-test weighing. Note: The pouch must be open during desiccation in order to permit moisture to escape from the filter.

The filter package (I23F) consists of one filter, one pouch, and two Teflon inserts. The total weight of these four pieces is assigned to I23F in the weight records. The blank filter package (I23BF) consists of one filter and two Teflon inserts. The pouch is not necessary but may be desirable. The total weight of these three or four pieces is assigned to I23BF in the weight records. The third and fourth Teflon inserts are marked BF to avoid confusion between them and the other two during unloading.

4.2.4.3 SAMPLING TRAIN PREPARATION

Preparation of the sampling train is basically the same as that for a Method 17 run. The one major difference is that the equipment is modified to permit the use of smaller orifices when lower flow rates are required. The other difference is that a metal condenser and preweighed drying column (Figure 1) are commonly used in lieu of the glass impingers. All manometers should be leveled, leak checked, and zeroed. Then the backhalf of the sampling train should be leak checked as described below.

4.2.4.4 LEAK CHECKS

In general the backhalf of the sampling train must be tested at the beginning and the end of each field test (and again if components are changed or the equipment is moved). Each impactor will be checked at least twice, and possibly four times. The last two tests are acceptance tests and the first two may be thought of as screening tests aimed at finding and correcting leaks in an advantageous manner. The first test (optional) is performed in the lab before the impactor is carried to the stack. The second (optional) is made before the impactor is warmed up. If leaks are found during the prerun hot leak checks they must be corrected before the run may proceed. As the impactor may cool down during this time, one may be forced to repeat the 45 min. to 1 hr. warmup time.

The significance of a leak and the acceptance limits assigned to a leak depend on where it occurs. For example, a leak around a nozzle attachment means that all the gas does pass through the precollector and impactor thus impactor performance is not affected. Likewise, a leak between the precollector and impactor inlet flange means the gas passed through the impactor but bypassed the precollector. A leak downstream of the impactor would not be acceptable because the dry gas meter reading is greater than the actual amount of gas sampled by the impactor. Once the impactor run has been

completed it could compromise the data to disassemble the unit and try to isolate the location of a leak. Leaks affect not only the indicated amount of gas sampled but also the calculated D_{50}'s, thus data cannot be salvaged by making leak rate corrections.

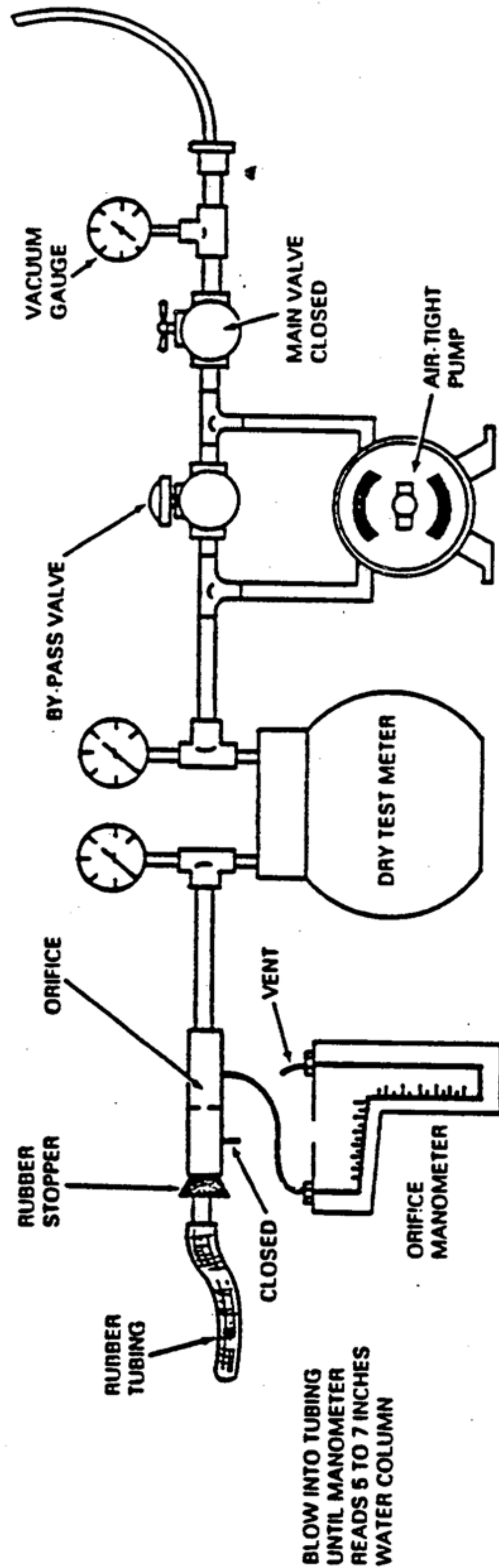
Many different techniques are available for leak checking a sampler. The particular techniques used to perform any pre-test cold checks are optional as these are all aimed at finding leaks before the run is performed. Although the pre-test cold leak checks are optional, it is highly recommended that some form of check be made prior to warmup. Such checks can locate leaks early and prevent unnecessary delays. The pre-test hot leak test and the post-test hot leak check are mandatory. It is these tests which accept or reject a run with respect to leaks. The techniques used for these tests are spelled out in detail in the following paragraphs.

Initial Set-Up Check of Meter Box Backhalf: Each time the sampling train is set up (desired orifice installed on the dry gas meter) the meter box should be checked as described below. The normal leak check procedure will not detect leaks on the positive pressure side of the pump as such leaks are discharged to ambient, never reach the dry gas meter, and thus less volume is recorded than sampled. Once this check has been performed it need not be repeated until the meter box is moved or the orifice is changed. If this initial check (and any equipment change checks) is not made, all subsequent leak checks are subject to question. The results of this check should be recorded in a field test log book (a chronological record of what took place during the field test). The procedure (see Figure 10) follows (the same as used with a Method 5 train): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing attached to 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 5 to 7 in. water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box. Leaks, if present, must be corrected (A soap solution is helpful for locating the source of leaks in a pressurized system.)

4.2.4.4.1 LAB LEAK CHECKS

A simple vacuum check is sufficient. Assemble the impactor and precollector. Connect a vacuum source to the impactor outlet (pump off). Plug the nozzle and turn the pump on, adjusting the pump valves to about 8 inches Hg negative differential to ambient. Then close off the line between the impactor exit and pump and see if the system holds this vacuum. If it falls a leak is present. The rate at which it falls indicates the size of the leak. If leaks are present, one may switch to a slightly positive pressure (6 in. of water) and use a soap solution to locate the source(s) of the leak(s). Usually these will be due to missing o-rings, loose fittings, etc. these should be corrected before the sample is sent to the sampling platform. Note: Release the vacuum at the nozzle to avoid damage to the filter.

FIGURE 10



Leak check of meter box.

4.2.4.4.2 COLD LEAK CHECKS

At the sampling platform the sampler is connected to the probe and a cold leak check is performed (optional). As shown on the run sheet, the criterion is a leakage rate $\leq$ 0.02 ACFM. The test is first done at –15 in. Hg with the precollector and sampler attached. If the system fails this test, the operator should attempt to fix the leak by checking the most common problem areas such as loose connections, etc. The test may then be repeated at the –5 in. Hg level (line B on the run sheet). If it still fails to meet specifications, one needs to isolate the source (sampler or the train). Line C may be used for this purpose. Any leaks should be located and corrected before warming the impactor, otherwise the pre-test hot leak test may prohibit the run from being started. Wrapping the entire impactor assembly with aluminum foil at this time is advantageous. This prevents the outer surfaces and joints from accumulating particulate matter during warmup and sampling. Such an accumulation can make disassembly difficult or even result in the loss of a run if any of the material is dislodged onto a substrate when one impactor is unloaded.

4.2.4.4.3 HOT PRE-RUN AND POST-RUN LEAK CHECKS

After the warmup is completed, the hot sampler is removed from the port, the cover is removed from the nozzle, and the hot pre-run leak check is performed. Plug the nozzle with a material that will be able to withstand the nozzle's high temperature than turn on the pump and draw a vacuum in the system equal to or greater than the maximum value reached during the previous sampling run. Record this rate as L_N. Table 1 (Leak Test Criteria) gives instructions and criteria in a flow chart form. Note that unlike Method 5, flow rate corrections are not permitted because such corrections affect the D_{50} as well as the total volume sampled.

After the run is completed and the hot sampler is removed from the last port, the hot post-run leak check is performed to verify that no leaks developed during the run. The criteria of Table 1 are used for this purpose. One must not attempt to remove the nozzle or disassemble that sampler at this time in order to isolate a leak. The only permissible leak is at the nozzle and a comparison is made between pre-run and post-run leak rates. The sampler is removed and the train is checked to verify that all measured gas went through the sampler.

The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with the by-pass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the by-pass valve until the desired vacuum is reached. Do not reverse direction of the by-pass valve. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak-check as shown below and start over. When the leak-check is completed, first slowly remove the plug from the inlet to the sample nozzle and immediately turn off the vacuum pump. This prevents water from being forced backward and keeps silica gel from being entrained backward.

4.2.4.5 RUN SHEET INSTRUCTIONS

The run sheet accompanies the impactor at all times. All information and comments relating to the run are recorded on this document. Figure 6 shows the side of the run sheet used by lab personnel to record identifying equipment numbers and to record observations made while unloading the impactor. This data form is specific to the University of Washington impactor configured with the precollector, six jet plates, control blank, and filter, as this is the recommended ARB preferred instrumentation and configuration. Use of other impactor or configurations will require minor alterations to this form. Figure 7 shows the other side of the run sheet. This side is used by the testing personnel during the run, example data is shown in Figures 8 and 9. Appendix A shows a an alternative version of the run sheet prepared by the Computer Programs. Entries to the alternative form are smaller to those described herein for the “manual” version shown in Figure 7. The circled numbers relate to additional information given below. The prefixes L and U are used to identify information recorded by laboratory personnel during loading (L) and unloading (U). Unprefixed members identify information recorded by testing personnel at the sampling location before, during, and after the run. The number sequence represents the normal sequence one would use in recording the information. One major difference between impactors and a Method 5 train is the use of a constant flow rate. On a Method 5 run the operator monitors point velocities and adjusts the sampler flow rate to maintain isokinetic sampling at each traverse point but impactors require a constant flow rate. With impactors a Method 2 velocity traverse is performed before the run and the techniques described in Section 4.2 are used to select the traversing procedures for one or more runs, each of which is made at constant but possibly differifng flow rates. The desired flow rate for a run will be obtained for stack conditions when the train is operated at the Target H (pressure drop across for the orifice) listed on the run sheet.

Table 1 Leak Test Criteria

Definitions:

- L_N = leak rate with Nozzle, Precollector, Impactor and Trains
- L_T = leak rate, assembly removed from probe (Train only)
- L_a = 0.02 cfm or 4% Q_I whichever is smaller (acceptable leak rate
- L_M = 10% Q_i (maximum acceptable leak rate), 10% Trash Point

All pre-run testing is performed at the highest pressure drop obtained in most previous runs. The Post-run testing is performed at the highest pressure drop obtained in the actual run.

For Hot Pre-run Test, the term "Reject Run" means that the leaks must be corrected before the run may proceed. This will usually mean the unit must be returned to the lab and reassembled.

Pre-test, Hot

Plug Nozzle, Test (Record L_N)

$L_n < L_a$?	Yes: Acceptable
	No: Attempt to correct leaks, retest
$L'_N < L_a$?	Yes: Acceptable
	No: Continue
$L'_N > L_M$	Yes: Reject Run
	No: Remove Impactor Assembly, Retest (Record L_T)
$L_T < L_a$?	Yes: Acceptable
	No: Reject Run

Post-Test Hot

Plug Nozzle, Test (Record L_{Npost})

$\lvert L_{Npost} - L_{Npre} \rvert > L_M$?	Yes: Reject Run or tighten Nozzle and retest
	No: Continue, do not attempt to correct leaks. Do Not remove nozzle Remove Assembly (Precollector/Impactor) from Probe, Plug Probe, Test (Record L_{Tpost})
$L_{Tpost} < L_a$?	Yes: Acceptable
	No: Reject Run

4.2.4.5.1 LAB PRE-RUN ENTRIES (15 ITEMS)

(L1) Run Code: This key number is usually assigned in the written test plan and will generally include abbreviations for the plant name, sampling location (inlet, outlet) and sequence number at this location (see Manual Appendix A). This same code is also listed at (L8) on the Run Side.

(L2) Substrate Set Identification No.: This is the number assigned in the Weight Book to the substrate set. This set includes one or two filters and substrates for the precollector, zero jet (solid disk), six jet plates (donuts), and one blank collection plate (donut) as listed on the right side of the form. This set number together with the sequence information (P, D, 1-6, BX, F and BF) is marked on the petri dish for each member of the set (Example: 126F, Impactor substrate set No. 26, filter).

(L3) Person loading impactor and data loaded: With a small test crew many of these items are not important but on a larger test where eight to ten runs are made per day this can avoid a lot of confusion in answering questions related to the run.

(L4) Hardware Identification: When a substrate set is loaded in an impactor, this information must be completed and the run number marked on the impactor shell. This information identifies which jet plates were loaded in the impactor during the run. The Nozzle Diameter is the calibration value for the nozzle and is used in the calculation of the target ΔH value. Nominal Diameters are also shown in fractions.

(L5) First Jet Plate No.: This information has already been recorded on the stage configuration line in the Hardware Identification section. As such these blanks are optional and are simply added for clarity. These numbers are read from the back side of the plates. (The plates should have been permanently marked when the hole verifications were made.) At (L5B) one of the two choices “Blank” or “Behind Disk” should be circled to indicate where the extra collection plate was loaded, upside down and directly behind the collection plate of the last jet stage or right side up and directly behind the zero stage (entrance jet) solid disk collection plate to catch any overloading from the disk.

(L6) Lab Leak Check: The first check is performed with the precollector mounted on the impactor. If a leak is present which cannot be corrected by inspecting and tightening fittings, then the impactor should be checked without the precollector in order to determine if the leak is in the precollector or the impactor. Small leaks in the precollector are acceptable. Leaks in the impactor should be located and corrected before sending the assembly to the sampling site. Use of a slightly positive pressure (less than 8” H_2O) and a foaming leak detector liquid can be helpful in locating the leaks. Be careful not to repture the filter by causing air to rush through it in the wrong direction. Always release the vacuum slowly at the precollector inlet, not by turning the pump off.

(L7) Real or Blank: The lab personnel should circle the appropriate description. Although the presence of a filter (in place of the precollector) at the inlet of the impactor obviously identifies the run as a blank rather than a real, the circles are used to facilitate identification during data processing. Frequently this will be redundant since the Run code would normally identify the run as being a blank.

(L8) Run Code: Same as (L1), listed on both sides of the form.

(L9) Control Box ID: This is the assignment of the impactor to a specific sampling train. This is necessary because the orifices in the different sampling trains generally have different calibration constants. Consequently, an assignment must be made before the Target ΔH value can be calculated.

(L10) Gas Meter ID: When the Control box ID is specified, this selects the gas meter since it is an integral part of the Control Box. The gas meter must be identified so that the appropriate dry gas meter calibration factor (Y) can be used for data reduction.

(L11) Orifice ID: As impactors may require the use of orifices of different diameters to cover the broad range of flow rates which may be needed, it is necessary ot identify which specific orifice is to be installed by the testing personnel. The orifice calibration factor ($\Delta H@$) of the specified orifice is used in the calculation of the Target ΔH value.

(L12) Sampling assignment: The test plan will frequently identify the areas where sampling is to be performed and distinguish between these different areas by the abbreviations used in the Run Code. In that respect, this line is redundant. It has been included for the purpose of clarity. Frequently different stage configuration and flow rates will be used in the different sampling areas (inlet, outlet zone to be traversed, etc.) and the loaded impactor (stage configuration used) and calculated Target ΔH will only be appropriate for one of these areas. Thus, the need to clearly identify the sampling assignment is established.

(L13) Target H: This is calculated using the computer program in Appendix A and the equations given in Section 6 for the equipment arrangement shown in Figure 1. This pressure drop across the orifice (as specified in (L11)) should be maintained throughout the run.

(L14) Drying Column ID No.: Both an ice bath condenser and silica gel drying column are used. The triple beam balance (1/10 g) is usually maintained in the lab and to avoid confusion, the drying columns are numbered. This number shows which drying column was used with which impactor.

(L15) Drying Column Initial weight: The weight of the drying column specified above is recorded on the Run Sheet. The weight gain of the drying column is used in the determination of the stack moisture value (B_{ws}). Note: 1gm = 1mL, 1 mL liquid = 0.04707 ft^3 vapor at standard conditions (68° F, 29.92 in. Hg).

4.2.4.5.2 STACK ENTRIES (32 ITEMS)

At this point the Run Sheet, Drying Colmn, and Impactor are ready to be given to the testing personnel and carried to the appropriate sampling site. The following entries are made by the testing personnel.

1) Date: This is the date the run is performed. It may be different from the date it was loaded.

2) Differential Stack Pressure: This reading was made during the Method 2 pitot traverse performed prior to the impact run.

3) Ambient pressure: This may be directly if a barometer is at the sampling site (mark through LAB) or, if the barometer is in the lab (and the lab is at ambient pressure), altitude corrections can be made, 0.1 in. Hg/100 ft. If a reading is taken from the plant control room, be sure the reading is measuring ambient pressure and not absolute pressure at some point in the plant process.

4) Ambient Temperature: Temperature at the start of the test.

5) Prerun Leak Test: This is described in Section 4.2.4.4.3. The COLD TEST is optional but recommended. The HOT Pre-run and Post-run test are required. To end a leak test and avoid rupturing the filter, the vacuum should always be released at the nozzle with the pump running. This sets the direction of the flow through the filter so that the filter will be supported. Look at L6 to see if the precollector leaks. Even if the lab test indicates a leak, the stack test is a different kind of test (a quantitative measure) and may prove to be acceptable. If the system fails Test A (15 in. Hg) then Test B should be performed. If B fails and the lab test showed a leaking precollector, the precollector should be removed and Test B repeated. If it still fails then Test C should be performed to see if the leak is in the impactor or the train.

6) Condenser ID No: List the ID No. Some condenser designs do not permit all the water to be removed. Residual amounts are trapped. Before using such a condenser add some water to the condenser then pour it out using the same technique that will be used after the run is completed. This preloads the entrapment areas to permit an accurate reading the the subsequent catch.

7) Sampling location: This describes where the sample is run. To avoid replicate detailed drawings reference is often made to figures and to descriptions in the test plan. This should agree with the Sampling Assigment. Space is provided to permit a detailed description.

8) Sampler Orientation: This is an extention of (7). It is important to know if the sampler was operated horizontal, right side up, or upside down. If a sampler is operated upside down, flow must be maintained while the sampler is removed from port to port while traversing. The sampler must be right side up or horizontal before flow is stopped. Any gas sampled while moving from port to port should be discounted in data analysis. A written record of orientation may be useful later if problems are encountered in interpreting the data.

9) Operator: The test personnel must identify themselves so that they can be called upon at a future time to answer questions.

10) Blank Space: This may be used as desired. Frequently the time at which the impactor was inserted for warm-up will be listed (Example: start warm-up at 1322).

11) Start Time: This is the time the run actually stars. As a stop watch is normally used for the traversing dwell times, this and item #28 will generally be the only recorded clock times (unless item #10 is used as above). Sufficient warm-up must have been completed by this time. Usually this entry is made shortly after insertion for in-situ warm-up and indicates the scheduled start time. If something prevents the run from being started at this time, simply mark through the entry and write the correct actual start time. Note: During the end of the warm-up time the pump should be running with the shut-off valve closed.

12) Sampling Duration: This is the actual run time, theta. Usually this entry is made before the run is started and indicates the scheduled run time. If something happens to change it during the run, it should be properly noted on the bottom portion of the run sheet. The operator should then mark through this entry and write in the corrected actual run time. Lab personnel will certify this after the run and make the same entry in U7.

13) Gas Meter-Start: This is recorded here and in (16) after the probe has been leak checked and inserted for warm-up. This is recorded to the nearest 1/1000 ft (see example). Pump is running with shut off closed. This is one of the most important entries on the page.

14) Run Time Column: As shown in the example, this column and column 15 are usually completed before the run is started and show the scheduled dwell time at each traverse point. If the schedule is altered one can mark through the entry and either write the corrected entry to the left or use the blank column (19). Note: The implied meaning is that the listed time marks the end of the dwell (not the beginning) and the gas meter reading was recorded on the fly at the indicated time. Immediately after this indicated time, the probe is positioned to the

next traverse point. In the example on line 3 the implied meaning is that from stop watch time 10 to time 15 the probe was at position A3 and the DGM reading at time 15 was 795.64 (approximately, since the needle was moving). If desired, clock times may be used for very long runs. For a run of about two hours or less, use of stop watch time as shown in the example is recommended. Clock times may be entered to the left of the appropriate line number (or in the blank column) if so desired.

15) Port No./Traverse Point Column: See explanation in (14) above. The entry on the "Pre" line and on line "1" are the same. "Pre" implies at or near start.

16) Gas Meter Reading Column: "Pre" is same as (13). During the run (22) this is the approximate reading (moving) at the indicated stop watch time. See also (14).

17) Gas Meter Temp, Pre: The pump is not sampling stack gas at this time so this temperature will be lower than the run temperature. During the run (23) the operator should record the temperature at some point during the dwell at this traverse point.

18) Flue Gas Temp, Pre: The purpose of this entry and (20) is to remind the operator that the probe heater should be working. Probe heat prevents the accumulation of water (in the probe) which could back wash the filter and substrates.

19) Blank Column: May be used as desired (see (14)).

20) Probe Temp, Pre: Entry is to remind the operator to turn on the probe heater (see 18).

21) See (14) and (15).

22) See (14) and (16).

23) Gas Meter Temperature Column: This is the temperature of the dry gas meter, read shortly before the dry gas meter reading is taken.

24) Flue Gas Temperature Column: This is a reading of the temperature of the flue gas at this traverse point, read sometime during the dwell at this point.

25) Orifice ΔH Column: The Target ΔH value (L13) is the desired value. This column is intended to be a record of the actual ΔH as well as a

reminder to adjust the valves as necessary to maintain the flow at the Target ΔH value (compensate for filter loading).

26) Pump Vacuum Column: This is a pump inlet vacuum read toward the end of the dwell at this traverse point.

27) Probe Temperature Column: This is a probe temperature read sometime during the dwell at this traverse point. This is a reminder to verify that the probe heaters are working to prevent condensate from draining back to the filter. This information is not used during data reduction.

28) End Time: This is the 24 hr. clock time when the run was actually ended. The interval between start and stop will generally be longer than the sampling duration because the flow is normally cut off and the timer stopped when the probe is moved from one port to the next.

29) Gas Meter-Finish: This is the reading of the gas meter when the run is stopped by closing the shut-off valve with the pump still running.

30) Post-run Leak Test and Visual Check of Nozzle: After the run has been stopped (with pump running) and the final gas meter reading recorded, the probe is removed from the stack and the Post-run Leak Test described in Section 4.2.4.4.3. is performed. This is similar to the test described in (5) except that it is performed post-test. This test is mandatory and is used to accept or reject the run with respect to the leaks. At this time the operator should also visually check the nozzle to verify it was not damaged (banged, scraped, etc.) during the course of the run. If the nozzle appears undamaged place a check mark in the box. If the nozzle is damaged write in the word “Damaged” and make appropriate entries in the Notes and Observations section.

31) Condenser H_2O Catch: After the hot leak test has been completed, the sampler is removed from the probe. The operator will then shake the umbilical to drain water in the line into the condenser. The line to the drying column may also contain some water droplets and should be drained into the condenser. At this time the condenser is removed and a graduated cylinder is used to measure the amount of water that was captured by the condenser. This value is recorded here. The length of tubing connecting the drying column to the control box inlet should be disconnected at the drying column and the short length of tubing connecting the drying column to the condenser should be re-connected where the other tube was removed. This loop will close off the drying column to prevent any loss or gain of water. The drying column, with tubing, is ready to be returned to the lab for weighing.

32) Notes and Observations: Any notes or observations not yet recorded should be entered at this time.

4.2.4.5.4 LAB POST RUN ENTRIES (12) ITEMS

At this point the SAMPLER, RUN SHEET, and DRYING COLUMN are ready to be returned to the lab for analysis and turn around. The following entries are made by the lab personnel.

(U1) Drying Column Final Weight: The drying column is weighed and the value recorded here. Note: If the initial weight was done with a tube connected to the two ends, the final weight must be done with the same tube attached. The weight gain is calculated and recorded.

(U2) Total volume H_2O: This is the sum of the condenser catch and the drying column weight gain.

(U3) Notes and Observations: This space may be used as desired.

(U4) Person Unloading Impactor and Date Unloaded: Used to identify the person unloading the impactor and when it was unloaded (see also L3).

(U5) Observations: If you wish to record any observations made while unloading the precollector and impactor, this is the place to make the notes. Such observations as obvious indications of bounce or overloading, hunks of rust (from nozzle scrapings) in the precollector, ruptured or wet filter, damaged o-ring, dramatic color changes from stages to stage, etc. are listed on the appropriate line.

(U6) Total Gas Meter Volume: This is the value obtained by subtracting the START reading from the FINISH reading. The readings in the gas meter column (22) should be examined to verify that this is the actual start and finish values. <u>This is the most important number on the Run Sheet.</u>

(U7) Post-Test Calculations-Run Time: This is the same as (12) and is optional. The common usage is to examine the column to determine the total run time and be sure that the “planned” duration and the “actual” duration are the same.

(U8) Post-Test Calculations-Gas Meter Reading: This is the same as (U6), total volume sampled, and is operational.

(U9) Post-Test Calculations-Gas Meter Temperature: This is the simple average of the values listed in the column. Data reduction equations assume the gas meter was operated at a constant temperature. The average value is used as that value.

(U10) Post-Test Calculations-Flue Gas Temperature: This is the simple average of the values listed in the column. The data reduction procedures assume that the flue gas temperature was constant. The average value is used as that value.

(U11) Post-Test Calculations-Blank Column: If the blank column is used and if an average value is desired it is recorded here.

(U12) Post-Test Calculations-Orifice ΔH: This is the simple average of the values listed in the column. This value is not used in the data reduction but if it differs from the Target ΔH value the calculations of % isokinetic value (%I) will probably be different than 100%.

Summary: All written comments and data related to a given impactor run should be recorded on the run sheet. Only the substrate weight records and velocity traverse information are recorded on other forms. The three most important data elements recorded are the Sample Duration (0), Total Volume Measured by Gas Meter (V_m), and Total Volume H_2O collected (V_{1c}). All entries are important but these are essential.

4.2.4.6 PARTICULATE TRAIN OPERATION AND DATA RECORDING

Once preliminary velocity traverses, selection of stage configurations and nozzle diameters, and pre-test cold leak checks are completed, the nozzle is covered securely and the sampler is inserted into the flue gas and rotated out of flow for warm up. Aluminum foil and high temperature fiberglass tape serve well for covering the nozzle. Once the impactor is at the desired operating temperature the probe may be withdrawn from the stack, the cover removed and the pretest hot leak check performed. Once the leak test is completed the assembly is reinserted in the stack. The sampler must be at stack temperature when sampling begins. Depending on how long the leak check takes the second warmup may be as short as 5-10 minutes. The first warmup time will generally be about 45 minutes to one hour. Probe heaters are turned on at the start of the warmup time. This will insure that vapor does not condense in the portion of the probe outside the flue and drain back into the impactor backwashing the filter and lower collection plates during sampling.

Section 4.2.4.5 (Run Sheet Instructions) lists the various entries made to the run sheet before, during, and asfter the run. <u>This run sheet serves as both a record and a guide.</u> The most important data to be recorded before the run starts is the initial gas meter reading. The pump may be running during warmup with the cut off valve closed as the pump oil needs to be warm for the pump to be leak free. Using the Traversing Protocol described in Section 4.5.3.A.4, the impactor is positioned to the first sampling point and rotated into flow. The cut off valve is opened (with the pump running) and the flow adjusted to the Target ΔH value. The impactor is then moved to the second traverse point at the appropriate time. Valves are adjusted as necessary throughout the run to maintain the Target ΔH value and data is recorded on the run sheet. Flow is maintained

while the impactor is moved from one traverse point to another in the same port but the flow is stopped (ΔH=0.00) as the impactor is removed from one port and inserted into the new port. Flow is resumed at the first traverse point in the new port. [If, however, the impactor is operated in an upside down orientation (rather than a horizontal or upright orientation) the flow is maintained without interruption throughout the run until the impactor has been removed from the last port and oriented to a horizontal or upright position. Only then can the flow be stopped.] During traversing, move the impactor as smoothly and as quickly as possible without bumping or vibrating the sampler. When removing or inserting the sampler, take care not to scrape the nozzle on the port wall. Also, take care not to bump the sampler against the far inside wall of the flue.

When all the traverse points have been sampled for the desired dwell time the sample run is completed. Flow is then stopped and the sampler is removed from the stack. The post-test hot leak check is performed and the impactor/precollector assembly is then gently disconnected from the probe using as little motion as possible and allowed to cool before being transported to the lab. If the assembly was wrapped with foil, then foil should be removed at this time. The nozzle should be covered and the impactor oriented to an upright position. The condenser catch is measured and the drying column is removed for transport to the lab together with the sampler and run sheet. A wooden carrier is made especially for transporting hot impactors in an upright position is convenient for this purpose.

4.2.4.7 ISOKINETIC CHECK

At this point the % Isokinetic should be calculated as described in Section 4.7.17 using the computer programs described in Manual Appendix A. Acceptable results are: 80% ≤ I ≤ 120 %. If “I” exceeds these limits, the run may be rejected.

It should be noted that only the large particles are affected by nonisokinetic sampling. Consequently, the information on the lower stages may be valid even if the isokinetic check is not met. Where multiple runs are made and only one has poor isokinetics, the outlier test used in the averaging of multiple runs (Section 4.2.7) will probably reject the bad data from the run and retain the data in the unaffected smaller sizes.

4.2.5 SAMPLE RECOVERY

After the sampler has cooled down enough to be handled without gloves, it should be brought into the laboratory and carefully unloaded to remove the particulate matter caught. Great care is needed in this procedure to ensure that all the particulate matter is recovered and transferred to the appropriate containers.

If a cyclone precollector was used, remove the sample collected in the cyclone. With a small brush (a small nylon brush made for cleaning electric shavers is suggested), push the particles caught inside the nozzle down into the cyclone. Then, holding the cyclone upright on a table (or in a vise), carefully remove the cap and, holding the cap over the cyclone, brush the particles adhering to the bottom of the cap and to the outside of the

gas exit tube into the cyclone body. (A No. 7 camel's hair artist's brush is convenient here.) Then, lay the cap aside, being careful not to dislodge any of the particles inside the gas exit tube. Using a downward, pushing motion, brush the particles on the inside walls of the body of the cyclone down into the collection cup. Carefully detach the collection cup from the body and, holding the body over the cup, brush the particles adhering to the underside of the body into the cup. (At this point, all the particles caught by the cyclone should be in the cup.) If a cup insert was used, remove it with a pair of forceps for desiccation and weighing. If not, transfer the particles to a pre-weighed container. Wash the internal nozzle and cyclone surfaces with a solvent, such as acetone, into a preweighed bottle or aluminum cup. Cover the wash container loosely and allow the solvent to evaporate completely before desiccation and weighing.

If an impactor precollector was used, carefully remove the substrate with forceps as is done with impactor substrates. Brush the residue from the nozzle, body and outside of the gas exit tube onto the substrate or weighing container using the same techniques as for a cyclone precollector.

For either type of precollector, collect and weigh the particles adhering to the inside of the gas exit tube and to the connecting tubing from the precollector to the impactor as part of the catch for the first impactor stage. This may be done by washing and/or brushing this tube.

Carefully disassemble the impactor, and sequentially remove the substrates, inspecting each stage before it is placed on the weighing or storage container. Handle substrates sparingly with forceps, spatula, or clean dry fingers. Teflon o-rings are also used with the filter. Place the first filter on a thin aluminum foil envelope before and after the run to help prevent loss during handling. The envelope should be part of the initial and final weighings and should be labeled according to the filter is contains. The second filter is a control and is placed directly beneath the first filter, separated only by a set of Teflon o-rings. The second filter is clean and does not require an envelope.

Typically, some of the material that is deposited in an impactor is collected on surfaces other than the substrates, accumulating on interior surfaces such as gaskets or jet plates. Collecting this "misdirected" particulate matter is often troublesome. If the material is hard and dry, one may brush off the particles on to the appropriate substrate or into the weighing container. If the particles are sticky or wet, some type washdown procedure should be used. Use a solvent that is considerably more volatile than the particles. Also remove and weigh (with the sample) any pieces of substrate that stick to the stage. Generally, recovering material collected on the impactor wall is difficult, frustrating, and perhaps successful only on the inlet sections, where there may be a significant amount of material. By convention, all of the particulate matter collected between two consecutive primary collection surfaces is assigned to the second of the two stages. That is, all the material collected on surfaces between one substrate and another is considered to be part of the catch of the second, or lower, substrate. Material collected in the impactor inlet assembly is added to the first stage catch, (as is the nozzle catch if no precollector is used).

As the impactor is unloaded note the appearance of each stage, substrate, or cyclone in a notebook or run sheet such as was shown in Figure 9. Use a magnifying glass or low-power microscope to examine the deposits. The deposits below the impactor jets should appear as compact cones or spikes with little or no material appearing as streaks across the surfaces or “halos,” i.e., concentric rings around the main deposit.

4.2.5.1 UNLOADING IMPACTOR

See Table 3.

4.2.5.2 RELOADING IMPACTOR

See Table 2.

Table 2

Impactor Loading Procedure for the
University of Washington Mark III/V Cascade Impactor

Note: All parts must be cleaned prior to assembly

A. Outlet Section

1. Secure outlet section of impactor in vise.

2. Place o-ring in groove at base of threads.

3. Teflon tape threads, approximately 1½ wraps.

4. Place filter support plate and fine screen in outlet section, support plate first, fine screen second.

5. When using a second (blank) filter for QA purposes one Teflon ring (marked BF) and blank filter are placed on top of the fine screen. The second Teflon ring marked BF is then placed over the filter. The filter assembly is then placed on top of the blank assembly as follows: Teflon ring, filter, Teflon ring. If stack temperatures exceed 425°F, Kapton may be substituted for the Teflon.

6. Check to ensure that the Teflon rings and filters are lying flat. Place the filter collar onto the outlet section and turn gently until the alignment pin on the top of the outlet section matches up with the hole in the filter collar. The filter collar should now be properly seated.

7. The inside edge of the top Teflon ring should be visible along the inside edge of the collar. If not, it should be replaced as the collar will cut the filter when the impactor is tightened.

8. Place an o-ring in the groove at the top edge of the filter collar.

B. Impactor Substrates

1. If a blank collection plate is to be included in the run, place the proper foil substrate in a collection plate. Place the collection plate on the filter collar with the substrate facing the impactor outlet (upside down).

2. Starting with the foil designated as the last collection substrate, place the foil in a collection plate and put it on top of the blank with the substrate surface facing up. If a blank is not used, this plate is placed directly on the filter collar with the substrate surface up.

3. The last jet plate (smallest flow area) is then placed on top of the collection plate. The jet plate should be oriented so that the jets are at the bottom, closest to the collection plate.

4. Place o-ring in groove at top of jet plate.

5. The remainder of the donut-shaped substrates should be loaded in the same way and added to the stack, alternating collection plates with jet plates.

6. When the last of the donut-shaped substrates and the corresponding jet stages have been placed in the stack, the zero stage collection plate should be loaded with the disk-shaped substrate and placed on top of the stack.

7. Align the stack, then slide the impactor cylinder (outer shell) over it. Tighten the cylinder onto the outlet section until it seals against the outlet section o-ring.

C. Inlet Section

1. Wrap Teflon tape approximately 1 ½ times around the threads of the inlet section.

2. Screw the inlet section (with connecting tube attached) into the impactor shell. Hand tighten only. Excessive tightening of the inlet section into the shell can cut the back up filter.

D. Precollector

1. Wrap threads of top and bottom sections and the nozzle 1 ½ times with Teflon tape.

2. Screw bottom section and nozzle into precollector body.

3. Remove foil from petri dish and curl slightly.

4. Insert foil into precollector body, greased side facing nozzle inlet.

5. Screw top onto precollector body.

6. Tighten precollector onto connecting tube (impactor body). Make sure the precollector is aligned such that the bend in the connector-tube offsets the nozzle.

E. Leak Check

1. Connect the inlet of the precollector/impactor assembly to the suction end of a pump by attaching a hose to the nozzle. Cap the outlet.

2. Pull a vacuum of approximately 10 inches of mercury on the assembly and observe the vacuum pressure for about a minute.

3. After this observation period is over, release the vacuum at the inlet, not at the outlet. Opening the outlet to ambient can rupture the filter.

4. Pressure losses of approximately four to five inches should be expected. Drastic leaks indicate loose fittings or missing o-rings. Attempt to correct any leaks. Use of a slightly positive pressure (6 inches of water) and a soap solution may help to locate the source(s) of the leak(s).

5. If small leaks are present which cannot be corrected, a leak check should be performed without the precollector.

6. Enter leak check data in appropriate space on impactor lab sheet.

F. Wrapping

1. On two small pieces of high temperature tape, write the impactor run code. Place one on the impactor and the other on the precollector.

2. Wrap impactor body and precollector with aluminun foil and secure with tape.

3. Rewrite impactor run code on the wrapped impactor body.

Table 3

Impactor Unloading Procedure for
University of Washington Mark III/V

A. Preliminary

1. Hold impactor uprright at all times.

2. Remove foil wrapping and blow off any loose dust from the impactor/precollector assembly with compressed air or gas. Cover nozzle with thumb to prevent blowing into precollector. Exterior surface should be clean to prevent contamination during unloading.

3. Secure outlet section in vise for disassembly.

4. Remove impactor lab sheet from run sheet notebook. As substrates are unloaded, observations such as broken peaks or loose particulate should be noted on the lab sheet.

B. Precollector and Impactor Inlet Section

1. Separate precollector from impactor where precollector attaches to the connector tube.

2. Unscrew top of precollector and remove foil from body, placing in petri dish.

3. Remove nozzle from precollector body and using clean dry brush, brush any loose particulate on the inside of the nozzle or the top section of the precollector onto the foil. Place nozzle to the side so that it can be washed in Step 7.

4. Separate body from bottom section and (using the same brush) brush any loose particulate in either section onto the foil. Place the brush to the side so that it can be washed in Step 7. Note: particulate on the inside of the exit tube (bottom section) should be transferred to the first substrate of the impactor.

5. Carefully fold foil in half twice and then loosely fold a small ridge on each side to prevent loss of particulate. The fold must be loose to permit drying during desiccation.

6. The tube connecting the precollector to the impactor should remain connected to the inlet section of the impactor. Any particulate in this tube should be brushed (using a second clean brush onto the first substrate in the impactor. This is best done by tapping the sides of the tube over the substrate, then brushing the interior of the tube with a small nylon bristle brush. The interior surface of the precollector exit tube (bottom section) should also be brushed onto the first

substrate in the impactor. Set tube/inlet assembly, precollector exit tube, and brush, to the side so that they can be washed in Step 8.

7. Washdown techniques as described in Section 4.2 of Method 17 may be used to rinse the nozzle and brush with acetone. The collected rinse must then be evaporated desiccated, and weighed on a precision balance. Note: It is important that the brushes used were previously cleaned by an acetone rinse and allowed to dry before being used to brush the particulate. As short straight nozzles are used, it may not be necessary to perform this nozzle washdown.

8. The precollector exit tube and the connecting tube between the precollector and impactor should also be washed into a second sample bottle. The evaporated dry weight gain from this washdown is assigned to the impactor's zero stage are shown in Figure 4-11 (Example Weight Sheet).

C. Impactor Substrates

1. Loosen and remove the shell of the impactor. The impactor inlet section with attached connecting tube was removed in Step B8 above.

2. Inspect the interior of the shell for any evidence of internal leakage. If any such evidence is found, make a notation and try to identify the stage(s) with which it was associated.

3. Remove the zero stage collection plate from the stack. If the o-ring of the jet plate directly beneath the collection plate sticks, remove both plates from the stack.

4. Remove the disk-shaped substrate from the collection plate and place in its labeled petri dish. This is best accomplished by grasping the edge of the substrate with tweezers and rotating the disk gently.

5. If the jet and collection plates are stuck together, gently push the collection plate horizontally until the o-ring seal releases.

6. Each donut-shaped substrate should be removed in the same way and placed in its respective labeled petri dish.

7. Any particulate present on the surface of a jet plate should be brushed onto the substrate directly beneath it unless it is obvious that the material was removed or reentrained from the preceding substrate.

D. Outlet Section

1. Gently lift the filter collar and brush any part of the filter adhering to it in the foil envelope.

2. Removing the outlet section from the vise, insert the handle of the brush into the outlet neck and gently lift the filter support plates.

3. Remove filters and Teflon rings from the plates and place respectively, dirty filter and two Teflon rings into the foil envelope and clean filter with two Teflon rings (labeled "BF") into its labeled petri dish.

E. Reloading Preparation

1. All parts of impactor and precollector should be blown off with compressed air or gas before being reloaded as described in Table 2.

4.2.6 INSPECTION FOR PRACTICAL PROBLEMS

Manual Sections 3 and 4 discuss deviations from theory and practical problems. The purpose of this inspection is to verify that these problems have been successfully avoided or limited. This analysis consists of a visual examination of a completed impactor run and a study of the postrun dry weights. The analysis is summarized in the following paragraphs which give qualitative and quantitative guidelines. The problems discussed include cover nozzle scraping, bounce, overloading, underloading and negative weight changes. Additional inspection information is given in Section 6.2.

4.2.1.6 NOZZLE SCRAPING

It is extremely easy to scrape a nozzle when inserting or removing the impactor from a port. If this happens, the results can be devastating. If the nozzle is significantly damaged as determined by the visual inspection made at the time of the postrun hot leak check it may be necessary to reject the run. Even if the nozzle is not damaged, scrapings from the port may invalidate the precollector catch. For this reason the precollector catch and zero stage collection plate (solid disk) should be inspected for particles that are obviously too large to have been suspended in the gas stream for sampling, or which appear from their shape, coloration, etc. to be foreign material.

4.2.6.2 PARTICLE BOUNCE

The "D_{50} product" guidelines elsewhere are intended to prevent a situation where bounce could be a problem. Visual inspection, however, is always necessary. Bounce can occur even when stages are not overloaded. Bounce occurs when the collection plate substrate material fails to capture and hold a particle that strikes its surface. If bounce has occurred the most direct indication is the filter. The filter loading will be very high and observation with a 10x occular will show the presence of particles much larger than the D_{50} of previous stages. When bounce occurs it is usually a substrate problem, meaning that a different substrate material must be used or the D_{50} products of the stages must be reduced by sampling at a lower flow rate. Sometimes the same end result can occur from scouring due to excessive jet velocities. The D_{50} product

guideline used in the impactor flow rate/stage selection section will indicate those cases where a different jet stage or impactor flow rate should be selected.

4.2.6.3 OVERLOADING

The maximum individual stage loading which should be permitted (excluding the precollector and filter) is 15mg. The impactor is normally operated in a horizontal mode, consequently captured particulate may fall away from the substrate and migrate to some other part of the impactor unless the substrate material holds the particulate in place. Greased substrates normally work well for this purpose. Matted materials such as quartz or fiberglass will trap the particulate in the fiber mat. Visual observations can provide some indication of whether the “capture” ability of the substrate material has been exceeded. If so, such a run is in question and subsequent runs should sample for shorter durations.

4.2.7 MULTIPLE SAMPLING RUNS

Multiple impactor runs are required to characterize a given test condition (inlet, outlet etc.). Cascade impactors are labor intensive instruments with typical run times of two to six hours (at the outlet of a high efficiency control device). The cost per run is quite high, yet if results are to be believable, multiple runs must be performed. The absolute minimum number of good runs is three. This does not include the mandatory blank run or the exploratory initial run. The recommended minimum number of good runs is five since these two additional runs decrease the width of the confidence interval at the 95% confidence level to about ½ the interval for three readings (a 50% gain in confidence). To obtain an additional 50% gain over the three run confidence interval (50% decrease in the width of the confidence interval associated with the five runs) one would need to make a total of about 14 runs. Admittedly 14 runs is impractical. Seven runs is reasonable and yields roughly one-half the benefit of increasing the number of runs from 5 to 14. For this reason five good runs is the recommended minimum, seven is desirable, while three is the absolute minimum requirement. If, as described in Section 4.2.7, a skewed velocity profile requires multiple regions (multiple runs)... to complete a full traverse, the number of runs must be multiplied by the number of regions. The rationale for requiring a minimum of three traverses and recommending seven is outlined in Appendix D. (Estimations of the uncertainties Associated with Cascade Impactor Data and in Measured Fractional Efficiencies of Control Devices.

The computer program documented in Manual Appendix A has provisions for averaging multiple runs performed at the same test conditions (location, plant load, etc.). Spline curve fitting techniques are applied to the cumulative mass data from each individual run. Averaging and all additional analysis is then performed using only the fitted coefficients for this set of common diameters.

The outlier analyses which can be performed in the averaging process may allow some use to be made of data from runs which might otherwise have to be rejected. Data in individual size ranges of a run which might be affected by gross weighing errors, nozzle

scrappings, etc. will probably be rejected by the (optional) outlier analysis if the data from several runs are being combined.

4.2.8 ANALYTICAL BALANCE PROTOCOL

Two potential moisture related problems may be encountered as one tries to determine accurate pre-run and post-run weights for impactor runs. One is that any moisture accumulated on the substrate (filter) during sampling should be removed and the second is that at some industrial sources the particulative collected (or condensed) during the run may act as a desiccant. Thus even though we remove all the moisture accumulated during sampling this hygroscopic particulate may gain weight upon exposure to room air. The amount of such weight gains depends on the relative humidity of the room air, exposure time, amount of such particulate on the substrate (filter), and hydroscopic propensity of the particulate. In cases where sulfuric acid was collected, the hydroscopic propensity of the acid was stronger than the drying agent in the desiccator and the substrate (filter) gained weight when placed in the desiccator. The use of a spot check second weighing at the end of a second desiccation period serves to verify that moisture uptake has not occurred during desiccation and that the substrates were sufficiently dry at the time of the first weighing (pre-test and post-test). A second moisture uptake test is recommended to determine uptake from room air prior to weighing. If this test shows significant uptake, steps must be taken to minimize exposure to moisture laden air. One step is to remove a single substrate (filter), place it in the weighing chamber (containing a small disk filled with desiccant) and complete this weighing before removing a second substrate from the desiccator. This “one at a time” technique is cumbersome but does minimize the exposure of the substrate to undesiccated air. If the lab has controlled 50% humidity, this technique is probably not necessary but if the lab humidity is high this may well be necessary. This “one at a time” technique should be used unless a test is performed where a complete set of substrates (with filter) is weighed one at a time in an undesiccated weighing chamber after various amounts of exposure time to room air. If the results of such a test show that moisture uptake from room air is not a problem, then and only then should one remove an “entire set at a time” from the desiccator.

4.2.8.1 PRE- AND POST-TEST DESICCATION (Table 4)

Table 4
Desiccation of Substrate Sets
(Pre-test and Post-Test)

1. Substrate sets should desiccate for approximately 6 to 12 hours immediately prior to the first weighing (Pre-test and post-test).

2. A small tray of fresh desiccant should be placed in the weighing compartment of the balance (to prevent moisture uptake during weighing) and the exposure of the substrate (filter) to undesiccated air should be minimized unless a moisture uptake test shows that exposure to room air does not result in significant weight changes. This test is made by performing multiple weighings on the same substrate after different amounts of exposure time to room air. Weighing procedures are given in Table 5.

3. The substrate set should desiccate for a second 6-12 hour period before the second weighing. This second weighing may be a spot check unless the difference between the two weighings is greater than 0.05 mg. Second weighings should always be performed on the filters and on post-test weighings of the precollection (and most heavily loaded) substrates.

4. If the difference between the first and second weighings is greater than 0.05 mg, a third weighing should be performed after further desiccation.

Each sample to be weighed should be desiccated to a constant weight, with periodic checks to establish constancy. Hard, nonvolatile particles may be dried in a convection oven at 100°C (212°F), then stored in a dessicator until they cool to room temperature. Weigh them, then check-weigh them 2 hours later. Volatile particles present special problems which have to be dealt with according to the characteristics of the particulate matter and the sampling goals. One technique that has been used for particles which are volatile at elevated temperatures is to dry them in a dessicator 24 hours at room temperature before weighing. Whatever the technique, constant weight of the samples after further drying is the criteria which is normally to be used. Record the results of the weighings (Figure 11, Example Weight Sheets) and any notes in a notebook.

Occasionally samples are collected which are inherently unstable in weight. This can occur if the collected particulate matter is reactive, if it is so hygroscopic that it continues to absorb water even in a conventional desiccator, or if it contains a component sufficiently volatile at room temperature to evaporate during the dessication period. For these situations special weighing protocols may have to be devised using insight into the nature of the offending process. For example, one may deal with steady loss of

volatile components by immediate “warm” weighing of the real and blank substrates followed by periodic reweighings to establish an estimate of the dry, “time zero” weight. Similar techniques or improved dessication techniques may be used with hygroscopic weight gains. Occasionally it has proven useful to chemically alter a hygroscopic component. In particular, neutralization of sulfuric acid by exposure to trace amounts of ammonia vapor may allow otherwise weight-unstable substrates to be dried to a stable weight.

4.2.8.2 BALANCE OPERATIONS (Table 5)

On some impactors such as the UW Mark 5, the inlet throat serves as the first jet stage. The D_{50} of the precollector is frequently close to, or perhaps smaller than, that of the first stage. The minimum stage D_{50} ratio should be 4:3 (x 1.3 or log D = 0.124). For stage D_{50}'s more closely spaced, the weight change on the lower stage tends to be affected too much by the lack of sharpness in the collection efficiency of the upper stage (see Manual, Section 2 – Theoretical and Empirical Basis for Cascade Impactors). For this reason if the D_{50} of a stage is too close to that of an adjacent stage its weight is combined with that of the next lower stage and it is omitted from the analysis. If the D_{50} of the precollector is less than that of the first stage, the weight change of the first stage provides a measure of the reentrainment from the precollector. The weight sheet records record the individual weights, these are combined by the computer program options described in Manual, Appendix A.

As shown in Figure 11, the filter, foil pouch, and two Teflon insert rings are weighed as an assembly rather than individually. The blank filter and two Teflon insert rings marked “BF” are also weighed as an assembly. The weight sheet (Figure 11) provides a section for recording washdown weights and a description of the tare weights used. The check marks on Figure 11 indicate that the reproducibility criteria were satisfied for the control weight, blank substrate, and blank filter as specified in Section 7.1 (Acceptable Results).

Table 5

Balance Procedures for 1/100 mg Analytical Balance
(see also Figure 11 Example Weight Sheet)

Note: The procedures listed in this table are generic and should be considered minimal. Modifications should be made as appropriate for a specific vendor's model number.

A. Precautions

1. Calibration and tare weights should be handled with smooth edged tweezers. These tweezers should not be used on substrates.

2. When substrates are weighed, check to make sure the substrate is not touching the side of the weighing chamber.

3. Door to weighing chamber should be kept closed except when changing substrates or weights.

4. To protect tare weights, the boxes containing these weights should be closed. Tare weights must be protected from dust and lint.

5. Balance and weighing chamber should be equilibrated in temperature with their surroundings to avoid thermal drift of the zero and scale factor (calibration dial). Room temperature in the weighing room should be regulated to less than 85°F and maintained at this temperature ± 5°F throughout the weighing session. Wide swings in temperature can be advertsely affect accuracy.

6. Adequate warmup time must be allowed to assure electrical stability (10-30 min.) and thermal stability. It is best to allow the balance to remain in a power on (standby) mode for days before and during a test. Be sure that sunlight does not shine directly on the balance weighing chamber.

7. Place a small dish filled with indicating type silica gel (desiccant) inside the weighing chamber. Be sure this dish does not interfere with the pan movement.

B. Weighing Procedures

1. Check to make sure electrical tare indicator is off.

2. Range dial should be set to 200 mg range.

3. Check zero. If readout does not indicate 00.00, adjust coarse and fine zero dials until the readout is 00.00.

4. Remove 200 milligram calibration weight from container with smooth edge tweezers and place on weighing pan.

5. Allow balance sufficient time to equilibrate. If readout is not 199.99 adjust with calibration dial. This adjustment sets the scaling factor.

6. Record calibration and zero data to balance log book along with date and time.

7. Weigh each tare weight and enter this data in the balance log book. The 50, 100, and 200 mg tare weights should be weighed (without tares). The two 500 mg tare weights should be weighed with the 100 mg and 200 mg weights used as tares.

8. If extreme changes (0.05 mg) in the weights of the tares are noted, the zero and calibration of the balance should be checked and these values, along with any adjustment, should be noted in the log book. The tare weights should then be reweighed as described above. The problem can be that one of the tare weights is dirty and needs to be cleaned.

9. After the tares are weighed, the zero should be rechecked and recorded in the log book, along with any required adjustment.

10. Remove the first substrate from the desiccator. These should be weighed “one at a time” to avoid moisture uptake.

11. The entire control weight set, A through D, should be weighed as part of the first substrate set. These weights should be recorded on the control set weight sheet in the balance log book as well as on the weight sheet.

12. The zero should be checked and recorded, along with any adjustments, each time tares are changed and between substrate sets (as shown on the weight sheet).

13. After the first substrate set is weighed, only control weight C need be reweighed with each subsequent set. If an extreme change in the weight of the control occurs, the zero and calibration of the balance should be checked. The entire control set should then be reweighed. If the weight change is still occurring, check for a dirty tare on control (clean if found) and reweigh each tare. Proceed with the weighing of the substrate sets only when this problem has been corrected.

14. Unless weight changes requiring recalibration of the balance occur, the calibration only needs to be checked every two hours.

15. When the weighing session is concluded, the balance zero and calibration should be checked a final time. Do not turn the balance off. Power should only be

turned off when all weighings for the field test have been completed. This avoids long delays as the balance warms up and obtains thermal stability.

5. CALIBRATION

One central laboratory/on-site log of all calibrations should be maintained. Entries from this log should be posted in the equipment maintenance records. The following paragraphs describe the calibration procedures for the instrumentation used with cascade impactors.

5.1 PITOT TUBE

As shown in Figure 1 a pitot tube is not used as an integral part of the impactor sampling train. At many commonly encountered flow rates, the presence of the precollector could result in a flow interference at the pitot head causing it's coefficient, C_p' to differ from the baseline value even when the pitot tube is dimensioned as described in Method 2. This interference is dependent on nozzle size and stack velocity. For this reason the pitot is omitted from the sampling train.

A separate Method 2 Pitot Probe is used to measure the velocity profile at various times during a test program. This probe and it's components should be calibrated per Section 4 of Method 2.

5.2 PRECOLLECTOR NOZZLE

Each nozzle shall be permanently and uniquely inscribed with an identification number. All calibrations and maintenance repairs shall reference this number. Each nozzle shall be inspected and calibrated before initial use. If nicks, dents, or corrosion are discovered, the maintenance logs shall be noted, the nozzle repaired and recalibrated as described below. Figure 12 is a data form that may be used for this purpose. A micrometer capable of measuring inside diameters to the nearest 0.025 mm (0.001 in.) shall be used to make three measurements of the inside diameter of the nozzle (undamaged nozzles only) each on a different axis as shown on the form. The average of these three measurements is then calculated. The difference between the high and the low numbers should not exceed 0.1 mm (0.004 in.).

5.3 DRY GAS METER

Wet test meter calibrations of the Dry Gas Meters are performed prior to initial use, and later as required, by comparison to a "standard" dry gas meter. After each field use the calibration of the metering system shall be checked by comparison to a standard dry gas meter as described in Section 4.3 of Method 5. Leak checks shall be performed as described in Section prior to any calibrations or comparisons.

The maximum acceptable leak rate (pump warm and running) is 0.00057 m^3/min (0.02 cfm) for systems to be used at flows higher than 0.02 cfm. For low flow rate sampling

situations (flow rates 0.2 cfm) the leak rate should not exceed 0.00014 m^3/min (0.005 cfm). Leaks producing rates greater than these should be repaired before calibration. If leakless pumps suitable for low flow rate operation cannot be obtained, it may be necessary to place the pump downstream of the gas metering system. The field setup programs described in Manual Appendix A make provision for this configuration.

Calibration procedures using a wet test meter are described in APTD-0576. Note—If the dry gas meter coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either 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.

5.4 ORIFICE FLOW METER

Calibration of the metering system orifice flow meter is described in Section 4.3 of Method 5.

5.5 DIFFERENTIAL PRESSURE METER

Calibration of the metering system Differential pressure meter is described in Section 2.2 of Method 2.

5.6 TEMPERATURE DEVICES

Calibration of the temperature metering system is described in Section 2.3 of Method 2.

5.7 BAROMETER

Calibration of barometers is described in Section 2.5 of Method 2.

5.8 GAS DENSITY DEVICES

Calibration and operation of the molecular weight determination equipment (Fyrite analyzer) is described in Method 3.

5.9 IMPACTOR STAGE CONSTANTS

As described in Manual Section 2.4 (Verification of Impactor Theory) normal treatment of field data is to use stage impaction constants calculated from the modified Marple theory rather that stage sconstants determined during laboratory calibration. The focus of laboratory impactor calibrations has been to validate the theory over a wide range of variations in each of the important parameters used in the model. The significance is that only impactor designs which have been validated by laboratory calibration should be used. Manual Appendix B lists commercially available impactor designs which have been validated together with the physical parameters (stage geometry constants) used by the computer program of Manual Appendix A to calculate the theoretical stage

constants for the given test conditions of temperature, pressure, gas composition, particle density and impactor flow rate. Stage geometry constants are: number of holes, average hole diameter, and jet-to-plate spacing (distance). In the data reduction program, MPPROG, the stage impaction constants, $\overline{VP50}$, are designated as SI (i). It should be noted that program MPPROG requires the operator to select either theoretical or fixed calibration values (manually entered in the program DEF/IMP for the impaction constants $\overline{VP50}$. Selection of theoretical calibration values also incorporates adjustments to the stage constants due to particular type of substrate material used (bare metal, coated metal, or fiberous matt). Choice of impactor flow rate and stage selection should be such that the Reynolds number (Re) is greater than 50. Calibrations have shown the theory to be questionable for some jet configurations at Re (50).

5.10 ANALYTICAL

The operating procedures for the analytical balance (Section 4.2.8) provide for frequent calibration using Class S standard weights traceable to the National Bureau of Standards.

Figure 11 *Example of a completed Weigh Sheet.*

SUBSTANCE SET NO I23	DATE OF INITIAL WEIGHING 1 4 - 10 - 84
(☐ APIEZON H)	DATE OF INITIAL WEIGHING 2 4 - 11 - 84
☐ FIBERGLASS ☐ BARE	DATE OF FINAL WEIGHING 1 4 - 21 - 84
☐ HERC. POLY. ☐ OTHER	DATE OF FINAL WEIGHING 2 4 - 22 - 84

WASH DOWN

$Ca = 5 \times 10^{-6}$ mg/ml

SOLVENT (☐ ACETONE) ☐ DISTILLED WATER

PRECOLLECTOR NOZZLE AND BODY: EVAPORATOR DISH:		PRECOLLECTOR EXIT TUBE AND SOLID DISK: EVAPORATOR DISH:	
ID	I 23 N	ID	I 23 T
INITIAL Wt (mg)	416.72	INITIAL Wt (mg)	418.53
FINAL Wt (mg)	420.16	FINAL Wt (mg)	419.23
Δ (mg)	3.44	Δ (mg)	0.70
WASH VOLUME (mL)	156 ml	WASH VOLUME (mL)	161 ml
RESIDUE, W_{aN}	0.0008	RESIDUE, W_{aT}	0.0008
CORRECTED WASH WEIGHT	3.44 mg	CORRECTED WASH WEIGHT	0.70 mg

(ADD THESE WEIGHTS TO THE DRY WEIGHTS TO GET TOTAL WT GAIN)*

DESCRIPTION	ID NO.	INITIAL TARE (mg)	INITIAL 1 (mg)	INITIAL 2 (mg)	FINAL TARE (mg)	FINAL 1 (mg)	FINAL 2 (mg)	TOTAL WT. GAIN (mg)
PRECOLLECTOR	I23P	100	30.66	30.69	100	48.79	48.81	21.57*
SOLID DISK	I23D	700	4.31	4.29	700	5.16	5.17	1.55*
	ZERO		00.00	00.01		-00.01	00.00	
DISK DONUT:								
CONTROL	CTRL	1050	57.14	57.15	1050	57.14	57.14	✓
S1	I23-1	↓	58.32		↓	59.98		1.56
S2	I23-2		53.03			57.87		4.84
S3	I23-3		65.07	65.05		66.67		1.60
S4	I23-4		64.06			64.95		0.89
S5	I23-5		56.87			56.96		0.09
S6	I23-6		56.02			55.89		-0.13
BLANK	I23-B	1050	64.91		1050	64.73		(-0.18)
FILTER 1 *	I23-F	600	53.03	53.01	600	54.06		1.36 ***
FILTER 2 **	I23-BF	500	62.01	62.00	500	62.34		N/A
	ZERO		00.01	-00.01		00.00	00.01	

(Margin note: 3.11)

SEE ALSO: (1) LAB LOAD/UNLOAD SHEET
(2) OPERATOR'S RUN SHEET

RUN NO. SAMPLE CALC
DATE 4-20-84

COMMENTS:

FILTER TYPE: (☐ 2500 QAS QUARTZ)
☐ REEVE ANGEL 934AH FIBERGLASS ☐ ACID WASHED ONLY
☐ GEIAH TEFLON ☐ ACID WASHED AND STACK CONDITIONED
☐ OTHER ☐ STACK CONDITIONED ONLY

DESCRIPTION OF TARES USED:

* FILTER + 2 TEF. RINGS + POUCH
** BLANK FILTER + 2 TEF. RINGS (BF)
*** COMBINED WEIGHTS SINCE BF STUCK TO F DURING RUN

100 → 100
700 → 500 + 200
1050 → 500 + 500 SS + 50
600 → 500 SS + 100
500 → 500

5598-11C

C-12

18.13	0.85	1.03
3.44	0.70	0.33
[illegible]	1.55	1.36

FIGURE 12 *Nozzle calibraton*

DATE/TIME	CALIBRATED BY	NOZZLE ID NUMBER	NOZZLE DIAMETER (INCHES)			ΔD	D_{avg}
			D_1	D_2	D_3		

WHERE:

$D_{1,2,3}$ = THREE DIFFERENT NOZZLE DIAMETERS AT 60 DEGREES TO EACH OTHER. EACH MEASURED TO THE NEAREST 0.001 INCH

ΔD = MAXIMUM DIFFERENCE BETWEEN ANY TWO DIAMETERS, $\Delta D \leq 0.004$ INCH

$D_{avg} = (D_1 + D_2 + D_3) \div 3$

INSTRUCTIONS

1. INSPECT THE NOZZLE FOR NICKS, DENTS, AND CORROSION. IF THESE ARE FOUND THEY SHOULD BE CORRECTED BEFORE CALIBRATION.
2. PLACE A REFERENCE MARK ON THE NOZZLE. PLACE THE NOZZLE AT THE CENTER OF FIGURE, ALIGNED WITH POINT 1. MEASURE AND RECORD D_1.
3. ROTATE THE NOZZLE SO THAT THE REFERENCE MARK IS ALIGNED WITH POINT 2. MEASURE AND RECORD D_2.
4. ROTATE THE NOZZLE SO THAT THE REFERENCE MARK IS ALIGNED WITH POINT 3. MEASURE AND RECORD D_3.
5. CALCULATE ΔD AND D_{avg}.

5.11 TRIPLE BEAM BALANCE

The lab balance is calibrated using a 50g Class P (or equivalent) analytical weights. After set up in the on-site lab, a silica gel drying column is placed on the balance and the reading is recorded. The 50g Class p weight (1.2 mg tolerance) is added to the drying column on the balance pan and this second reading is recorded. The difference between the two weights must be between: 49.50g and 50.50g.

6 CALCULATIONS AND DATA REPORTING

6.1 VARIABLES

6.1.1 NOMENCLATURE

Variables are defined as they are used in the equations.

The following paragraphs give equations involved in the setup, operation, and data analysis of cascade impactors. In practice, the calculations are performed by the computer programs documented in Appendix A of this report. Further explanation as to the use of the equations is given in various sections of this report, to include Section 4 (Field Protocol) and Section 5 (Data Reduction and Analysis Procedures).

6.1.2 MOISTURE CONTENT ESTIMATE

An initial guess at the stack moisture is used in the preliminary calculations for stage selection, impactor flow rate, and Target ΔH for use with the initial run. Accurate moisture data is obtained during the initial run or by application of Method 4, but an estimate must be made prior to the run. Plant operating personnel will frequently be able to provide stack moisture information. This data may also be available from previous test reports. If necessary, one may use a preweighed drying column and the meter box from the sampling train. Simply record the initial gas meter reading and pull filtered stack gas through the preweighed drying column until the indicating silica gel shows some moisture collection. Record the final gas meter reading and determine the final weight of the drying column. The weight change of the drying column and the gas meter change are used in Section 4.7.13 to estimate the stack moisture.

6.1.3 GAS DENSITY

A Method 3 analysis (Fyrite or Orsat) is used to determine the dry gas volumetric fraction for oxygen (O_2) and carbon dioxide (CO_2). The preliminary moisture content estimate (B_{ws}) is then used together with the O_2 and CO_2 values to calculate the dry mean molecular weight (M_d) and the wet mean molecular weight (M_w) of the flue gas as follows:

$$M_d = 32B_{O_2} + 44B_{CO_2} + 28(B_{N_2} + B_{co}) \quad (1)$$

where B_{O_2}, B_{CO_2}, B_{N_2}, and B_{CO} are dimensionless dry volumetric fraction for O_2, CO_2, N_2, and CO respectively. M_d has dimensions of lb/lb mole. Dry air has a value of 29 lb/lb mole.

$$M_s = M_d (1 - B_{ws}) + 18 B_{ws} \quad (2)$$

where B_{ws} is the volumetric fraction for water (stack moisture), dimensionless.

6.1.4 POINT VELOCITY

A Method 2 pitot is used to measure the temperature (T_i) and velocity pressure head (ΔP_i) at each Method 1 traverse point across the duct. This data is used to calculate the velocity at this point (i_i) as follows:

$$i_i = K (\Delta P_i \ T_i) ½ \quad (3)$$

where

i_i = pitot velocity (ft/sec) at point i,

T_i = absolute temperature at point i (°R = °F + 460),

ΔP_i = pitot pressure reading (inches H_2O) at point i,

K = pitot-gas composition factor, given by:

$$K = 2.9 C_p (29.92 R'/P_s) ½ \quad (4)$$

where

$$P' = 28.95/M_s \quad (5)$$

$$P_s = P_{bar} + P_g \quad (6)$$

C_p = Pitot calibration coefficient (dimensionless). For a Type S pitot which matches the criteria of Method 2, this coefficient has a value of 0.84. A type S pitot which does not meet the criteria of Method 2 should be calibrated as described in Section 4 of Method 2. A standard pitot is constructed such that it has a coefficient of 0.99,

M_s = Wet mean molecular weight,

P_s = Absolute stack pressure (inches Hg),

P_{bar} = Ambient pressure, barometric pressure at the stack measurement site (inches Hg),

P_g = Stack gauge pressure, differential (=) to atmosphere, (inches Hg, 13.6 inches H_2O = 1.00 in. Hg). As described in Method 2 this value is measured by disconnecting the downstream side of the pitot tube so that we read the differential between ambient and the downstream side of the Type S pitot. The pitot manometer reads in inches H_2O so we must convert the ± reading to inches Hg by dividing by 13.6.

6.1.5 VELOCITY PROFILE

The velocity profile is determined by calculating the velocity at each point of the Method 2 traverse. These point velocities may then be averaged over the whole traverse or over regions of the full traverse (see Section 4.5.3.A.4). The average velocity for the full traverse (υ_s) and the average temperature (T_s) are as follows:

$$\upsilon_s = \frac{1}{n}\sum \upsilon_i (i = 1,n) \tag{7}$$

$$T_s = \frac{1}{n}\sum T_i (i = 1,n) \tag{8}$$

where n is the number of points in the traverse. The Impactor Traversing Protocol (Section 4.5.3.A.4) gives equations for a division of the Method 1 traverse points into two or more regions, calculation of required sampling velocity for each region, and averaging over only the points in each region.

6.1.6 HARDWARE SELECTION

The first decision related to hardware selection is to decide upon the sampler flow rate. Each impactor has a designed range of flows, the exact limits of which depend on stack temperature, viscosity, and the substrate material being used. At outlets one generally desires a high flow rate and at inlets one usually desires a low flow rate. These factors are discussed in Section 4.5.3.A (Preliminary Determinations). When selecting a flow rate (Q_I) one is interested in calculating the approximate run time (t_{50mg}) associated with this value of Q_i. An initial guess is obtained by calculating the time required to collect a total sample of 50mg (sum of the precollector, all stage, and filter weights). The following equations are used for this calculation:

6.1.6.1 TIME FOR 50 mg

$$t_{50mg} = 0.77162/(Q_I G_A) \tag{9}$$

where

Q_I = actual impactor flow rate (ACFM),

G_A = mass loading (gr/ACF).

Note:

$$G_A = 17.65\ c_s\ (1 - B_{ws})\ P_s/T_s \qquad (10)$$

where

C_s = mass loading (gr/SCF) corrected to standard conditions, (dry, 68°F, 29.92 in. Hg),

T_s = Absolute Stack Temperature (°R = °F + 460),

P_s = Absolute Stack Pressure (inches Hg) as given by Eq. 4-6.

NOTE: 1.00 lb = 7,000 grains = 453.6 gm (gr is the abbreviation for grains)

One should select a flow rate that will allow for reasonable run times, subject to the $i\,D_{50}$ limits for the selected stages.

6.1.6.2 NOZZLE CHOICE AND FLOW RATE

Only a discrete set of nozzles is available, thus one should modify the selected Q_I to permit the impactor to be operated isokinetically to the average velocity (i_{si}) (over the traverse region i) while using one of the real nozzle sizes. The following equations are used for this purpose. Using the flow rate obtained from the t_{50mg} calculation, calculate an ideal nozzle size then pick a real nozzle close to this size and calculate the corresponding Q_I. Note different nozzles may be used for the different regions.

$$D_n = 1.748\ (Q_{i}/i_{si})\ ½ \qquad (11)$$

where

D_n = nozzle diameter (inches),

Q_I = impactor flow rate (ft^3/min) actual stack conditions

i_{si} = average velocity over region "i" (ft/sec),

or

$$Q_I = 0.3272\ i_{si}\ D_n^2 \qquad (12)$$

To see what Q_I results when a given nozzle is selected.

6.1.6.3 STAGE CONFIGURATION

The following equations are used to select the stage configuration by calculating the size cut for a given impactor stage, given the stage calibration constant (K_s), impactor temperature (T), gas viscosity (μ), particle density, and several pressures:

$$D_{50i} = K_s\ (\mu P_s / Q_I \rho_P P_A C_{i-1})^{1/2} \qquad (13)$$

where

D_{50i} = the value of the ith iteration for the D_{50} for this stage (cm)

Note: To convert from cm to μm multiply by 10^4 μm/cm

K_s = stage calibration constant, a function of geometry and substrate materials calculated by the modified Marple Impactor Theory described in Section 2.4,

P_s = local absolute pressure downstream of the stage jet (inches Hg),
Q_I = impactor flow rate (cm^3/sec),

P_i = absolute pressure at impactor stage inlet (inches Hg).This is the same as the stack pressure, P_s, less the accumulated pressure drop from the preceding stages.

ρ_p = particle density (gm/cm^3) determined by helium pychometer measurements,

C_{i-1}= i-1 iteration for the Cunningham slip correction factor as described below,

μ = gas viscosity (gm/cm/sec) as described below:

The D_{50} is a function of the Cunningham slip correction factor (C) and the Cunningham slip correction factor is a function of the D_{50}, consequently our approach is to make an initial guess at the Cunningham slip correction factor (C_o) and calculate the corresponding value for the D_{50}, D_{501}. This value, D_{501}, is then used to calculate a new value for the correction factor, C_1, which is in turn used to calculate a new diameter, D_{502}. We continue to iterate in this manner until two successive C_i values satisfy the closeness criteria given below:

$$\left|1 - (C_{i-1} / C_i)\right| \langle 0.001 \qquad (14)$$

The equation for the Cunningham correction factor is as follows:
An initial guess, C_o' is used to calculate D_{501}' subsequent C_i using $D_{501\ are}$ given by:

$$C_i = 1 + (2L/D_{50i})\ [1.23 + 0.41\ EXP\ (-.44\ D_{50i}/L)] \qquad (15)$$

where

D_{50i} = diameter (cm) as obtained by using the D_{50i} equation above and the previously calculated value for C (C_{i-1}),

L = mean free path of the gas (cm).

For a stack temperature of 180°C, pressure of 30 inches Hg, and flue gas composition close to that of ambient air the Cunningham correction factor is approximately 1.03 for a 1×10^{-3} cm (10 μm) particle and approximately 2.03 for a 3×10^{-5} cm (0.3μm) particle. A good initial guess for C then is C_0 = 1.03.

For standard air the mean free path (L) (over the range of 0°C to 410°C) is given by:

$$L = (1.04\ \mu/P_s)\ (1 + 0.00367\ T)^{1/2} \quad (16)$$

For T (°C), μ in (gm/μm/sec) as given below, P_s (inches Hg), and L (cm).

For standard air the viscosity (μ) (over the range 0°C to 410°C) is given

$$\mu = (174.4 + 0.406\ T) \times 10^{-6} \quad (17)$$

For T (°C) and μ (gm/cm-sec).

A rigorous algorithm for the calculation of the viscosity of a gas mixture in terms of its components has been given by Wilke (1950). A simplified version for combustion gases has been adapted by Williamson (1983). The simplified version is as follows:

$$\mu = C_1 + C_2 T + C_3 T^2 + C_4 F_{H_2O} + C_5 F_{O_2} \quad (18)$$

μ = gas mixture viscosity (micropoise),

F_{H_2O} = stack gas moisture fraction (by volume),

Fo_2 = stack gas oxygen fraction (by volume),

T = absolute temperature of the gas mixture (°R) and for T in °R, the coefficients are as follows:

C_1 = 51.05, C_2 = 0.207,

C_3 = 3.24×10^{-5}, C_4 = -74.14, C_5 = 53.15.

6.1.7 PERFORMANCE CRITERIA

The Reynolds number, Re, is given by Equation 2-1. In this section the symbol i will be used to represent jet velocity, not stack gas velocity. The $i\,D_{50}$ criteria has units of μm m/sec. The D_{50} is given by Equation 4-13 for units of cm. This value must be multiplied by 10^4 μm/cm to obtain the needed units for the $i\,D_{50}$ product. The stage jet velocity (i_i) is the velocity at each of the jets on stage i and is given by Equation 4-20 below:

$$i_i = K\,(P_s/P_i)\,(Q_A/n_iA_i) \qquad (19)$$

where:

P_s = Pressure at the inlet to the impactor. This is the same as the stack pressure (Eq. 4-6),

P_i = Pressure at the inlet to stage i (Eq. 5-23),

Q_A = Actual impactor flow rate at inlet to impactor, stack conditions,

n_i = Number of holes in stage i,

A_i = Average jet area (all jets must have the same nominal diameter) given by the following:

$$A_i = \pi\,D^2/4$$

K = A unit conversion constant

For i_i (m/sec), Q_A (ft^3/min), and A_i (cm^2), K has the value K = 4.72 (m cm^2 min/sec ft^3)

In terms of D_i (cm) we have the following:

$$i_i = 3.71\,(P_s/P_i)\,(Q_A/n_iD_i^2) \qquad (20)$$

For the above units.

6.1.8 TARGET ΔH

The target ΔH control parameter (ΔH) is given below. The development of this equation is described by Aldina and Jahnke (1979) in Appendix C of EPA 450/2-79-006 “APTI Course 450 Source Sampling for Particulate Pollutants-Student Manual,” December 1979.

$$\Delta H = [846.72\,D_n^4\,\Delta H_@\,C_p^2\,(1 - B_{ws})^2\,\frac{M_dT_mP_s}{M_sT_sP_m}]\,\Delta P \qquad (21)$$

where:

ΔH	=	Target ΔH control parameter (inches H_2O),
D_n	=	Nozzle diameter (inches),
C_p	=	Pitot tube coefficient, Type "S" or standard (dimensionless),
B_{ws}	=	Stack moisture fraction as defined above,
M_d	=	Mean molecular weight, dry, of the stack gas, as defined above,
M_s	=	Mean molecular weight, wet, of the stack gas at the pitot, as defined above,
T_m	=	Average absolute temperature of the dry gas meter (°R = °F + 460),
T_s	=	Average stack temperature for this traverse region (°R = °F + 460),
P_m	=	Absolute pressure at the dry gas meter (inches Hg) as described below,
P_s	=	Absolute pressure at the stack (inches Hg) as given by equation 4-6,
ΔP	=	Average pitot pressure drop for this traverse region,
$\Delta H_@$	=	Orifice meter calibration constant, defined as the ΔH which yields 0.75 cfm at 528°R, 29.92 inches Hg, and M_d = 29.00.

Further explanation is given by the following:

$$P_m = P_{bar} + \frac{\Delta H}{13.6} \qquad (21)$$

for ΔH in inch H_2O, P_m and P_{bar} in inches Hg

Note: Here we have a term which is dependent on ΔH itself. To be rigorous we would need to iterate until a convergence requirement is satisfied. To do this one would calculate ΔH_1 using an assumed initial value of ΔH_0 = 1.75, use ΔH_1 to calculate P_m and a new ΔH_2, test for convergence then continue iterating until convergence is obtained. In practice, however, this is not necessary because of the small range of ΔH values (.1 + 5) and the 13.6 divisor. This type of iterative approach will be required for other

calculations such as the D_{50} equation and its dependence on the Cunningham correction factor.

Note: For impactor operation a Target ΔH control parameter (ΔH) is calculated for each traverse region using the average velocity for the respective regions (i_{sk}). The above equation was originally intended for calculation of a ΔH for isokinetic sampling at each point in the traverse. Adaptation of this equation to impactor operation (where a constant flow rate is maintained throughout the run) is accomplished by the following equation:

$$\overline{\Delta P_k} = \left(\frac{1}{j}\sum_{i=1}^{j} \sqrt{\Delta P_i}\right)^2 \qquad (23)$$

for all points in region k

thus we have average the square roots of the pitot pressure at each point then square this value.

The basic orifice equation is given below. The development of this equation is described in Appendix C of EPA 45012-79-006 "APTI Course 450 Source Sampling for Particulate Pollutants-Student Manual", December 1979.

$$Q = K\left[\frac{T\Delta H}{PM}\right]^{1/2} \qquad (24)$$

Where Q is the actual flow rate through the orifice, T and P are the absolute temperature and pressure of the gas passing through the orifice, M is the mean molecular weight of the gas and K is a proportionately constant determined by calibration. The value of K is dependent on geometry and choice of units.

Method 5 expresses the calibration constant in terms of $\Delta H_@$ where $\Delta H_@$ is defined to be the pressure drop across the orifice which would result in a flow rate of 0.75 ft^3/min for dry standard air at 68 °F (528°R), 29.92 in. Hg, and mean molecular weight of 29.0, thus in terms of K

$$\Delta H_@ = \frac{0.9244}{K^2} \qquad (25)$$

Orifice calibration procedures are described in Section 4.6.4 which yield $\Delta H_@$ values for each orifice.

6.1.9 TRAVERSE POINT DWELL TIME

Velocity weighted dwell times are not recommended since all points in any given region are within ±20% of the sampling velocity (Section 4.5.3.A.4). Equal dwell times are

used for all traverse points in a given Region. Thus the dwell time (t) for each traverse point in a given region is obtained from

$$t = e/n \qquad (26)$$

where e = Total Run Time (min),
n = number of traverse points in a given Region.

6.1.10 AVERAGE GAS METER TEMPERATURE, AVERAGE EMISSION GAS TEMPERATURE, AND AVERAGE ORIFICE PRESSURE DROP (ΔH)

The average dry gas meter temperature, flue gas temperature, and orifice pressure drop (ΔH) are calculated using the form shown in Figure 4-7. Figure 4-9 shows example data. The average inlet dry gas meter reading and the average outlet dry gas meter reading are used to determine the average dry gas meter temperature.

6.1.11 DRY HAS METER VOLUME AND LEAKAGE CORRECTION

The sample volume measured by the dry gas meter (DGM), V_m, must be corrected to normal (or engineering standard) conditions, V_m (std), (68°F, 29.92 in. Hg) by the following equations:

$$V_m\,(std) = 17.64\,(P_m/T_m)\,V_m Y \qquad (27)$$

where

P_m = Absolute pressure at the dry gas meter (inches Hg) as given by Equation 4-22

T_m = Average dry gas meter temperature (°R = °F + 460) as calculate on the run sheet,

Y = Dry gas meter calibration constant,

V_m = Actual sample volume as measured by the dry gas meter (ft^3). Final DGM reading minus initial DGM reading.

If the post-test hot leak check with the sampler removed shows a leak rate in excess of either 4% of the impactor flow rate or 0.02 ft^3/min then the run should be rejected. If the leak is less than this value no volume correction is required. If the leak test with the sampler in place showed a leak in excessive of 10% of the impactor flow rate the run is rejected. If the leak is less than the 10% limit (and the “sampler removed” test is less than the limit above) no correction is required because the flow calculated by the dry gas meter reading is correct.

6.1.12 VOLUME OF WATER VAPOR

The total moisture catch from the condenser and drying column is calculated on the Run Sheet at position U2 as shown in Figure 4-7 (see also Section 4.5.3.D.5 Instruction for Using the Run Sheet). The Total Volume H_2O (V_{lc}) in mL is converted to vapor equivalent by the following equation:

$$V_w(std) = \left[(\rho_w / M_w)(RT_{std} / P_{std})\right]V_{lc} \quad (28)$$

$$V_w(std) = K_2 \, V_{lc} \quad (29)$$

where: K_2 = 0.04707 ft^3 water vapor (at 68°F, 29.92 in. Hg) per mL liquid water.

6.1.13 MOISTURE CONTENT

The moisture content (B_{ws}) is calculated by the following:

$$B_{ws} = V_{w(std)} / \left(V_{m(std)} + V_{w(std)}\right) \quad (30)$$

6.1.14 ACETONE BLANK CONCENTRATION

Acetone is used to washdown the nozzle, precollector, and connecting tube. This washdown liquid/particulate solution is then evaporated, desiccated and weighed. This weight includes both the weight of the particulate removed by the washdown and the residue (impurities) of the solvent used to perform the washdown. To determine the weight of the particulate alone, we mut correct for the residue present in the washdown solvent. The acetone blank concentration (C_a) is used to make this correction. By measuring the volume of the acetone used to perform the washdown and applying this residue concentration factor (C_a), we can determine the weight of the residue and subtract this number from the total weight change to determine the weight of the particulate alone.

Approximately 200 mL of the acetone used for washdown is placed in a beaker labeled "Acetone Blank". This solvent is then measured (volume or weight), evaporated, desiccated, and weighed. The acetone blank residue concentration, C_a (units of mg residue per mL liquid acetone) is then calculated from the following:

$$C_a = m_a / (V_a \rho_a) \quad (31)$$

where m_a = mass of residue of acetone blank after evaporation and desiccation (mg),

V_a = Volume of acetone blank (mL),

ρ_a = Density of acetone liquid (mg/mL). Used to convert between liquid volume and liquid weight. Specified by manufacturer on bottle's label.

Note: Acetone used for washdown must be stored in glass bottles. C_a is calculated for each separate bottle. For acetone to be acceptable as a washdown solvent the following criteria must be met:

$$C_a \times 100\% < 0.001\% \quad (32)$$

6.1.15 % ISOKINETIC

Calculation of % Isokinetic is the same as with Method 5/17 except that volume corrections are not made for measured leak rates and the average velocity is the average for a given region. This equation is as follows:

$$I = \frac{T_s V_{m(std)} P_{std} 100\%}{T_{std} \upsilon_s \theta A_n P_s 60(1 - B_{ws})} \quad (33)$$

$$= K_4 \frac{T_s V_{m(std)}}{P_s \upsilon_s A_n \theta (1 - B_{ws})} \quad (34)$$

where

K_4 = 0.09450 for English units given below,

T_s = Absolute Stack Temperature (°R = °F + 460),

$Vm_{(std)}$= Dry Gas Meter Volume (ft^3) corrected to 68°F, 29.92" Hg as given by Equation 4-27,

P_s = Absolute Stack Pressure (in. Hg) as given by Equation 4-22,

υ_s = Average stack gas velocity (ft/sec) for this Region. The average of the point velocities for all points in this region, Equation 4-7,

θ = Total Sampling time (minutes),

B_{ws} = Stack moisture fraction (given by Equation 4-30) for this run,

100% = Conversion factor to percentage,

60 = Conversion factor, 60 sec per minute,

A_n = Cross sectional area (ft^2) of the circular nozzle given by:

$$A_n = \pi d^2 / (4 \times 144) \quad (35)$$
$$= 0.005454\ d^2$$

for d = nozzle diameter (inches),
144 = conversion factor, 144 in^2/ft^2.

6.1.16 ACETONE WASH RESIDUE

The weight of residue from the acetone used to perform a washdown must be subtracted from the evaporated/desiccated weight in order to determine the true weight of the particulate removed by the washdown procedure. The weight of the residue is referred to as the acetone wash blank, W_a (mg), and is calculated by the following:

$$W_a = C_a V_{aw} \rho_a \tag{36}$$

where

C_a = Acetone blank residue concentration as given by Equation 4-31 (mg residue/mL liquid acetone),

ρ_a = Density of acetone liquid (mg/mL). Used to convert between liquid volume and weight of liquid,

V_{aw} = Volume of acetone used to perform the washdown (mL).

This residue weight contribution (W_a) is then subtracted from the washdown evaporated/desiccated weight. In no case shall a blank value (W_a) greater than 0.001% of the weight of the acetone used for a washdown ($V_{aw}\rho_a$) be permitted (i.e., $C_a \times 100\% < 0.001\%$).

With an impactor precollector two separate washdowns are performed (1) nozzle, body of precollector, and brush and (2) exit tube of precollector, connecting tube, and brush.

6.1.17 TOTAL PARTICULATE WEIGHT AND BLANK WEIGHT CORRECTIONS

If the blank impactor run shows reproducible weight changes, corrections may be calculated to be applied to the measured stage weight gains. If the weight changes are not reproducible, alternate substrate materials should be selected. Consider the set (w_i) consisting of all weight changes for substrates from the Blank Impactor run together with the weight change for the Blank Substrate from each real run. If the range of this set is less than $\pm$ 0.25 mg the set may be considered reproducible and the average for this set should be applied as a correction to all the weight sheet records. Separate blank corrections are determined for the filter using the weight change values from the two filters in the blank impactor run together with the blank filter in each of the real runs. The corrections (substrate and filter) are calculated as follows:

Calculate the average:

$$\overline{w} = \frac{1}{n}\sum_{I} w_i \qquad i = I, n \tag{37}$$

for w_i = Final Weight (mg) – Initial Weight (mg).

Test for Reproducibiltiy:

$$\overline{w} - c \langle w_{min} \langle w_{max} \langle \overline{w} + c \tag{38}$$

where c = 0.25 mg or 10% of the stage catch of the most lightly loaded substrate in real runs; which ever figure is smaller.

If Equation 4-38 is satisfied for the set of all blank substrates (filters) the new weight change ($\Delta m'_i$) is calculated as follows:

$$\Delta m_i' = \Delta m_i - \overline{w} \tag{39}$$

where Δm_i is the weight change for a substrate (filter) and $\overline{w}$ is as calculated by Equation 4-37 for the appropriate set. One for the substrates and a different correction factor for the filters.

If the values from the blank runs are reproducible but individual runs violate the criteria of Equation 4-38 the outlier tests described in Section 5.4 may be used to selectively reject individual runs. Note that the data from such runs may include substrates where the blank weight change is a small percentage of the change for any given substrate. In such cases, we need only reject those substrates where the blank change exceed 10% of the weight change for this substrate.

The total particulate weight may be calculated by summing all corrected catch weights (precollector, collection stages, filter) and the washdown weights (corrected for the respective wash blanks, W_a).

6.1.18 PARTICULATE CONCENTRATION

The stack loading or particulate concentration is calculated from the following:

$$C_s = (0.001\ g / mg)(M / V_{m_{(std)}}) \tag{40}$$

where

C_s = Particulate concentration, dry basis, connected to dry standard conditions (g/dscf) for the above equation,

M = Total particulate weight (mg),

$Vm_{(std)}$ = Dry gas meter volume (ft^3) corrected to standard condition (68°F, 29.92 in. Hg).

Note: The dry gas standard particulate concentration, C_s may be expressed in different units (the same symbol, C_s is used). Common units for C_s are grains per dry standard cubic foot (gr/dscf), pounds per dry standard cubic foot (lb/dscf), and grams per dry normal cubic meter (g/dncm). Conversion factors are as follow:

From	To	Multiply By
ft^3	m^3	0.02832
g	gr	15.43
g	lb	2.205×10^{-3}
lb	gr	7,000
g/ft^3	g/m^3	35.51
gr/ft^3	gm/m^3	2.288
lb/ft^3	gm/m^3	1.602

The particulate concentration may also be expressed in terms of actual stack conditions, wet. The volume $V_{m(std)}$ must be converted to stack conditions and the moisture fraction taken into consideration as follows:

$$Vm(A) = \left[T_s / (17.65\ P_s)\right]\left[V_{m(std)} / (1 - B_{ws})\right] \quad (41)$$

$$G_A = (0.001\ g/mg)\ (M/V_{m(A)}) \quad (42)$$

where

G_A = Particulate concentration at actual, wet, stack conditions (g/dscf),

$V_{m(A)}$= Volume of the dry gas meter (ft^3) expressed as actual wet stack gas sampled through the impactor, stack temperature (T_s, °R), stack pressure (P_s, in. Hg) and stack moisture content (B_{ws}),

17.65 = 528°R/29.92 in. Hg,

M = Total particulate weight (mg) Section 4.7.17.

Note: The wet actual particulate concentration, G_A, may be expressed in different units (the same symbol, G_A, is used). Common units for G_A are grains per actual cubic foot, wet (gr/acf), pounds per actual cubic foot, wet, (lb/acf), and grams per actual cubic meter, wet (g/acm).

6.1.19 STAGE CUT POINTS

Section 5 (Data Reduction and Analysis Procedures) gives the equations used to calculate the Stage Cut Points. Section 4.7.6 gives the D_{50} equation (Equation 4-13). Figure 4-5 shows the D_{50} for various stages of the Pollution Control Inc. University of Washington Mark 5 Impactor at 300°F for dry air at various flow rates. Equation 4-13 in Section 4.7.6 (Hardware Selection) also gives the D_{50} equation. Optionally, the calculations may be performed by the computer programs described in Appendix A.

6.2 DATA FORMS

Data forms used with cascade impactors include Method 2 velocity profile forms (Figure 5 of Method 2), the manual version of the run sheet (lab and field) as shown in Figure 6 and 7, and the weight sheet shown in Figure 11. A run sheet form for use with the computer programs is given in Manual Appendix A, Figure 1. The weight book consists of the completed weight sheet forms (one for each substrate set) together with the balance record book (chronological record of setup checks, zero's, repairs, etc.), controls weight sheet (date, time, and weight values for control A, B, D, and D), and tares "weight sheet" (date, time, and weight values for tares used).

Calibration forms include Figure 12 for nozzles, and Figure 8 of Method 5 for dry gas meter and orifice calibrations using a wet test meter. Manual, Appendix C includes figures which may be used as photocopy masters for all of these forms.

A central record of calibration data and equipment maintenance records should be maintained separately. Appropriate copies should be made from records in this central file and stored with the field test data sheet. A bound notebook providing a chronological record of what happened during a test should also be maintained. This is used to prevent potentially important information from being lost or forgotten. This notebook becomes a part of the permanent test records. It is usually maintained by the leader of the test crew. Files should also be maintained for "other forms" such as velocity traverses, flue gas composition measurements, barometric pressure readings, reports of post-test measurements such as flue analysis (ultimate and proximate for coal, etc.), physical density by helium pycnometer, Bahco particle size analysis of bulk fly ash samples, etc. Other files may be needed for plant data records (load conditions, product feed rates, etc.) and for data reduction computer printouts. Computer printouts to set-up parameters are normally filed with the appropriate run sheets. Data reduction printouts include printouts of both input data and outputs such as tabulated data and graphs. Computer programs often evolve or are modified for various reasons, so it is advisable to maintain diskettes (computer storage media) of both input data and source listings of the data reduction routines so that future questions about "which version of the program was used" may be easily answered.

In summary, the field test data records can be divided into seven sections as follows: (1) chronological record, (2) run sheets (run side and lab side), (3) weight records, (4)

calibration and maintenance records, (5) other forms, (6) plant data records, and (7) computer printouts and diskettes.

6.3 REPORTING REQUIREMENTS

Any written reports should include all the appropriate sections used in a report from a Method 5 test such as a description of the plant process, sampling port locations, control equipment, fuel/feed stocks being used, general plant load conditions during the test (descriptions of plant production equipment problems, etc.), and anything else necessary to characterize the condition being tested.

All raw data (weight sheets, run sheets, calibration records, velocity profile data) should be listed in an appendix to the report and the following outputs should be given in a graphical form (tabulated form should be included in the appendix) for the average from multiple runs: (1) Plots of cumulative percent vs. aerodynamic diameter and (2) plots of dM/dLogD vs. aerodynamic diameter, and (3) plots of cumulative concentration vs. aerodynamic diameter.

Additional information may be required for any given project. The information listed above is to be considered as the minimum amount that should be included to characterize a given operating condition.

6.4 COMPUTER PROGRAMS

Most of the calculations outlined in this report can be performed by the optional set of computer programs given in Manual, Appendix A. This appendix includes complete documentation, operating instructions, and illustrations for the computer programs.

7. QUALITY ASSURANCE AND CONTROL

7.1 ACCEPTABLE RESULTS

The following criteria are used to determine the acceptability of test results.

7.1.1 GENERAL TEST CRITERIA

7.1.1.1 BLANK IMPACTOR GAINS

Blank Impactor Gains: A blank impactor run is mandatory in order to demonstrate the suitability of the selected substrate material. The maximum recommended range (deviation from the average) in the substrate weight changes for this blank run is 0.25 mg.

7.1.1.2 MINIMUM NUMBER OF RUNS

Minimum number of runs: It is recommended that seven (7) sets (multiple runs synthesizing a complete traverse) be performed. The minimum number of sets that may be used to characterize a condition is three (3).

7.1.2 CRITERIA FOR INDIVIDUAL RUNS

7.1.2.1 REPRODUCIBILITY OF CONTROL WEIGHTS

Reproducibility of Control Weights: The control weights used in the operation of the analytical balance should be reproducible to within ± 0.05 mg. The precision associated with the stage weight gains is determined by the reproducibility of the control weights.

7.1.2.2 REYNOLDS NUMBER LIMIT

Reynolds Number Limit: The combination of selected jet stage and impactor flow rate must be such that Reynolds numbers are greater than 50. Reynolds numbers greater than 200 are desirable.

7.1.2.3 BOUNCE PREVENTION

Bounce Prevention: The combination of selected jet stage and impactor flow rate must be such that the product of the jet velocity (v) and aerodynamic stage cut point (D_{50}) does not exceed the following values: for bare metal substrate, 5 um-m/s; for fiber mat substrate, 15 um-m/s; for greased substrated, 25 um-m/s.

7.1.2.4 IN-SITU SAMPLING

In-Situ Sampling: Extractive sampling into an impactor is not permitted, even when heat traced lines are used and the impactor is placed in a heated oven. The nature of the problem is that excessive particulate losses occur in extractive probes. The ability of an extractive probe to remove particles of a given size is dependent on flow rate, tube diameter, number of bends, and a host of other factors. Size selective losses occurring in the probe invalidate the data from the impactor.

7.1.2.5 STRAIGHT NOZZLE

Straight Nozzles: Only straight nozzles may be used. Method 5 type goose neck (button hook) or other 90° bend nozzles may not be used. The impactor must either be rotated into the gas stream so that a straight nozzle can be used or a right angle precollector should be used to permit the impactor to be operated perpendicular to the direction of the gas flow.

7.1.2.6 MINIMUM NOZZLE DIAMETER

Minimum Nozzle Diameter: The primary problem associated with the use of small nozzles is pluggage of the nozzle by large particles. For this reason, 1.4 mm is recommended as a particle minimum nozzle ID. In practice, however, a smaller nozzle may be used if one is willing to accept the increased risk of a nozzle pluggage. A secondary problem may be a shift of the D_{50} of the entry stage to the system (i.e. precollector or the first impactor stage depending upon the configuration).

7.1.2.7 IN-SITU HEATING

In-Situ Heating: If the stack temperature is above 347°F (175°C), sampling may usually be performed at stack temperature. At stack temperatures less than this limit, it may be necessary to heat the impactor to at least 18°F (10°C) above the stack temperature by the use of external heaters wrapped around the impactor. The decision to externally heat the impactor depends primarily on the properties of the flue gas. Thus, high moisture stacks or high SO_3 levels may require in-situ heating of the impactors. The postrun visual examination of the impactor substrates will indicate the presence or absence of condensation problems.

7.1.2.8 WARM-UP REQUIREMENT

Warm-Up Requirements: Warm-up times should be 45 minutes to one hour. Shorter times may result in condensation occurring on various surfaces of the impactor.

7.1.2.9 MINIMUM RUN TIME

Minimum Run Time: The shortest permissible run time is 60 seconds. A desirable minimum run time is three minutes. If high loadings require run times shorter than 60 seconds, a lower flow or different sampling device should be used if possible. Great care must be taken when operating with such short run times.

7.1.2.10 LEAK TESTS

Leak Tests: The impactor must satisfy both the pre-test hot leak test criteria and the post-test hot leak test criteria given in Table 1.

7.1.2.11 ANISOKINETIC SAMPLING LIMITS (POINT)

Anisokinetic Sampling Limits: At each traverse point sampled during a given impactor run, the point velocity (v_i) must be within ± 20% of the inlet velocity (v) for the impactor, thus $.8v \leq V_i \leq 1.2v$.

7.1.2.12 NOZZLE INSPECTION

Nozzle Inspection: The nozzle must pass the post-test nozzle damage visual check.

7.1.2.13 SUBSTRATE INSPECTION

Substrate Inspection: When the impactor is unloaded, the stage catches are inspected to see if overloading, scouring, bounce, condensation, handling losses, etc., have occurred such that the data are compromised or invalidated.

7.1.2.14 ISOKINETIC REQURIEMENT (RUN)

Isokinetic Requirements: The calculated % Isokinetic (I) for a given run must satisfy the following:

$$75\% \leq I \leq 125\%$$

(as calculated by Equation 34).

7.1.2.15 MAXIMUM STAGE LOADINGS

Maximum Stage Loadings: Excluding the precollector and filter, the individual substrate catch should not exceed 15 mg. If this limit is exceeded one runs a risk of overloading the substrate. The actual point where overloading occurs depends on the design of the impactor used, the type of substrate material selected, and the properties of the material collected. The postrun visual examination is the best check for overloading. Other tests include unrealistic filter weight changes and microscopic examination of the filter and substrates for the presence of grossly oversized particles.

7.1.2.16 BLANK SUBSTRATE WEIGHT CHANGES

Blank Substrate Weight Change: The recommended range in weight changes for the blank substrate is 0.25 mg (or 10% of the expected weight change for the loaded substrates). The weight change of the blank substrate provides a cumulative measure of all balance errors (drift in the analytical balance), handling losses, flue gas-substrate interactions, etc., that might affect the weight change determinations for an impactor run. The change for each run should be compared to the grand average of all other blank substrates ("blank" impactor run and blank substrate from each real run). Any given run is suspect if its change is significantly different (an outlier) from this grand average. Any temporal variations in the substrate flue gas interactions can be detected by use of the blank substrate in each run. The outlier tests described in Section 5.4 may be used to reject individual runs.

7.1.2.17 BLANK FILTER WEIGHT CHANGES

Blank Filter Weight Change: Some criteria as above except that the criteria are applied to the set of all blank filter weight changes rather than the set of all blank substrate weight changes.

7.2 SPECIAL CONSIDERATIONS

There are a number of problems inherent in cascade impactor sampling which could result in the invalidation of whole sets of data. The intent of this section is to outline measures, which if integrated into standard impactor operating procedures, would reduce these potential errors to acceptable levels.

7.2.1 PRETEST SITE SURVEY

Some prior knowledge of the test site and flue gas conditions is required for efficient test preparation. One method of obtaining the necessary information is a pretest site survey by one or two experienced individuals.

The goal of the survey is to gather information needed by the sampling crew for adequate planning of the test. The minimum data required are the identification of special or unusual problems so that work can begin on tasks which must be completed prior to testing (such as installation or enlargement of ports). Usually, the more complete the survey, the more efficient and worthwhile the testing will be.

In cases where the sampling crew is unfamiliar with both the site and the type of process stream to be sampled, data concerning the process itself should be collected during the pretest survey. It is important to ensure that enough information is available so that sampling can be performed under typical operating conditions, particularly if a batch or cyclical process is to be tested or if the source is occasionally operated in an anomalous mode. Other important plant information includes availability of facilities and supplies such as electrical power, water, ice, and laboratory space. An additional aspect of the plant survey which must not be neglected is a thorough safety inspection.

In addition to the plant data mentioned above, a site survey should include careful annotation of gas stream conditions expected at the sampling points. Information concerning gas temperature, pressure, composition, and approximate particulate loading will be needed to select the optimum equipment and sampling strategy. If possible, an impactor should be operated during the survey to identify potential problems. Such a test can be valuable in the determination of mass loading, proper sampling duration, and collection substrate and impactor suitability.

The precision of testing performed during a survey should not be expected to equal that of the actual test, but it should be close enough so that problems that might be encountered in the actual test can be anticipated from the results of the survey. This will make decisions regarding the correct equipment and techniques possible. If a pretest survey is not possible, it may be necessary to use the first impactor runs of the test series as "trash" runs to provide information for the proper setup of the remaining test runs.

In situations where the source is of a type previously tested and sampling conditions at the site are familiar to the sampling team, only a site inspection may be needed. This

visit should be made by a member of the sampling team who should establish contact with plant personnel, inspect sampling ports for size, location, and suitability, request needed items or work (such as port enlargement or replacement, sampling platforms, laboratory space, and electrical power), and identify sources of possible problems. Port size, port extension, inside duct dimensions, and port adapter configuration can be determined with a tape measure. Generally, the pretest site inspector should look for unusual problems or circumstances that will need attention before the test date.

7.2.2 CYCLIC PROCESSES

As previously mentioned, cyclic processes can introduce greater difficulty into a sampling program. The test procedure should be planned and coordinated with plant personnel so as to span an integral number of process cycles, if possible.

7.2.3 SUBSTRATE COLLECTION SURFACE

Extensive studies of substrate media have shown that suitable substrates exist for most applications if caution is exercised in selection and use. It should be noted that impactor calibration and performance depend upon the type of substrate used and that calibration is required for each type. Also, the stability of the substrate should be checked in each gas stream being sampled. Both greases and glass fiber mats typically experience anomalous weight changes when exposed to stack gases.

The pretest survey should include a series of blank impactor runs to aid in the selection of the substrate material. A good rule of the thumb is that the maximum allowable change in weight of the blank substrate should be no more than 10% of the mass of the particulate matter that is expected to be collected on the impactor stage collecting the least mass. In most instances, a blank substrate weight change of 0.25 mg is excessive. Reproducibility of blank weights is of greater concern that the absolute magnitude of the change. If the changes are reproducible, corrections for them can be made to the data with confidence that valid results will be obtained.

7.2.4 IMPACTOR JET STAGES

Most commercially available impactors come with a fixed set of stages which are used at all times and no decision as to which stages to use is required. However, in some cases, most notably the University of Washington Mark V impactor, a variety of jet stages are available and those most suited to the sampling conditions to be used.

A trade-off exists between three major condiserations when choosing jet stages. Because of the non-ideal behavior of jet stage efficiency curves, a separation should not be smaller than about a factor of 1.5. Excessive jet velocities can result in low Reynolds numbers and uncertainty in the value of the impaction perameter.

If data regarding a particular particle diameter are desired, the cutpoint of two stages should bracket this diameter for reliable interpolation of the mass less than this

diameter. If the target diameter is large, the cutpoint of the largest stage should be as close to the desired diameter as possible to reduce extrapolation errors.

7.2.5 SMALL NOZZLE SIZE

The particle size cuts of cyclones and impactors are dependent on a number of factors. Other than the selection of stages, the sampling flow rate is the only variable affecting the cut sizes which can be adjusted by the user. If a multi-stage device is used to measure the complete size distribution, some latitude is available in setting the flow because interpolation can be used to determine the concentration of particles in any designated size range within the operating limits of the sampler.

If a given stage is required to produce a stated size, say 10 um, the sample flow rate required to obtain that cut will be dictated by the sampler used (given the gas composition and temperature of the process stream being measured). This means that if a cut at a specified target diameter must be obtained, one may not have the latitude in selecting the sampler flow to be used that one has in simple total particulate measurements or even for standard impactor runs. The matching of the sample inlet velocity with the gas stream velocity for isokinetic sampling must be accomplished entirely through the cross-sectional area of the sampling nozzle. This means that a much larger array of nozzles must be available than those used in Method 5 sampling. If the isokinetic error is no larger than 20%, the maximum error in the measured emission rate of 10 um particles will be about 15% and the errors for smaller particles will be lower. Errors for large particles will be approximately equal to the isokinetic error. Deviations of 20% from iskonetic can probably be tolerated. If sampling is to be done within 20% of isokinetic, an array of nozzles must be available that step by 10% in diameter from one to the next.

Once the flow rate is determined, it can be used with the gas velocity to select the appriproate nozzle to use. Only straight nozzles should be used as “gooseneck” or bent nozzles will, in most cases, severly perturb the results.

If there is no requirement for a specific size cut as may be required in PM_{10} sampling, the operator has more flexibility to choose a flow rate suitable to the requirements of his sampler and the particulate loading of the gas stream. Typically the average velocity of the points to be traversed is determined using EPA Method 2. Next a nozzle is selected whose isokinetic flow rate at this average velocity is judged to be suitable for the particular site and impactor. The flow rate determined in this way is maintained at all sampling points on the traverse. If the velocity distribution is poor, several runs may have to be made, each covering a part of the duct, to synthesize a complete traverse.

The flow rate mentioned above is considered to be suitable for a particular impactor if it falls within the recommended operating limits of the impactor and restricts bounce and reentrainment of particles.

Studies have been conducted which have supplied the following operating criteria which, if met, may be expected to yield acceptable impactor samples:

1. If bare metal substrates are used, the vD_{50} products should not exceed 5 um•m/s.

2. If glass or quartz fiber substrates are used, the vD_{50} products should not exceed 15 um•m/s.

3. If greased substrates are used, the vD_{50} products should not exceed 25 um•m/s.

4. The spacing between the D_{50}'s of adjacent stages should not exceed a factor of about 2.5. If this spacing is exceeded, particles having momenta too high for reliable collection will be passed to the succeeding stage.

5. Operation at flow rates which result in very low Reynolds numbers should be avoided.

These are very generalized guidelines and should not be considered as hard and fast rules for all situations. The properties of the particles (e.g., hard dry particles or sticky particles) may dictate some modification of these criteria. An impactor run during the pretest site survey is recommended to properly assess these considerations.

The time required to collect an adequate sample depends on the mass loading of the aerosol, the size distribution of the particles, and the gas flow rate in the sampler. If the results of a mass test are available, the mass loading can be obtained from them. If not, an estimate should be made based on the pretest survey or other information. Given the mass concentration, an estimate of the sampling time for initial tests can obtained from nomographs. Results from the initial tests can then be used to more accurately establish the optimum sampling time.

The amount collected on each stage also depends on particle size distribution. If the flue gas contains mostly large particles, the precollector and upper stages of the impactor will contain more particulate matter than the filter or the lower stages. Two conflicting criteria complicate the choice of the sampling time. It is desirable, for minimizing weighing errors, to collect several milligrams on each stage, however, most size distributions are such that the upper stages are overloaded and particles become entrained before the lower stages collect as much as a few milligrams. A rule of thumb is that no stage should be loaded above 15 mg, but the determining factor is whether or not reentrainment occurs. The deposit on each stage must always be visually observed to judge the "quality" of the deposits and the appropriate sampling time.

7.2.6 CALIBRATIONS

In most projects involving impactor sampling, the accuracy, precision, and comparability of gas volume and flow rate measurements are critical to the project data quality

objectives. For this reason the flow metering system of each sampling train should have dependable calibrations. A pretest calibration check of the dry gas meter and orofice, using the procedure outlined in EPA Method 5 for post test calibration checks, is suggested but not required. This is especially true if the system has not been used for an extended period of time.

The type S pitot tube should be calibrated prior to testing according to the procedure in Method 2. All temperature sensors in the system should be checked for proper calibration using the procedures outlined in Method 5.

7.3.7 ON SITE OPERATIONAL CHECKS

There are a number of in-field checks of the sampling system that can be performed to ensure the quality of data collected. Although the procedures outlined below cannot detect all possible problems, the suggestions listed can help eliminate several sources of error. One operational check that should never be neglected is a leak check of the entire sampling train. This is best done in three steps: the assembled collection device only, the sampling train without the collection device, and the sampling train with the collection device mounted on the probe.

The procedure to leak check the impactor should be performed after the impactor is loaded and assembled. If a precollector is to be used, this should be attached to the impactor and the whole assembly leak checked as a unit. The inlet to the collection device should be plugged and the outlet attached to the suction side of a small pump. The vacuum side of a mercury manometer or vacuum guage should be connected in parallel to the impactor with the positive pressure side open to ambient. The pump valving should be adjusted until the manometer registers a vacuum of approximately 11 inches Hg. The impactor should then be sealed off. Field use of this leak check procedure has indicated that impactor assemblies experiencing pressure losses of less than 5 to 6 inches Hg in 60 seconds generally pass the EPA leak check criterion when checked with the entire sampling train. More significant leaks should be corrected. To prevent rupturing the impactor backup filter, the vacuum should be released at the sample nozzle.

It should be noted that the intent of this leak check procedure is not the elimination of every leak, but rather the detection of major problems such as missing o-rings. Small leaks are tolerated in this test because they do not significantly affect the quality of the impactor data. This is true for two reasons. First, the volume of the impactor is so small that a 60 second pressure drop of 5 to 6 inches Hg corresponds to a flow rate well within the EPA criterion of 0.02cfm. Furthermore, most impactors are not designed to be leak tight near the inlet of the device. This is due to the fact that during operation, the pressure drop to ambient at this point is essentially zero.

A negative guage pressure leak check of the sampling train both with and without the collection device, should be performed as described in Section 5. When leak checking

the system with the impactor mounted on the probe, care should be taken to prevent rupturing the backup filter by backflow through the impactor.
An internal audit of the flow metering system is suggested as another method of detecting problems with the sampling train. To perform this system check, the metering orifice ΔH is set to achieve a desired flow rate. It is recommended that the flow rate chosen be an actual calibration point for the 1.0 orifice. This recommendation is made on the basis that, occasionally, the curve fitted to orifice calibration data introduces significant error into the flow rate determination. Given the calibration flow rate for the orifice and the dry gas meter flow rate (obtained by measuring the length of the time for an arbitrary volume, such as 2.000 ft^3, to pass through the meter) correct these two dry gas meter flow rates (calibration and audit) to standard conditions then determine their percent difference. An acceptance criterion of ±5 percent is suggested but the needs of the sampling program may dictate adjustments to this value.

Problems such as impactor leaks, impactor stage overloading, bounce or reentrainment of particles can often be detected by examining the impactor substrates as they are unloaded. Note the appearance of each stage, substrate, or cyclone in a notebook or run sheet such as was shown in Section 4. A magnifying glass or low-power microscope will be useful when examining the deposits.

The shape of the deposits will provide some indication of whether or not bounce or reentrainment occurred during the run. An acceptable velocity through the jets usually results in a well-defined, cone-shaped pile of particulate matter while an excessive jet velocity yields a diffuse deposit. In extreme cases virtually none of the particles will be collected directly under the jets. Reentrainment is also more likely to occur at higher sampling flow rates. Streaks of particulate radiating out from the deposits may indicate that blow-off occurred and clumps of agglomerated material on the inlet surfaces of the jet plates almost certainly indicate that blow-off has occurred.

In addition to visual inspection, reentrainment due to stage overloading can be detected by running two otherwise identical tests for different sampling durations. If the size distribution measured in the longer run shows a pronounced bias toward smaller particles, overloading and reentrainment should be suspected. the operator must be aware, however, that substrate weight changes due to chemical reaction will not necessarily be the same for different sampling periods. Additional blank runs may be needed to resolve any doubts caused by possible substrate reactions.

If an internal leak in the impactor occurs, it can be found by careful inspection of the internal surfaces of the impactor as it is being unloaded. An unusual deposition pattern or an unusually dirty spot near a seal is a good indication. Also, an internal leak sometimes gives results similar to those obtained from reentrainment. Internal leaks are usually caused by improper impactor assembly. If an internal leak or improper assembly is suspected, reassemble the impactor before using it. Other internal leaks may be caused by nicked or warped metal or hardened rubber o-rings.

Although the choice of substrate surface should minimize substrate weight changes caused by reaction with the flue gas, blanks should still be run to quantify this effect. Blank substrates and backup filter can be included in each impactor run made if the construction of the impactor allows. The blank substrate should be added to the impactor set just before the backup filter with the collection plate turned upside down so that the substrate surface is out of flow. The blank filter should be placed directly behind the backup filter in the impactor, separated by Teflon or Kapton gaskets from the backup filter.

Entire impactor sets can also be run as blanks. Blank runs are made by attaching a prefilter to an impactor (no precollector is necessary) and operating the assembly in the same gas stream and under the same conditions of flow rate and sampling duraction as a regular test run. The blank impactor is then unloaded and the substrates desicoated and weighed as usual. The changes in weight of the substrates in the blank run should then indicate the amount of the changes in weight (background) to be expected for the substrates in the regular test run. At least one blank run should be made each day when sampling sources where substrate weight changes may occur; in practice, this means virtually everywhere. If the blank run appears normal, the weight changes for all blank substrates of the same geometry are averaged and the average value is substracted as a background correction from the weight gains observed for the regular test runs. Relatively large weight changes can be tolerated if they are uniform and reproducible from stage to stage and from one blank run to another.

Control runs are recommended as a means of quantifying any substrate weight changes caused by faulty standard handling procedures. Although such mechanical losses are not likely to be a factor with greased foils as with fiber mats, control runs are still suggested in either case. To perform a control run, an impactor is loaded as for a regular run. The inlet and outlet are plugged and the impactor is carried to the sampling site. The impactor is not operated, but is kept at the sampling site until the actual run is completed. Then the control is carried back to the laboratory and unloaded in the same way as the impactors for the regular runs. Every aspect of the treatment of the control is the same as that of a real run except that it is not operated in the stack. If the substrate loses or gains more than an average of 0.05 mg, additional care must be taken to improve the handling and/or weighing procedures.

Prior to performing the first impactor run, the isokinetic setup table should be checked to insure that the orifice and nozzle size chosen are acceptable. The recommended lower limit of orifice pressure drop, H, is 1.0 inch of water. Smaller values of H make it difficult to adjust to the correct flow rate. In cases where a particular cutpoint is desired from the sampler, such as 10 um, the proper flow rate can be critical. In most cases, the sample flow rate for an impactor will be much smaller than the flow rate used for Method 5 or Method 17 and the orifices used in the system for these methods will be too large to provide effective flow metering. In such a situation one of the smaller orofices should be used to obtain a larger H for the same impactor flow rate.

The sample flow rate required for the near isokinetic sampling with this nozzle should also be checked to insure it falls within the suggested operating limits or the impactor and does not contribute to the occurrence of bounce and reentrainment. Improper sample flow rates can be changed if a different nozzle size is used. If changes are made in either nozzle or orifice size, a new isokinetic setup table should be calculated.

A "wet" weighing of the undesiccated substrates from the first impactor run should be made to determine approximate stage loadings. Any adjustments in run time indicated should be made in subsequent runs.

At least one post-test dry weight of each substrate should be recorded on site. If possible, second weighings should also be performed in the field. Second weighings of every substrate may be avoided by performing second weighings on a random selection of 10 to 20 percent of the substrates. If the first weight in each case is reproduced to within 0.05mg, the first post-test weighing may be accepted as the final dry weight of all the substrates.

The final dry weight change of each substrate should be corrected for any blank weight changes. The magnitude of this correction is determined by averaging the weight changes for all blank substrates of the same geometry. This average value is subtracted as a background correction from substrate weight gains for each test run.

Field data sheets should be checked during and after each run to ensure that all needed information is (or has been) recorded. Pressure in the field to complete the sampling often leads to an attitude that one can fill in information at a later time from memory—this is a very poor practice and should be avoided.

7.3 SPECIAL SAMPLING CONDITIONS

The following paragraphs discuss various special sampling situations.

7.3.1 HIGH PARTICULATE CONCENTRATIONS

Most impactors are designed for sampling at relatively low concentration outlets, downstream of particulate control equipment. Consequently many of these impactors are not suitable for sampling upstream of control equipment (inlet sampling situations) where the particulate concentrations may be as much as 10,000 times greater than at the outlet. Some impactors permit the operator to select from multiple stages, permitting the impactor to be configured for low flow rates.

7.3.2 WET STACKS AND SUPPLEMENTAL HEATING

In sampling situations where the process stream contains entrained moisture or is near dew point, one must first define the measurement objectives: (1) Characterize only the particulate to be released to the atmosphere or (2) characterize both the particulate and entrained liquid/condensibles present in the flue. If the former is desired, as is normally

the case, one must provide supplemental heating to the impactor to prevent condensation from occuring in the impactor and to reevaporate entrained liquid droplets that would be evaporated in the downwind plume. Heat is usually supplied either by a heating pad properly sized for the impactor/precollector or by lengths or electrical heating tape. Glass fiber cord or tape may be used to secure the heating devices to the precollector, connecting tube, and impactor. Insulation should then be placed around the assembly and secured. A layer of aluminum foil wrap helps keep the insulation dry and aids in cleanup.

The temperature of the gas exiting the impactor should be monitored by a thermocouple exposed to the sample gas flow immediately upstream of the final filter, but the heating elements should be controlled by a second thermocouple between the impactor and the heater. A setting should be selected for this second thermocouple that will not damage the impactor but will raise the temperature of the exit gas about 20°F above the stack gas temperature (as monitored by the first thermocouple).

7.3.3 HIGH TEMPERATURE

Most source sampling is performed at sampling sites where the gas temperature is less than 350°F, as industrial processes generally use economizers which utilize heat from the exhaust stream to preheat incoming combustion air. Consequently, the temperature of the gas exiting the stack is generally maintained at temperatures of about 300°F. These low temperatures permit the use of coated metal substrates, Viton o-rings, and Teflon inserts. When it becomes necessary to sample at temperatures where the upper limits of these materials are exceeded one must use high temperature substitutes such as quartz substrates, metal o-rings, and Kapton inserts. Also, high temperature heater tapes would need to be used in the probe rather than the more durable moisture resistant silicone insulated heater tapes. Longer pre-run warmup times may also be required.

7.3.4 TOP ENTRY PORTS

In sampling situations where the duct is horizontal and the access ports are on the top of the duct, a special adapter must be used to attach the impactor to the probe. This adapter performs two major functions: (1) it rotates the impactor 180° so that it can be operated in an upright position rather than upside down and (2) it helps prevent the filter from being backwashed by water which might condense inside the probe and drain down to the end of the probe. Probe heaters are used and the adapter is wrapped with heater tapes and insulation. A thermocouple is used to monitor the probe exit temperature. Heater tapes on the adapter and probe are maintained at sufficiently high temperatures to assure that the gas exiting the probe is well above the dew point.

7.3.5 SMALL DUCTS

Special procedures and equipment must be used in small ducts when the cross-sectional blockage of the duct by the impactor/precollector assembly exceeds 5 percent

of the duct cross section area. In such situations one should attempt to rotate the impactor into the flow and use straight nozzles, provided cross-sectional blockage for this configuration does not exceed the 5 percent limit. A second option would be to connect a long pipe nipple to the port and install a longer connecting tube to the precollector so that only the precollector body is in the gas flow, the body of the impactor being located out of flow inside the long nopple. If such a configuration is used, one should construct a special removable curved flow shield around the connecting tube between the precollector and impactor body to prevent major flow interruptions being introduced by the port opening. This can be very significant when the port diameter is a substantial percentage of the duct diameter. The long pipe nipple will need to be heated and insulated and it may be necessary to use supplemental heating on the impactor body.

7.3.6 SIZE SEGREGATED SAMPLES FOR CHEMICAL ANALYSIS

If it is desired that size segregated samples be obtained for chemical analysis, special substrate material will be necessary. It is not possible to collect bulk quantities with cascade impactors but one can collect milligram quantities that may be analyzed by using trace element techniques such as x-ray analysis and Neutron Activation Analysis (NAA). Special substrates and filters must be used which give very low background signature for the elements desired. The polypropylene polymers substrate coatings, and quartz filters provide relatively clean signatures.

8 REFERENCE AND LIST OF CASCADE IMPACTORS

Reference

"Recommended Methodology for the Determination of Particle Size Distributions in Ducted Sources," Southern Research Institute, May 1986 (ARB Contract No. A3-092-32).

LIST OF CASCADE IMPACTORS

Mark III Impactor
Andersen Samplers Division of
Andersen Group
4215 Wendell Drive
Atlanta, GA 30336

Model 1502 (MRI) Impactor TransTechnology
Belfast Instrument Co.
Subsidiary of TransTechnology Corp.
727 South Wolfe Street
Baltimore, MD 21231

Mark III and Mark IV Impactors

Flow Sensor Division of
Andersen Group
4215 Wendell Drive
Atlanta, GA 30336

Mark III and Mark V Impactors
Pollution Control Systems Corp.
4530 Union Bay Place, N.E.
Seattle, WA 98105

Model 226, 228, and 2210 Impactors
Sierra Instruments Division of
Andersen Group
4215 Wendell Drive
Atlanta, GA 30336

Brink Model C Impactor
Zoltek Corporation
3101 McKelvey Road
St. Louis, MO 63044

APPENDIX L

AASI LABORATORY ACCREDITATION

STATE OF LOUISIANA
DEPARTMENT OF ENVIRONMENTAL QUALITY

Is hereby granting a Louisiana Environmental Laboratory Accreditation to

Ambient Air Services Inc
106 Ambient Airway
Starke, Florida 32091

Agency Interest No. 100329

According to the Louisiana Administrative Code, Title 33, Part I, Subpart 3, LABORATORY ACCREDITATION, the State of Louisiana formally recognizes that this laboratory is technically competent to perform the environmental analyses listed on the scope of accreditation detailed in the attachment.

The laboratory agrees to perform all analyses listed on this scope of accreditation according to the Part I, Subpart 3 requirements and acknowledges that continued accreditation is dependent on successful ongoing compliance with the applicable requirements of Part I. Please contact the Department of Environmental Quality, Louisiana Environmental Laboratory Accreditation Program (LELAP) to verify the laboratory's scope of accreditation and accreditation status.

Accreditation by the State of Louisiana is not an endorsement or a guarantee of validity of the data generated by the laboratory. To be accredited initially and maintain accreditation, the laboratory agrees to participate in two single-blind, single-concentration PT studies, where available, per year for each field of testing for which it seeks accreditation or maintains accreditation as required in LAC 33:I.4711.

Lourdes Iturralde, Administrator
Notifications and Accreditations Section
Public Participation & Permit Support Services Division

Certificate Number: 04064

Expiration Date: June 30, 2016
Issued On: July 1, 2015

STATE OF LOUISIANA
DEPARTMENT OF ENVIRONMENTAL QUALITY
Issue Date: July 1, 2015

Ambient Air Services Inc
AI Number: 100329
Expiration Date: June 30, 2016

106 Ambient Airway, Starke, Florida 32091

Certificate Number: 04064

Air Emissions

Analyte	Method Name	Method Code	Type	AB
100025 - Sampling	EPA 104	674	State	LA
3880 - Opacity	CEMS Performance Specification 1	753	State	LA
100025 - Sampling	EPA 10A	1232	State	LA
100025 - Sampling	EPA 10B	1233	State	LA
3885 - Oxides of nitrogen	EPA 20	1250	State	LA
3895 - Oxygen	EPA 20	1250	State	LA
4010 - Sulfur dioxide	EPA 20	1250	State	LA
3995 - Stack gas velocity, volume flow rate	EPA 2B	1272	State	LA
4000 - Stack gas velocity, volume flow rate in small stacks/ducts	EPA 2D	1274	State	LA
3995 - Stack gas velocity, volume flow rate	EPA 2E	1275	State	LA
3995 - Stack gas velocity, volume flow rate	EPA 2F	1276	State	LA
3995 - Stack gas velocity, volume flow rate	EPA 2G	1277	State	LA
3995 - Stack gas velocity, volume flow rate	EPA 2H	1278	State	LA
100025 - Sampling	EPA 21	1844	State	LA
4055 - Visible emissions from coke oven batteries	EPA 22	1846	State	LA
100025 - Sampling	EPA Method 29	1861	State	LA
100025 - Sampling	NCASI Vents	1971	State	LA
1441 - Sampling	40 CFR Part 50 1984 App G	2198	State	LA
3780 - Carbon monoxide	CEMS Performance Specification 4B	2371	State	LA
3970 - Total reduced sulfur	EPA Method 16C	2565	State	LA
1095 - Mercury	CEMS Performance Specification 12	2571	State	LA
4020 - Sulfuric acid mist, sulfur dioxide	EPA CTM-013B	2740	State	LA
4020 - Sulfuric acid mist, sulfur dioxide	EPA CTM-013A	2741	State	LA
4010 - Sulfur dioxide	EPA CTM-013	2742	State	LA
4017 - Sulfur trioxide	EPA CTM-013	2742	State	LA
4019 - Sulfuric acid mist	EPA CTM-013	2742	State	LA
3850 - Moisture content	Oregon Method 4	2841	State	LA
100025 - Sampling	Oregon Method 4	2841	State	LA
100025 - Sampling	EPA CTM-013A	2843	State	LA
100025 - Sampling	EPA CTM-013B	2844	State	LA
4010 - Sulfur dioxide	AASI-SOP TEI Model 43C	2983	State	LA
4010 - Sulfur dioxide	AASI-SOP TEI Model 43i	2984	State	LA
3780 - Carbon monoxide	AASI-SOP TEI Model 48i	2985	State	LA
1845 - Nitrogen dioxide	AASI-SOP TEI Model 42i	2986	State	LA
100709 - Barometric Pressure	AASI-SOP CM102083	2987	State	LA
100708 - Temperature	AASI-SOP CM102083	2987	State	LA
100706 - Wind Direction	AASI-SOP CM102083	2987	State	LA
100705 - Wind Speed	AASI-SOP CM102083	2987	State	LA
100707 - Precipitation	AASI-SOP NCM 260	2988	State	LA
100025 - Sampling	40 CFR Part 50 Appendix B	10000304	State	LA
3973 - Total Suspended Particulate (TSP)	40 CFR Part 50 Appendix B	10000304	State	LA
3950 - Particulates <10 um	40 CFR Part 50 Appendix J	10000507	State	LA
100025 - Sampling	40 CFR Part 50 Appendix J	10000507	State	LA
3805 - Fine particulates <2.5 um	40 CFR 50 Appendix L	10000709	State	LA
100025 - Sampling	40 CFR 50 Appendix L	10000709	State	LA
100025 - Sampling	EPA 0011	10001806	State	LA
100025 - Sampling	EPA 0061	10003608	State	LA
100025 - Sampling	EPA 18	10011300	State	LA

Clients and Customers are urged to verify the laboratory's current certification status with the Louisiana Environmental Laboratory Accreditation Program.

Air Emissions

Analyte	Method Name	Method Code	Type	AB
3885 - Oxides of nitrogen	CEMS Performance Specification 2	10214627	State	LA
4010 - Sulfur dioxide	CEMS Performance Specification 2	10214627	State	LA
3755 - Carbon dioxide	CEMS Performance Specification 3	10214638	State	LA
3895 - Oxygen	CEMS Performance Specification 3	10214638	State	LA
3780 - Carbon monoxide	CEMS Performance Specification 4	10214649	State	LA
3970 - Total reduced sulfur	CEMS Performance Specification 5	10214661	State	LA
100215 - Calibration Drift and Relative Accuracy Tests	CEMS Performance Specification 6	10214672	State	LA
3995 - Stack gas velocity, volume flow rate	CEMS Performance Specification 6	10214672	State	LA
100018 - Volatile organics	CEMS Performance Specification 8	10214694	State	LA
100025 - Sampling	EPA CTM-027	10214707	State	LA
100076 - Traverse Points	EPA Method 1	10246614	State	LA
3780 - Carbon monoxide	EPA Method 10	10246625	State	LA
100023 - Total Gaseous Organic Compounds	EPA 18	10246636	State	LA
3885 - Oxides of nitrogen	EPA Method 19	10246647	State	LA
3940 - Particulates, SO2, NOx, sulfur removal efficiency	EPA Method 19	10246647	State	LA
3780 - Carbon monoxide	CEMS Performance Specification 4A	10246650	State	LA
100076 - Traverse Points	EPA Method 1A	10246658	State	LA
3995 - Stack gas velocity, volume flow rate	EPA Method 2	10246669	State	LA
100025 - Sampling	EPA Method 23	10246705	State	LA
100077 - Gaseous Nonmethane Organic Emissions	EPA Method 25	10246738	State	LA
100025 - Sampling	EPA Method 25	10246738	State	LA
100025 - Sampling	EPA Method 25A	10246749	State	LA
100023 - Total Gaseous Organic Compounds	EPA Method 25A	10246749	State	LA
3755 - Carbon dioxide	EPA Method 3A	10247684	State	LA
3895 - Oxygen	EPA Method 3A	10247684	State	LA
100142 - Emission Rate Correction Factors	EPA Method 3B	10247695	State	LA
100025 - Sampling	EPA Method 3B	10247695	State	LA
100024 - Modified Method 5 Sampling Train	EPA 0010	10250201	State	LA
100025 - Sampling	EPA 0010	10250201	State	LA
100025 - Sampling	EPA 308	10274507	State	LA
4815 - Formaldehyde	EPA 323	10274585	State	LA
100025 - Sampling	EPA 101A	10401204	State	LA
1441 - Sampling	EPA 102	10401306	State	LA
100025 - Sampling	EPA 103	10401408	State	LA
100025 - Sampling	EPA 12 (FAA)	10401908	State	LA
100025 - Sampling	EPA 13A	10402003	State	LA
100025 - Sampling	EPA 13B	10402105	State	LA
3845 - Hydrogen sulfide, carbonyl sulfide, carbon disulfide	EPA 15	10402207	State	LA
100025 - Sampling	EPA 15	10402207	State	LA
100025 - Sampling	EPA 15A	10402309	State	LA
3830 - H2S, methyl mercaptan, dimethyl sulfide, dimethyl disulfide	EPA 16	10402401	State	LA
100025 - Sampling	EPA 16	10402401	State	LA
100025 - Sampling	EPA 16A	10402503	State	LA
4010 - Sulfur dioxide	EPA 16A	10402503	State	LA
100025 - Sampling	EPA 16B	10402605	State	LA
100025 - Sampling	EPA 17	10402707	State	LA
3805 - Fine particulates <2.5 um	EPA 201A	10402901	State	LA
100665 - Particulate Matter between 2.5 and	EPA 201A	10402901	State	LA

Air Emissions

Analyte	Method Name	Method Code	Type	AB
10 um				
3915 - Particulates	EPA 201A	10402901	State	LA
3950 - Particulates <10 um	EPA 201A	10402901	State	LA
100025 - Sampling	EPA 201A	10402901	State	LA
100045 - Condensible Particulate Matter	EPA 202	10403006	State	LA
3915 - Particulates	EPA 202	10403006	State	LA
100025 - Sampling	EPA 202	10403006	State	LA
100025 - Sampling	EPA 26	10403108	State	LA
1540 - Bromide	EPA 26A	10403200	State	LA
1575 - Chloride	EPA 26A	10403200	State	LA
1770 - Hydrochloric acid (Hydrogen chloride (gas only))	EPA 26A	10403200	State	LA
100096 - Hydrogen Bromide (HBr)	EPA 26A	10403200	State	LA
1775 - Hydrogen fluoride (Hydrofluoric acid)	EPA 26A	10403200	State	LA
3835 - Hydrogen halides and halogens	EPA 26A	10403200	State	LA
100025 - Sampling	EPA 26A	10403200	State	LA
4000 - Stack gas velocity, volume flow rate in small stacks/ducts	EPA Method 2A	10403744	State	LA
4000 - Stack gas velocity, volume flow rate in small stacks/ducts	EPA Method 2C	10403755	State	LA
3765 - Carbon dioxide, oxygen, dry molecular weight	EPA Method 3	10403766	State	LA
100025 - Sampling	EPA 306 (ICP)	10403904	State	LA
1095 - Mercury	EPA 30B	10404203	State	LA
100025 - Sampling	EPA 30B	10404203	State	LA
3850 - Moisture content	EPA Method 4	10404258	State	LA
3915 - Particulates	EPA 5	10404305	State	LA
100025 - Sampling	EPA 5	10404305	State	LA
3915 - Particulates	EPA 5A	10404407	State	LA
100025 - Sampling	EPA 5A	10404407	State	LA
3915 - Particulates	EPA 5B	10404509	State	LA
100025 - Sampling	EPA 5B	10404509	State	LA
3915 - Particulates	EPA 5D	10404601	State	LA
100025 - Sampling	EPA 5D	10404601	State	LA
3935 - Particulates from wool fiberglass insulation	EPA 5E	10404703	State	LA
100025 - Sampling	EPA 5E	10404703	State	LA
3915 - Particulates	EPA 5F	10404805	State	LA
100025 - Sampling	EPA 5F	10404805	State	LA
3930 - Particulates from wood heaters	EPA 5G	10404907	State	LA
100025 - Sampling	EPA 5G	10404907	State	LA
3930 - Particulates from wood heaters	EPA 5H	10405002	State	LA
100025 - Sampling	EPA 5H	10405002	State	LA
3915 - Particulates	EPA 5I	10405104	State	LA
100025 - Sampling	EPA 5I	10405104	State	LA
100025 - Sampling	EPA 6	10405206	State	LA
100025 - Sampling	EPA 6A	10405308	State	LA
100025 - Sampling	EPA 6B	10405400	State	LA
4010 - Sulfur dioxide	EPA Method 6C	10405411	State	LA
100025 - Sampling	EPA 7	10405502	State	LA
3885 - Oxides of nitrogen	EPA Method 7E	10405911	State	LA
100025 - Sampling	EPA 8	10406005	State	LA
3880 - Opacity	EPA Method 9	10406403	State	LA
100025 - Sampling	NCASI 8A	60031223	State	LA
4010 - Sulfur dioxide	NCASI 8A	60031223	State	LA

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Air Emissions

Analyte	Method Name	Method Code	Type	AB
4017 - Sulfur trioxide	NCASI 8A	60031223	State	LA
100143 - Sulfuric acid mist	NCASI 8A	60031223	State	LA
100025 - Sampling	NCASI CI/SG/PULP-94.02	60031245	State	LA

Non Potable Water

Analyte	Method Name	Method Code	Type	AB
NONE	NONE	NONE	NONE	NONE

Solid Chemical Materials

Analyte	Method Name	Method Code	Type	AB
NONE	NONE	NONE	NONE	NONE

Biological Tissue

Analyte	Method Name	Method Code	Type	AB
NONE	NONE	NONE	NONE	NONE

APPENDIX M

3RD PARTY LABORATORY VALIDATION

Note: Information in this Appendix supplied by MultiMac JV.

Quality Assurance Laboratory Data Review
Naval Station Guantanamo Bay Cuba Air Curtain Incinerator Emissions Testing

Introduction

Amec Foster Wheeler Environment & Infrastructure, Inc. (Amec Foster Wheeler) conducted a third party Quality Assurance (QA) laboratory data review for Naval Facilities Engineering Command Southeast (NAVFAC SE) in support of air curtain incinerator emissions testing at the Naval Station Guantanamo Bay, Cuba. The testing was performed by Ambient Air Services, Inc. (AASI) during 15 April – 01 May 2016.

The review was conducted following the EPA National Functional Guidelines for Inorganics and Organics Superfund Data Review (EPA 2014a and EPA 2014b) and the US Army Corps of Engineers Chemical Quality Assurance for Hazardous, Toxic, Radioactive Waste Projects engineer manual (USACE 1997) where applicable and not superseded by the sampling or analysis methods used for the project. Data were reviewed for adherence to project requirements to assist the end user in determining usability. For example, the results reported for samples analyzed outside of established holding times or for those exceeding the established temperature requirements for shipping may be biased low. However, these data were generated as part of a testing regime that included areas outside of the scope of this review. This report assumes that end users understand the implications of nonconforming analyses noted herein and will evaluate them within the larger scope of the project test data to determine their ultimate usability.

This report was originally completed July 28, 2016. This version has been updated to include review of an additional particle size distribution laboratory package.

Data Reviewed

Laboratory data packages generated for samples collected during separate day and night monitoring periods during the last two weeks in April 2016 were reviewed. The packages included data for the following parameters:

- Particulate Matter (PM)
- Condensable Particulate Matter (CPM)
- Particle Size
- Dioxins/Furans (D/F)
- Polychlorinated Biphenyls (PCB)
- Polycyclic Aromatic Hydrocarbons (PAH)
- Semi-volatile Organic Compounds (SVOC)
- Volatile Organic Compounds (VOC)
- Hydrogen Chloride (HCl)
- Hydrogen Cyanide (HCN)
- Metals
- Aldehydes

The data packages were reviewed for:

- Parameter list matching the AASI sampling plan
- Completeness [Field Sampling Forms (w/ preservation data), Hold Times, chains of custody (CoC), Case Narrative, Quality Control Samples, Raw Data]
- Analyses within established holding time
- Quality Control (QC) samples within established criteria [Method Blank (MB), Matrix Spike/Duplicate (MS/MSD), Laboratory Control Sample (LCS), Internal Standards, Surrogates]
- Traceability of reported values to raw laboratory data (20 percent of field samples)

Laboratories

The following laboratories produced data packages reviewed for this report:

Table 1 – Team Laboratories

Laboratory Name and Location	Data Packages Reviewed
Ambient Air Services, Inc. Starke, FL	Particulate Matter – USEPA Method 5 (NARA 2016a) Condensable Particulate Matter – USEPA Method 202 (NARA 2016b) Particle Size – CARB Method 501 (CARB 1990)
Enthalpy Analytical, Inc. Durham, NC	Aldehydes – NCASI Method A105.01 (NCASI 2005)
TestAmerica Laboratories, Inc. Knoxville, TN *Pittsburgh, PA	Dioxins/Furans – 40 CFR Part 60, Appendix A-7 to Part 60 – Test Method 23 (NARA 2016c) Polychlorinated Biphenyls – USEPA Method 1668A (EPA 2003) Polycyclic Aromatic Hydrocarbons – KNOX-ID-0016 (KNOX 2010) Semi-volatile Organic Compounds – SW846 8270C (EPA 1996a) Volatile Organic Compounds – SW846 5041A (EPA 1996b), SW846 8260B (EPA 1996c) Hydrogen Chloride – KNOX 0050/26A (KNOX 2009) Hydrogen Cyanide – USEPA Method 9014 (EPA 2014c)
Element One, Inc. Wilmington, NC	Metals – USEPA Method 29 (NARA 2016d)
MVA Scientific Consultants Duluth, GA	†Particle Size Distribution – MVA Method 316

*Hydrogen cyanide analyses only
†Additional package reviewed during November 2016

Results of Review

Review results are presented in Tables 2 and 3. The field samples verified for traceability to raw laboratory data are listed in Table 4 – all were traceable from the data report to raw data.

Table 2 – Results of Laboratory Data Review: Day

Data Package	Parameter List (y/n)	Package Complete (y/n - comment)	Hold Times Met (y/n)	Quality Control w/in Criteria (y/n)
Particulate Matter Condensable Particulate Matter	y	n – missing case narrative	na	y
Particle Size	y	n – missing case narrative	na	y
Aldehydes	y	y	y	y
Dioxins/Furans Polychlorinated Biphenyls Polycyclic Aromatic Hydrocarbons Semi-volatile Organic Compounds	y	y – some samples received broken (documented by laboratory)	y	n – PAH: MB biphenyl high; some internal standard failures (both addressed in narrative) SVOC: LCS failures – noted in lab report ("entire sample consumed"); some surrogate failures (addressed in narrative)
Volatile Organic Compounds*	y	y – LCS/LCSD were run in lieu of MS/MSD due to limited sample volumes; 4 samples not reported due to internal standard failures (noted in narrative)	y	n – Samples received at 12.3C; matrix issues resulted in surrogate and internal standard failures (addressed in narrative)
Hydrogen Chloride	y	y	y	y
Hydrogen Cyanide	y	y	y	n – Samples received at 8.5C; results reported exceeded holding time (addressed in narrative)
Metals*	y	y	y	n – Matrix spike low for selenium (addressed in narrative)
Particle Size Distribution	y	y – There is no batch QC required for the method utilized.	na	na

*Parameters not in the original sample plan. Reported parameters match promulgated methods.

Table 3 – Results of Laboratory Data Review: Night

Data Package	Parameter List (y/n)	Package Complete (y/n - comment)	Hold Times Met (y/n)	Quality Control w/in Criteria (y/n)
Particulate Matter Condensable Particulate Matter	y	n – missing case narrative. (note: one page of day test raw data included)	na	y
Particle Size	y	n – missing case narrative	na	y
Aldehydes	y	y	y	n – Samples received at 18.4C (0-10C required). Deviation not addressed
Dioxins/Furans Polychlorinated Biphenyls Polycyclic Aromatic Hydrocarbons Semi-volatile Organic Compounds	y	y	y	n – PAH: Some internal standard failures (addressed in narrative)
Volatile Organic Compounds*	y	y – LCS/LCSD were run in lieu of MS/MSD due to limited sample volumes; six samples received broken and four were broken during sample preparation (documented by laboratory)	y	n – matrix issues resulted in surrogate and internal standard failures (addressed in narrative)
Hydrogen Chloride	y	y	y	y
Hydrogen Cyanide	y	y	y	y
Metals*	y	y	y	n – Matrix spike low for selenium (addressed in narrative)
Particle Size Distribution	y	y – There is no batch QC required for the method utilized.	na	na

*Parameters not in the original sample plan. Reported parameters match promulgated methods.

Table 4 - Samples Verified for Traceability to Raw Laboratory Data

Data Package	Samples Reviewed
Particulate Matter Condensable Particulate Matter	Day: R1 – 2, R4 – 1, H621, H671, H682 Night: 4319, 4316, H685, H731, H735, H680
Particle Size	Day: H628, H639, H640, H648, H656, 5011F, H663, H669 Note: Blank corrections listed but not applied to reported data. Night: H689, H694, H697, H705, H720, H727, H728, 5015F (two labeled 5016F on consecutive days) Note: Blank corrections listed but not applied to reported data.
Aldehydes	Day: Day2-A, Day4-A Night: Day3-A run spike, Day5-A
Dioxins/Furans Polychlorinated Biphenyls Polycyclic Aromatic Hydrocarbons Semi-volatile Organic Compounds	Day: SVOC/PCB/PAH - M8J3C, M8J3H, M8J3N, M8J3Q, M8J3X; D/F - M8J3A, M8J3F, M8J3K, M8J3P, M8J3V Night: SVOC/PCB - M8K4A, M8K4G, M8K4M, M8K4P, M8K4W, M8K43; PAH - M8K4A, M8K4G, M8K43, M8K47; DF - M8K39, M8K4E, M8K4J
Volatile Organic Compounds	Day: M8JV9, M8JWF, M8JWG, M8JWL, M8JWN, M8JWR, M8JWX, M8JW2, M8JXF, M8JXJ Night: M8K1X, M8K11, M8K19, M8K24, M8K3J, M8K3Q, M8K3X, M8K34
Hydrogen Chloride	Day: M8MJ89 Night: M8K49
Hydrogen Cyanide	Day: D-29-1 Run 1, D-29-3 Run 3 Night: N1-3, N3-3
Metals*	Day: D1 Night: N4
Particle Size Distribution	Day: D1 Night: N3

*The original metals package contained many repeat sample runs with several masses listed for a given parameter and several dilutions. The data and narrative provided were not sufficient to trace reported data to raw data. The laboratory provided a results key upon request (Attachment 1).

References

U.S. Environmental Protection Agency (EPA). 2014a. National Functional Guidelines for Inorganic Superfund Data Review (ISM02.2)

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U.S. Environmental Protection Agency (EPA). 2003. Method 1668, Revision A: Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS

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U.S. Environmental Protection Agency (EPA). 1996a. SW-846 Test Method 8270C - Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)

U.S. Environmental Protection Agency (EPA). 1996b. SW-846 Test Method 5041A: Analysis for Desorption of Sorbent Cartridges from Volatile Organic Sampling Train (VOST)

U.S. Environmental Protection Agency (EPA). 1996c. SW-846 Test Method 8260B: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS)

TestAmerica – Knoxville (KNOX). 2009. Method 0050/Method 26 or 26A - Method for Determining HCl and Cl_2 Emissions in Stack Gas

U.S. Environmental Protection Agency (EPA). 2014c. SW-846 Test Method 9014: Cyanide in Waters and Extracts Using Titrimetric and Manual Spectrophotometric Procedures

U.S. National Archives and Records Administration (NARA). 2016d. Code of Federal Regulations. Title 40, Appendix A-8 to Part 60. Method 29 - Determination of Metals Emissions from Stationary Sources

Attachments

Attachment 1 – Metals Laboratory Results Key
Attachment 2 - Laboratory Case Narratives

----- End of Report -----

Attachment 1

Metals Laboratory Results Key

ICP Result Location Summary

Element	DI Total µg	D2 Duplicate Total µg	D2 Duplicate Total µg	D3 Spike Total µg
----------------	--------------	--------------	--------------	--------------
	27414-1	27414-2	27414-2	27414-3
Beryllium	6/9/16 @ 1347	6/9/16 @ 1350	6/9/16 @ 1352	6/9/16 @ 1355
Phosphorus	6/9/16 @ 1245	6/9/16 @ 1247	6/9/16 @ 1250	6/9/16 @ 1252
Chromium	6/9/16 @ 1531	6/9/16 @ 1533	6/9/16 @ 1536	6/9/16 @ 1538
Manganese	6/9/16 @ 1531	6/9/16 @ 1533	6/9/16 @ 1536	6/9/16 @ 1538
Cobalt	6/9/16 @ 1245	6/9/16 @ 1247	6/9/16 @ 1250	6/9/16 @ 1252
Nickel	6/9/16 @ 1531	6/9/16 @ 1533	6/9/16 @ 1536	6/9/16 @ 1538
Copper	6/9/16 @ 1531	6/9/16 @ 1533	6/9/16 @ 1536	6/9/16 @ 1538
Zinc	6/9/16 @ 1147	6/9/16 @ 1150	6/9/16 @ 1153	6/9/16 @ 1155
Arsenic	6/9/16 @ 1531	6/9/16 @ 1533	6/9/16 @ 1536	6/9/16 @ 1538
Selenium	6/9/16 @ 1531	6/9/16 @ 1533	6/9/16 @ 1536	6/9/16 @ 1538
Silver	6/9/16 @ 1347	6/9/16 @ 1350	6/9/16 @ 1352	6/9/16 @ 1355
Cadmium	6/9/16 @ 1531	6/9/16 @ 1533	6/9/16 @ 1536	6/9/16 @ 1538
Antimony	6/9/16 @ 1245	6/9/16 @ 1247	6/9/16 @ 1250	6/9/16 @ 1252
Barium	6/9/16 @ 1147	6/9/16 @ 1150	6/9/16 @ 1153	6/9/16 @ 1155
Thallium	6/9/16 @ 1347	6/9/16 @ 1350	6/9/16 @ 1352	6/9/16 @ 1355
Lead	6/9/16 @ 1531	6/9/16 @ 1533	6/9/16 @ 1536	6/9/16 @ 1538

Element	D4 Total µg	D5 Total µg	N1 Total µg	N2 Duplicate Total µg	N2 Duplicate Total µg
----------------	--------------	--------------	--------------	--------------	--------------
	27414-4	27414-5	27414-6	27414-7	27414-7
Beryllium	6/9/16 @ 1400	6/9/16 @ 1403	6/9/16 @ 1405	6/9/16 @ 1408	6/9/16 @ 1411
Phosphorus	6/9/16 @ 1258	6/9/16 @ 1300	6/9/16 @ 1303	6/9/16 @ 1306	6/9/16 @ 1308
Chromium	6/9/16 @ 1544	6/9/16 @ 1546	6/9/16 @ 1549	6/9/16 @ 1552	6/9/16 @ 1554
Manganese	6/9/16 @ 1544	6/9/16 @ 1546	6/9/16 @ 1549	6/9/16 @ 1552	6/9/16 @ 1554
Cobalt	6/9/16 @ 1258	6/9/16 @ 1300	6/9/16 @ 1303	6/9/16 @ 1552	6/9/16 @ 1554
Nickel	6/9/16 @ 1544	6/9/16 @ 1546	6/9/16 @ 1549	6/9/16 @ 1552	6/9/16 @ 1554
Copper	6/9/16 @ 1544	6/9/16 @ 1546	6/9/16 @ 1549	6/9/16 @ 1552	6/9/16 @ 1554
Zinc	6/9/16 @ 1201	6/9/16 @ 1203	6/9/16 @ 1206	6/9/16 @ 1306	6/9/16 @ 1308
Arsenic	6/9/16 @ 1544	6/9/16 @ 1546	6/9/16 @ 1549	6/9/16 @ 1552	6/9/16 @ 1554
Selenium	6/9/16 @ 1544	6/9/16 @ 1546	6/9/16 @ 1549	6/9/16 @ 1552	6/9/16 @ 1554
Silver	6/9/16 @ 1400	6/9/16 @ 1403	6/9/16 @ 1405	6/9/16 @ 1408	6/9/16 @ 1411
Cadmium	6/9/16 @ 1544	6/9/16 @ 1546	6/9/16 @ 1549	6/9/16 @ 1552	6/9/16 @ 1554
Antimony	6/9/16 @ 1400	6/9/16 @ 1403	6/9/16 @ 1405	6/9/16 @ 1408	6/9/16 @ 1411
Barium	6/9/16 @ 1201	6/9/16 @ 1203	6/9/16 @ 1206	6/9/16 @ 1408	6/9/16 @ 1411
Thallium	6/9/16 @ 1400	6/9/16 @ 1403	6/9/16 @ 1405	6/9/16 @ 1408	6/9/16 @ 1411
Lead	6/9/16 @ 1544	6/9/16 @ 1546	6/9/16 @ 1549	6/9/16 @ 1552	6/9/16 @ 1554

Element	N3 Spike Total µg	N4 Total µg	N5 Total µg	FB Total µg
----------------	--------------	--------------	--------------	--------------
	27414-8	**27414-9**	**27414-10**	**27414-11**
Beryllium	6/9/16 @ 1419	6/9/16 @ 1424	6/9/16 @ 1427	6/9/16 @ 1429
Phosphorus	6/9/16 @ 1602	6/9/16 @ 1608	6/9/16 @ 1610	6/9/16 @ 1613
Chromium	6/9/16 @ 1602	6/9/16 @ 1608	6/9/16 @ 1610	6/9/16 @ 1613
Manganese	6/9/16 @ 1602	6/9/16 @ 1608	6/9/16 @ 1610	6/9/16 @ 1613
Cobalt	6/9/16 @ 1602	6/9/16 @ 1608	6/9/16 @ 1610	6/9/16 @ 1613
Nickel	6/9/16 @ 1602	6/9/16 @ 1608	6/9/16 @ 1610	6/9/16 @ 1613
Copper	6/9/16 @ 1602	6/9/16 @ 1608	6/9/16 @ 1610	6/9/16 @ 1613
Zinc	6/9/16 @ 1219	6/9/16 @ 1224	6/9/16 @ 1227	6/9/16 @ 1230
Arsenic	6/9/16 @ 1602	6/9/16 @ 1608	6/9/16 @ 1610	6/9/16 @ 1613
Selenium	6/9/16 @ 1602	6/9/16 @ 1608	6/9/16 @ 1610	6/9/16 @ 1613
Silver	6/9/16 @ 1419	6/9/16 @ 1424	6/9/16 @ 1427	6/9/16 @ 1429
Cadmium	6/9/16 @ 1602	6/9/16 @ 1608	6/9/16 @ 1610	6/9/16 @ 1613
Antimony	6/9/16 @ 1602	6/9/16 @ 1608	6/9/16 @ 1610	6/9/16 @ 1613
Barium	6/9/16 @ 1219	6/9/16 @ 1224	6/9/16 @ 1227	6/9/16 @ 1230
Thallium	6/9/16 @ 1419	6/9/16 @ 1424	6/9/16 @ 1427	6/9/16 @ 1429
Lead	6/9/16 @ 1602	6/9/16 @ 1608	6/9/16 @ 1610	6/9/16 @ 1613

Attachment 2

Laboratory Case Narratives

Case Narrative:
Metals – USEPA Method 29

Day/Night

Element One, Inc.

Element One Analytical Narrative

Client:	Ambient Air Services, Inc.	Element One #:	27414
Client ID:	NSGB	Analyst:	DMR
Method:	29	Dates Received:	05/18/16
Analytes:	Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, P, Se, Ag, Tl & Zn	Dates Analyzed:	06/09/16

Summary of Analysis

The impinger fractions for the M29 samples were digested on the hot plate with trace metals grade concentrated nitric acid. The filters were cut into small strips using Teflon scissors and placed in corresponding impinger beakers with 10mL of trace metals grade concentrated nitric acid and 10mL DI. The filters were heated below boiling for one hour. After digestion the samples were combined with the reconstituted organic beakers and brought to a final volume of 100mL with DI.
The samples were analyzed for metals by EPA Method SW-846 6020A on a PerkinElmer Elan 6100 ICP-MS.

Detection Limits

The ICP-MS instrument reporting limits were 0.25µg/L for beryllium, 20.0µg/L for phosphorus and 1.0µg/L for the metals.

Analysis QA/QC

Duplicate analyses relative percent difference (RPD), spike sample recovery, and second source calibration verification data are summarized in the Quality Control Section.
*Ref to page 11; the selenium spike recoveries for D3 Spike and N3 Spike were outside of the laboratory guidelines of 75% to 125% with 71% and 73% at a five-fold dilution respectively. The samples were analyzed at a ten-fold dilution resulting in spike recoveries of 86% for D3 Spike and 86% for N3 Spike, indicating matrix interference.
All other QA/QC data was within the criteria of the method.

Additional Comments

The reported results have not been corrected for any blank values or spike recovery values. The reported results relate only to the items tested or calibrated.

The ICP analysis of the field blank sample revealed notable concentrations of metals. The sample was reanalyzed at multiple dilutions with consistent results.

Rev. 06.22.16; to correct the client project ID.

Case Narrative:
Aldehydes - NCASI Method A105.01

Day

Enthalpy Analytical, Inc.

Enthalpy Analytical Narrative Summary

Company	Ambient Air Services, Inc.
Analyst	KAM
Parameters	NCASI Method A105.01

Client #	Cuba - GTMO
Job #	0316-127
# Samples	10, 1 Blank, 2 Spikes

Custody

Jon Escobedo received the samples on 4/26/16 after being relinquished by Ambient Air Services, Inc. The samples were received at 7.5°C and in good condition. Prior to, during, and after analysis, the samples were kept under lock with access only to authorized personnel by Enthalpy Analytical, Inc.

Analysis

The samples were analyzed for acetaldehyde, formaldehyde and propionaldehyde using the analytical procedures in NCASI Method ISS/FP-A105.01, "Impinger Source Sampling Method for Selected Aldehydes, Ketones, and Polar Compounds".

The initial volumes of the combined aqueous BHA/hexane samples were measured. The combined samples were transferred to separatory funnels for the first extraction. The samples were shaken for 30 seconds and the hexane and BHA layers allowed to separate. Two additional extractions were performed by adding fresh hexane to the aqueous BHA samples in the separatory funnels, shaking for 30 seconds and allowing the hexane layers to separate. The hexane extracts were combined for each sample. The final hexane and BHA volumes were measured and recorded.

The Agilent Technologies Model 6890, Gas Chromatograph "Lolita" (S/N US00000347) was used for these analyses.

Calibration

The calibration curve is located in the back of this report and referenced in the Analysis Method column on the Detailed Results page.

For each calibration curve used, the first page of the curve contains all method specific parameters (i.e., curve type, origin, weight, etc.) used to quantify the samples. The calibration curve section also includes a table with the Retention Time (RetTime), Level (Lvl), Amount (corresponding units), Area, Response Factor (Amt/Area) and the analyte Name. The calibration table is used to identify (by retention time) and quantify each target compound.

Chromatographic Conditions

The acquisition method LOLITA0098.M is included in the Raw Data section of this report.

Enthalpy Analytical Narrative Summary
(continued)

QC Notes

None of the compounds of interest were identified at concentrations greater than the detection limit in the analyses of the laboratory or client blanks.

A Laboratory Duplicate (LD) was prepared and analyzed along with the samples using an aliquot of sample ***4 Day Side B***. The initial and duplicate analyses did not differ by more than 0.4%.

The laboratory prepared an aqueous spike solution containing 988 µg/mL of acetaldehyde, 1,005 µg/mL of propionaldehyde and 1,014 µg/mL of formaldehyde. Four vials of the spike solution were provided to the client prior to sample collection while a vial was retained by the laboratory to prepare laboratory control samples (LCS). Two LCS were analyzed along with the samples and yielded average recoveries ranging from 91.4% to 97.1%.

Reporting Notes

Acetaldehyde and propionaldehyde are identified as two peaks ("1" and "2"). This is normal for the method's derivatization process, and results for both peaks are combined on the chromatograms and in the Results.

These analyses met the requirements of the TNI Standard. Any deviations from the requirements of the reference method or TNI Standard have been stated above.

The results presented in this report are representative of the samples as provided to the laboratory.

Case Narrative:
Aldehydes - NCASI Method A105.01

Night

Enthalpy Analytical, Inc.

Enthalpy Analytical Narrative Summary

Company	Ambient Air Services, Inc.
Analyst	JBB
Parameters	NCASI Method A105.01

Client #	Guantanamo Bay: Cuba
Job #	0713-213
# Samples	9, 2 Spikes

Custody

Patricia Mann received the samples on 5/5/16 after being relinquished by Ambient Air Services, Inc. The samples were received at 18.4 °C and in good condition. Prior to, during, and after analysis, the samples were kept under lock with access only to authorized personnel by Enthalpy Analytical, Inc.

Analysis

The samples were analyzed for formaldehyde, acetaldehyde, and propionaldehyde using the analytical procedures in NCASI Method ISS/FP-A105.01, "Impinger Source Sampling Method for Selected Aldehydes, Ketones, and Polar Compounds".

The initial volumes of the combined aqueous BHA/hexane samples were measured. The combined samples were transferred to separatory funnels for the first extraction. The samples were shaken for 30 seconds and the hexane and BHA layers allowed to separate. Two additional extractions were performed by adding fresh hexane to the aqueous BHA samples in the separatory funnels, shaking for 30 seconds and allowing the hexane layers to separate. The hexane extracts were combined for each sample. The final hexane and BHA volumes were measured and recorded.

The Agilent Technologies Model 6890, Gas Chromatograph ("Lolita" S/N US00000347) was equipped with a Nitrogen-Phosphorus Detector for these analyses.

Calibration

The calibration curves are located in the back of this report and referenced in the Analysis Method column on the Detailed Results page.

For each calibration curve used, the first page of the curve contains all method specific parameters (i.e., curve type, origin, weight, etc.) used to quantify the samples. The calibration curve section also includes a table with the Retention Time (RetTime), Level (Lvl), Amount (corresponding units), Area, Response Factor (Amt/Area) and the analyte Name. The calibration table is used to identify (by retention time) and quantify each target compound.

Chromatographic Conditions

The acquisition method LOLITA0095.M is included in Raw Data section of this report.

Enthalpy Analytical Narrative Summary
(continued)

QC Notes

No blank samples were received from the field with these samples.

Formaldehyde was present in the laboratory method blank at a concentration above the MDL but below the LOQ. None of the other compounds of interest were identified at concentrations greater than the detection limit in the analysis of the laboratory method blanks.

A laboratory reagent (hexane) blank was also analyzed, and none of the compounds of interest were identified at levels above the MDL.

A Laboratory Duplicate (LD) was prepared using an aliquot of sample ***3A-Spk.HEX***. It was analyzed with the samples and yielded percent differences values which were all below 1.0%.

The laboratory prepared an aqueous spiking solution containing 1,014 µg/mL of formaldehyde, 988 µg/mL of acetaldehyde, and 1,005 µg/mL of propionaldehyde in 1-propanol. Four 12-mL vials of the spiking solution were provided to the client prior to sample collection while a 40-mL vial of this solution was retained by the laboratory to be used preparing Laboratory Control Samples (LCSs).

An LCS was generated by adding 100 uL of the spiking solution to 30 mL of BHA solution, and then extracting and analyzing it with the samples. LCS-1 yielded recovery values ranging from 78.4% to 84.0%.

Reporting Notes

Acetaldehyde and propionaldehyde are identified as two peaks ("1" and "2"). This is normal for the method's derivatization process, and results for both peaks are combined on the chromatograms. The detailed results pages label these summed compounds as "*Compound*-1+2". On the Summary results page we have simply identified the three analytes by name.

These analyses met the requirements of the TNI Standard. Any deviations from the requirements of the reference method or TNI Standard have been stated above.

The results presented in this report are representative of the samples as provided to the laboratory.

Case Narrative:
Dioxins/Furans - 40 CFR Part 60, Appendix A-7 to Part 60 – Test Method 23
Polychlorinated Biphenyls - USEPA Method 1668A
Polycyclic Aromatic Hydrocarbons - KNOX-ID-0016
Semi-volatile Organic Compounds – SW846 8270C

Day

TestAmerica Laboratories, Inc.

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The results reported herein are applicable to the samples submitted for analysis only. If you have questions regarding this report, please call (865) 291-3000 and ask to speak with the TestAmerica project manager listed on the cover page of this report.

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The original chain of custody documentation is included with this laboratory report.

Sample Receipt

Custody seals were not present on the sample shipments upon arrival at the laboratory.

The sample container for the Run 1 Back Half Rinse was received broken.

Quality Control and Data Interpretation

Unless otherwise noted, all holding times and QC criteria were met and the test results shown in this report meet all applicable NELAC requirements.

Combined Method 0010 Sampling Train With Method 23 Sampling Train Laboratory Processing

The field sample collection tasks included the use of a Method 0010 sampling train combined with a Method 23 sampling train. The Method 0010 / 23 sampling objectives included stack gas evaluations for the following classes of analytes:

- Semi-volatile compounds analyzed by SW-846 Method 8270 (Full Scan + TICs)
- PAHs analyzed by Low-level Selective Ion Monitoring (SIM) High Res GC/MS
- PCBs analyzed by EPA Method 1668A
- And dioxins and furans analyzed by SW-846 Method 8290.

The field sampling tasks included the collection of the standard sampling train fractions according to the requirements of SW-846 Method 3542 in addition to the additional fractions required for the collection of dioxin and furan samples. This standard sampling train breakdown renders six (6) sample fractions and two (2) toluene rinse fractions that are submitted to the laboratory for processing. The fractions are as follows:

- The particulate filter (collected in a Petri dish)
- The front-half nozzle, probe, and front-half of the filter holder acetone and methylene chloride solvent rinses,
- A separate front-half nozzle, probe, and front-half of the filter holder toluene solvent rinse (for D/Fs, only)
- An XAD-2 resin module
- The back-half of the filter holder and connecting glassware acetone and methylene chloride solvent rinses,
- A separate back-half of the filter holder and connecting glassware toluene solvent rinses,

- The condensate and impinger contents composite,
- And an acetone and methylene chloride solvent rinse of the connecting glassware behind the XAD-2 module and glassware connecting the impingers.

The Front-half fractions were composited in the laboratory for extraction in a Soxhlet apparatus. Extraction was conducted using methylene chloride and a second extraction was conducted using toluene. The sample process was followed for the Back-half fractions. The Condensate portions underwent extraction with methylene chloride, only.

Extracts from the Soxhlet process were combined in such a way as to acquire representative composites for each Front-half or Back-half fraction for the analyte types being determined by these sampling trains. Four (4) separate extract portions were then divided off of the final extract composites for each analyte type outlined above. Since the Condensate fraction composites are analyzed for only three (3) analyte types, and not analyzed for dioxins and furans, only three extract portions were divided off of the final extract composites for them.

A relatively low level contamination was introduced into the sampling train extracts by the Method 8270 surrogate spiking materials used. Biphenyl was determined to be a low level contaminate in the Method 8270 surrogate spiking material because it appears on the PAH SIM Low Level Method as a target analyte. The actual train XAD-2 resin fractions had large biphenyl hits in them which render the low levels introduced by the spiking program inconsequential in comparison. The contamination level in LCS, media blanks, and train blank samples can be used to evaluate the level of biphenyl contributed by the surrogate spikes.

Each analyte class can be summarized for a general analytical laboratory process understanding. The summaries are as follows:

PAHs by Low Level Selective Ion Monitoring (SIM) High Resolution GC/MS

The method 0010 sampling train components were extracted and analyzed for polyaromatic hydrocarbons (PAHs) using TestAmerica Knoxville standard operating procedures KNOX-OP-0009 and KNOX-ID-0016, based on the following extraction method:

SW-846 3542, "Extraction of Semivolatile Analytes Collected Using Method 0010 (Modified Method 5 Sampling Train)"

The sampling trains are prepared as three analytical fractions:

- The particulate filter and front half of the filter holder, nozzle and probe solvent rinses are combined as one sample.
- The XAD-2 resin trap and back half of the filter holder, coil condenser and connecting glassware solvent rinses are combined as a separate sample.
- The condensate, impinger contents and their related glassware solvent rinses make up a third sample.

The condensate fraction extracts were split three ways and the particulate filters and XAD-2 resin fractions were split four ways to accommodate the required analysis. The filters and XAD components are spiked with the appropriate amount of SIM PAH internal standards and the

components are Soxhlet extracted with methylene chloride. The condensate portion for this analyses were spiked with the appropriate levels of internal standards and extracted using a continuous liquid-liquid extractor. The condensate extracts were final concentrated to 0.5 mL while the Front- half and Back-half are final concentrated to 0.25mL and analyzed by by SIM-HRGC/LRMS.

A field QC sampling surrogate was added to the XAD-2 resin by the laboratory prior to the field sampling campaign. The results for the sampling surrogate recoveries appear with the "Internal Standard" percent recovery data.

Note that the labeled internal standards added prior to extraction serve both as a measurement of the extraction efficiency of the method as well as a measure of cleanup recovery efficiency.

The dilution factor reported on the sample result form represents a combination of factors (such as dilution, sample weight/volume adjustment, split ratio, etc.) used to adjust the reporting limits and method detection limits.

Due to the combined extraction where each sampling train composite fraction is split for the different required analysis, each sample was spiked with the necessary internal standards and surrogates before the extractions are commenced. Consequently, one of the target analytes was detected as a background contaminate in all the samples, method blanks, trip blanks and media checks above the reporting limit during the SIM-PAH analysis. A "Spike Interference Check", which contains all the necessary internal standards and surrogates required for each analysis, was analyzed and confirmed the presence of biphenyl in the spikes. When the concentration of biphenyl in the samples is approximately the same concentration found in the associated method blank, trip blank, and media check, the result should be considered to have been derived from the spiking program. However, high concentrations of biphenyl in the samples appear to be from the small amount in the spike plus the amount collected during the sampling event.

Several of the back-half samples were reported with elevated reporting limits for all PAH analytes. Dilution of the samples because of high analyte levels was necessary prior to analysis and the reporting limits were adjusted accordingly.

Note that the concentration of one or more target compounds in several of these samples exceeded the calibration range even at the maximum fifty-fold dilution allowed by this isotope dilution method. Since some compounds saturated the detector or were extremely high in concentration, the samples were analyzed at a further dilution by using a post-dilution spike technique to bring the concentration of the compound into the instrument calibration range. Due to the addition of the internal standards after extraction, isotope dilution technique correction does not apply to the affected samples. The reporting limits have been adjusted accordingly.

Several samples have one or more internal standard recoveries outside QC limits (high) due to apparent matrix interferences. Under these conditions an apparent low bias of the analytes associated with these internal standards will be incurred.

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Several samples have one or more internal standard recoveries outside QC limits (low). Even though the recoveries were below limits, the signal-to-noise ratio was greater than 10:1. The results are reported in accordance with our standard operating procedure and as indicated by the referenced method, isotope dilution techniques produce results that are corrected for the internal standard recovery and should be usable for their intended purposes.

On the analysis of the "Front Half" samples M23-0010 RUN 1 FH and M23-0010 RUN 4 FH had several internal standards outside QC limits on the original analysis and the diluted analysis. Sample M23-0010 RUN 1 FH, had the coeluting pair benzo(b)fluoranthene and benzo(k)fluoranthene reported from the diluted analysis. The interference that hindered the internal standard recoveries on the original analysis was removed on the dilution analysis. The other native analytes associated with an elevated internal standard recovery outside QC limits that were still reported from the original analysis; the dilution did not minimize the interference effect on the internal standard recoveries. These compounds associated with the high internal standards will have a low bias. Sample M23-0010 RUN 4 FH had internal standard recoveries outside QC limits. The diluted analysis removed the effects of the interferences on these internal standards. The native analytes associated with these internal standards were reported from the dilution analysis.

On the analysis of the 'Back Half" samples, it was noticed that there was a difference in chromatography and concentration between the maximum bench dilution analysis and the post-dilution spike analysis for benzo(a)pyrene; there appears to be a co-elution in the maximum bench dilution. The results from the maximum bench dilution are reported to give a maximum possible concentration, and are qualified with a "CI" to indicate that there is reason to suspect these may have a high bias.

On the analysis of the "Back Half" samples, matrix interferences were observed for several internal standards; the associated analytes were reported from the post-dilution spike analysis. In some cases, even if the recoveries were within acceptable range on the original analysis, the interferences were still present, so the analytes associated with these internal standards were reported from the post dilution spike.

On review of the data, it was noticed that in several samples, the peaks identified by the data system for multiple target analytes exhibited very slight retention time shift or a shoulder on the peak that could not be resolved. Therefore, these compounds have been flagged with "CI" to indicate that although they met the qualitative criteria of the method, there is reason to suspect these may be biased high.

Some benzo(b)fluoranthene and benzo(k)fluoranthene results were qualified with an "EST" flag to indicate that the value is estimated due to a co-eluting peak. These two compounds could not be resolved due to the difficult sample matrix.

<u>Semivolatile Full Scan Analyses Including TICs - (Method SW846 8270C)</u>

The semivolatile organic sampling train components were extracted and analyzed using TestAmerica Knoxville standard operating procedures KNOX-OP-0009 and KNOX-MS-0016, based on the following methods:

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- SW-846 3542, "Extraction of Semivolatile Analytes Collected Using Method 0010 (Modified Method 5 Sampling Train)"
- SW-846 8270C, "Semivolatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS)".

The sampling trains are prepared as three analytical fractions: The particulate filter and front half of the filter holder, nozzle and probe solvent rinses are combined as one sample. The XAD-2 resin trap and back half of the filter holder, coil condenser and connecting glassware solvent rinses are combined as a separate sample. The condensate, impinger contents and their related glassware solvent rinses make up a third sample.

The particulate filter and XAD-2 components are spiked with the method 8270C surrogates and the components are Soxhlet extracted with methylene chloride. The condensates are spiked with the surrogates and extracted using a separatory funnel. The extracts are concentrated to 1 mL and analyzed by GCMS.
Sample results were calculated using the following equation:

$$\text{Result, ug} = (\text{On column concentration, ng/uL}) \times \left(\frac{\text{Volume final extract, uL}}{\text{1 Sample}}\right) \times \left(\frac{\text{1ug}}{\text{1000 ng}}\right) \times \text{DF} \times \text{SF}$$

Where: DF = Bench Dilution Factor
SF = Extraction Split Factor

One or more surrogate recoveries for sample M23-0010 RUN 1 BH were outside QC limits. Since the recoveries were elevated above the laboratory QC limits, the results for the sample may be biased high.

The laboratory control sample and laboratory control sample duplicate results for batches 6118026, 6118027, and 6118028 were outside control limits for several analytes.

Several samples were reported with elevated reporting limits for all analytes due to required sample dilution. Based on screening results, a dilution was necessary prior to analysis and the reporting limits were adjusted accordingly.

Note that a dilution factor reported on the sample result form represents a combination of factors (such as dilution, sample weight/volume adjustment, split ratio, etc.) used to adjust the reporting limits and method detection limits.

Laboratory control sample/laboratory control sample duplicates are performed instead of a matrix spike/matrix spike duplicates for Method 0010 sampling trains in batches 6118026, 6118027, and 6118028.

Dioxin and Furan Analyses Analyzed by Method 8290

All positive 2378-TCDF results at or above the minimum level were confirmed on a DB-225 column. The raw data for the DB-225 analyses is included in the data package directly following the primary column analyses.

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Samples M23-0010 RUN 1 COMBINED, M23-0010 RUN 2 COMBINED, M23-0010 RUN 3 COMBINED, M23-0010 RUN 4 COMBINED, and M23-0010 RUN 5 COMBINED exhibited total TCDD above the calibration range. Samples M23-0010 RUN 3 COMBINED, M23-0010 RUN 4 COMBINED, and M23-0010 RUN 5 COMBINED also exhibited total TCDF above the calibration range. The method does not require further action be taken. The results were reported as is with an "E" qualifier.

The following flags are used to qualify results for chlorinated dioxin and furan results:

J – The reported result is an estimate. The amount reported is below the Minimum Level (ML). The qualitative definition of the ML is "the lowest level at which the analytical system must give a reliable signal and an acceptable calibration point". The ML was introduced in EPA Methods 1624 and 1625 in 1980 and was promulgated in these methods in 1984 at 40 CFR Part 136, Appendix A. For the purposes of this report, the ML is qualitatively defined as described above, and quantitatively defined as follows:

Minimum Level: The concentration or mass of analyte in the sample that corresponds to the lowest calibration level in the initial calibration. It represents a concentration (in the sample extract) equivalent to that of the lowest calibration standard, after corrections for method-specified sample weights, volumes and cleanup procedures has been employed.

Example: The lowest calibration level for TCDD in the initial calibration is 0.5 pg/uL. A mass of 10 pg of 2,3,7,8-TCDD in the sample would result in a concentration of 0.5 pg/uL in the sample extract (at a final volume of 20 uL). Since the concentration in the sample extract corresponds to the concentration in the lowest calibration standard, the 10 pg mass in the sample components is the ML. If the sample extract is further diluted, the ML will increase by the dilution factor.

Example: A 1/10 dilution is performed on the sample extract described above. The ML for 2,3,7,8-TCDD becomes 100 pg rather than the default of 10 pg.

E – The reported result is an estimate. The amount reported is above the Upper Calibration Level (UCL) described below. The quantitative definition of the UCL is listed below:

Upper Calibration Level: The concentration or mass of analyte in the sample that corresponds to the highest calibration level in the initial calibration. It is equivalent to the concentration of the highest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

Example: The maximum calibration level for TCDD in the initial calibration is 200 pg/uL. A mass of 4000 pg of 2,3,7,8-TCDD in the sampling components would result in a concentration of 200 pg/uL in the sample extract (at a final volume of 20 uL). Since the concentration in the sample extract corresponds to the concentration in the highest calibration standard, the 4000 pg mass in the sample components is the UCL. If the sample extract is further diluted, the ML will increase by the dilution factor.

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Example: A 1/10 dilution is performed on the sample extract described above. The UCL for 2,3,7,8-TCDD becomes 40,000 pg rather than the default of 4000 pg. In this example, all positive 2,3,7,8-TCDD results above 40,000 pg are flagged with an E.

B – The analyte is present in the associated method blank at a detectable level. For this analysis, there is no method specified reporting level other than the qualitative criterion that peaks must exhibit a signal-to-noise ratio of $\geq$2.5 to 1. Therefore, the presence of any reportable amount of the analyte in the blank will result in a B qualifier on all associated samples.

Q – Estimated maximum possible concentration. This qualifier is used when the result is generated from chromatographic data that does not meet all the qualitative criteria for a positive identification given in the method. These may include one or more of the following:

- Ion abundance ratios must be within specified limits (+/-15% of theoretical ion abundance ratio).
- Retention time criteria (relative to the method-specified isotope labeled retention time standard).
- Co-maximization criterion. The two quantitation ion peaks must reach their maxima within 2 seconds of each other.
- 2,3,7,8-TCDF result is reported from the non-isomer specific Rtx-5 column.
- Polychlorinated dibenzofuran purity. An interference may be present on the indicated polychlorinated dibenzofuran when a polychlorinated diphenyl ether peak is present and maximizes within +/- 3 seconds of the dibenzofuran candidate.

S – Ion suppression evident. The trace indicating the signal from the lock mass of the calibration compound shows a deflection at the retention time of the analyte. This may indicate a temporary suppression of the instrument sensitivity due to a matrix-borne interference.

C – Coeluting Isomer. The isomer is known to coelute with another member of its homologue group, or the peak shape is shouldered, indicating the likelihood of a coeluting isomer.

X – Other. See explanation in narrative.

Laboratory studies supporting risk assessment and Total Maximum Daily Load (TMDL) evaluations, frequently use qualified data reported as low as the Method Detection Limit (MDL), or the Estimated Detection Limit (EDL). Several of EPA's isotope dilution methods employ the EDL.[1,2,3] The EDL is based on a direct measurement of the signal-to-noise (S/N) ratio acquired during sample analysis. This S/N measurement is used to calculate the concentration in the sample corresponding to the minimum intensity of the smallest quantifiable peak. The EDL reflects the amount of the particular analyte which would be required to cause a positive result for the particular analysis. Because the S/N obtained covaries with recovery, instrument sensitivity and sample-specific cleanup efficacy, the EDL is a more valid measure of the sensitivity of the entire analytical process for the specific sample than is an MDL run periodically on a reference matrix.

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The EDL is typically calculated according to the following equation:

$$\text{Estimated Detection Limit} = \frac{N \times 2.5 \times Qis}{His \times RRF \times W \times S}$$

Where:

N	=	peak to peak noise of quantitation ion signal in the region of the ion chromatogram where the compound of interest is expected to elute
His	=	peak height of quantitation ion for appropriate internal standard
Qis	=	ng of internal standard added to sample
RRF	=	mean relative response factor of compound obtained during initial calibration
W	=	amount of sample extracted (grams or liters)
S	=	percent solids (optional, if results are requested to be reported on dry weight basis)

(The area of the internal standard is sometimes used instead of height, along with an area-to-height conversion factor.)

This method of estimating the detection limit differs from the MDL in that it does not carry the requirement that the sample be statistically distinguished as being from a contaminated population. As results approach the EDL, the risk of false positives and the analytical uncertainty increase significantly. However, a low false positive well below the ML or MDL is often closer to the true value than an assumption that the target analyte is present at the detection or reporting limits. For relatively clean samples, MDL studies may give an elevated estimate of the detection limit. Additionally, on contaminated samples, the MDL may give a falsely low estimate of the detection limit.

$$\text{Analyte Concentration} = \frac{As \times Qis}{Ais \times RRF \times W \times S}$$

Where:

As	=	Sum of areas of the target peaks
Qis	=	ng of internal standard added to sample
Ais	=	Sum of areas of the internal standard peaks
RRF	=	mean relative response factor of compound obtained during initial calibration
W	=	amount of sample extracted (grams or liters)
S	=	percent solids (optional, if results are requested to be reported on dry weight basis)

In sample data, peaks must have an intensity of $\geq$2.5 times the height of the background noise in order to be considered. Careful examination of the two equations above reveals that for the concentration of the smallest peak detectable (per the EDL equation) to exactly equal the smallest peaks that are calculated, requires that the average height to area ratio obtained during the calibration must equal the area to height ratio for every peak obtained near 2.5 times the noise. When the area to height ratio on a peak in a sample is less than the average obtained during calibration, the calculated result will correspond to a peak that would have been less than 2.5 times the noise on the calibration. This is the result of normal variability. Because

the source methods for the EDL (SW-846 8290 and 8280A) do not provide for censoring of results by any other magnitude standard than being 2.5 times the noise, the laboratory does not censor at the calculated EDL. Hence, detections may be reported below the estimated detection limits.

Footnotes:

1. Code of Federal Regulations, Part 136, Chapter 1, Appendix 1, October 1994: Method 1613 Tetra- Through Octa-Chlorinated Dioxins and Furans by Isotope Dilution High Resolution Gas Chromatography/High Resolution Mass Spectrometry.
2. U.S. EPA. Test Methods for Evaluating Solid Waste, Volume II, SW-846, Update III, December 1996. Method 8280A: The Analysis of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans by High Resolution Gas Chromatography/Low Resolution Mass Spectrometry.
3. U.S. EPA. Test Methods for Evaluating Solid Waste, SW-846. Third Edition. March 1995 Method 8290: Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans by High Resolution Gas Chromatography/High Resolution Mass Spectrometry.

PCBs Analyzed by Method 1668A

Due to the extraction technique where each sample is split for different analysis before extraction, each sample was spiked with the necessary internal standards and surrogates required for each analysis. Consequently, a target analyte, PCB 1, was detected in all method blanks above the minimum level (ML). A "Spike Interference Check", which contains all the necessary internal standards and surrogates required for each analysis, was analyzed and confirmed the presence of PCB 1 in the spikes. When the concentration of PCB 1 in the samples is approximately the same concentration found in the associated method blank the result may be considered attributed to the spike. Higher concentration in the samples may be considered attributed to the spike plus the amount collected during the sampling event.

For sample M23-0010 RUN 4 BH the recovery of internal standard 13C12-PCB 1 was 24%, which is below the lower acceptance criterion (30%). The minimum required signal-to-noise ratio was present, and the target estimated detection limit for associated analytes was met. The results are reported in accordance with the standard operating procedure. As indicated by the referenced method, isotope dilution techniques produce results that are independent of internal standard recovery.

For samples M23-0010 RUN 4 CONDENSATE and M23-0010 RUN 5 CONDENSATE the recovery of internal standard 13C13-PCB 54 was slightly above the upper acceptance criterion (140%) at 141%. The results are reported in accordance with the standard operating procedure. As indicated by the referenced method, isotope dilution techniques produce results that are independent of internal standard recovery.

For sample M23-0010 RUN 1 BH the recovery of surrogate standard 13C12-PCB 8 was 49%, which is below the lower acceptance criterion (50%). The minimum required signal-to-noise ratio was present. All other surrogates were within limits.

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Sample M23-0010 RUN 1 BH exhibited PCB 3 above the upper calibration level (UCL) at the maximum 10-fold dilution. No sample was available for re-extraction; therefore, the result was reported as is with an "E" qualifier.

Several samples were diluted 10-fold due to native PCB levels and/or severe ion suppression.

Nomenclature – The standardization strategy described in this report uses the naming convention of SW-846 Method 8290. This convention differs from Method 1668 in the following manner:

Standard Addition Occurs Prior to:	Method 1668	SW-846 Conventions Used in this Report
Sampling	None	Sampling Surrogate
Extraction	Labeled Toxics/LOC/Window Defining	Internal Standard
Cleanups	Labeled Cleanup Standard	Cleanup Standard*
Injection	Labeled Injection Internal Standard	Recovery Standard

* Cleanup Standard is also referred to as Surrogate Standard on report.

The shorthand notation used for congeners in this report is summarized in Table 2.

Qualifiers – The following flags are used to qualify results for HRMS PCB results:

J – The reported result is an estimate. The amount reported is below the Estimated Minimum Level (EML). EML is defined by the method as the lowest concentration at which an analyte can be measured reliably with common laboratory interferences present. This value has been determined for each congener by MDL and laboratory method blank studies. The value is adjusted to reflect sample specific initial and final volumes.

E – The reported result is an estimate. The amount reported is above the UCL described below.

The E qualifier is applied on the basis of the **Upper Calibration Level (UCL)**. The quantitative definition of the UCL is listed below:

Upper Calibration Level: The concentration or mass of analyte in the sample that corresponds to the highest calibration level in the initial calibration. It is equivalent to the concentration of the highest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

B – The analyte is present in the associated method blank at a reportable level. For this analysis, there is no method specified reporting level, other than the qualitative criterion that peaks must exhibit a signal-to-noise ratio of 2.5-to-1. Therefore, the presence of any

amount of the analyte present in the blank will result a B qualifier on all associated samples.

Note: Some laboratories do not report contamination in the blank unless it is above their lower calibration limit, or an established percentage of the level in the samples, or an established percentage of the regulatory limit. Likewise, some laboratories set a reporting limit at one half the lower calibration limit.

Q – Estimated maximum possible concentration. This qualifier is used when the result is generated from chromatographic data that does not meet all the qualitative criteria for a positive identification given in the method. The criteria include the following areas:

- Ion abundance ratios must be within specified limits (+/-15% of theoretical ion abundance ratio.)
- Retention time criteria (relative to the method-specified isotope labeled retention time standard).
- Co-maximization criterion. The two quantitation ion peaks must reach their maxima within 2 seconds of each other.

S – Ion suppression evident. The trace indicating the signal from the lock mass of the calibration compound shows a deflection at the retention time of the analyte. This may indicate a temporary suppression of the instrument sensitivity, due to a matrix-borne interference.

C – Coeluting Isomer. The isomer is known to coelute with another member of its homologue group, or the peak shape is shouldered, indicating the likelihood of a coeluting isomer. When the C flag is followed by a number, the number indicates the lowest numbered congener among the coelution set. For example, if 100 pg/L is detected at the retention time of PCB 156, and PCB 157 is known to coelute with PCB 156, the results will be flagged as follows:

PCB 156 100 pg/L C

PCB 157 100 pg/L C156

In certain electronic deliverables the result field for PCB 157 will be null, with "C156" appearing in the qualifier field in accordance with the CARP EDD specification.

X – Other. See explanation in narrative.

Results – The results for the analyses are summarized in the following pages. Please see comments regarding qualifiers, above. Additional information regarding qualifiers is explained in the legends at the end of each result summary. A summary of the shorthand conventions used in this report is provided in Table 2.

Detection Limits – For all analyte results a sample specific detection limit is calculated for that analyte. This is done by first determining the GC/MS peak height of the noise or interferent in the expected region of the analyte signal. This value is multiplied by the number 2.5, which serves as a safety factor. The 2.5 safety factor is disregarded if the noise present in the analyte region is a result of chemical interferences. The resulting signal response value is then used to estimate the minimum detectable analyte amount. The result is the estimated sample detection limit.

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When an analyte is not detected, an ND appears in place of the result. The value in the detection limit column is the estimated detection limit for the analyte in that particular sample.

EXAMPLE CALCULATIONS

The following formulas were used for sample calculations. Examples are given for calculating the percent recovery for internal standard $^{13}C_{12}$-PCB 1, the concentration of native PCB 1 and the EDL for PCB 1. All values used in the calculations below are typical (i.e. not extracted from a particular sample). Actual values are found on the IsoCalc Preliminary Sample Report (IPSR) at the position indicated (in parentheses, below):

INTERNAL STANDARD RECOVERY ($^{13}C_{12}$-PCB 1)

$$\text{Percent Recovery} = \frac{\Sigma A_{IS} \bullet W_{RS} \bullet 100\%}{\Sigma A_{RS} \bullet W_{IS} \bullet RRF}$$

ΣA_{IS} = Sum of areas for the Internal Standard quantitation ions. (IPSR – Column "Area", Row "13C12-PCB 1")

W_{RS} = Mass in ng of the Recovery Standard. (IPSR – Column "Std Amt", Row "13C12-PCB 9")

ΣA_{RS} = Sum of areas for the Recovery Standard quantitation ions. (IPSR – Column "Area", Row "13C12-PCB 9")

W_{IS} = Mass in ng of the Internal Standard. (IPSR – Column "Std Amt", Row "13C12-PCB 1")

RRF = Internal Standard mean relative response factor from the initial multipoint calibration. (IPSR - Column "RF", Row "13C12-PCB 1".)

Substituting typical values ,
$$\frac{1106275 \bullet 2.000\,(ng) \bullet 100\%}{1205581 \bullet 2.000\,(ng) \bullet 1.412} = 65\%\ \text{Recovery}$$

NATIVE ANALYTE QUANTITATION (PCB 1)

$$\text{Conc} = \frac{\Sigma A_X \bullet W_{IS}}{\Sigma A_{IS} \bullet V \bullet 0.001\,(mL/L) \bullet RRF}$$

ΣA_X = Sum of areas for analyte quantitation ions. (IPSR – Area Column "Area", Row "PCB 1")

W_{IS} = Mass in ng of Internal Standard. (IPSR – Column "Std Amt", Row "13C12-PCB 1")

ΣA_{IS} = Sum areas for the Internal Standard. (IPSR – Column "Area", Row 13C12-PCB 1)

V = Volume of sample extracted in mL. (IPSR – Header Column 2, Row "Initial Wt/Vol")

RRF = Native analyte mean relative response factor from the initial calibration, or daily response factor as appropriate. (IPSR – Column "RF", Row "PCB 1")

Substituting typical values, $\frac{8951 \bullet 2.000\ (ng)}{1106275 \bullet 2200\ (mL) \bullet 0.001\ (mL/L) \bullet 1.136}$ = 0.00647 ng/L = 6.47 pg/L

CALCULATION OF SAMPLE SPECIFIC ESTIMATED DETECTION LIMIT

This calculation uses the noise values found on the IsoCalc Preliminary Peak Report (IPPR), which follows the IPSR. All the other values used in the equation are found on the IPSR.)

$$\frac{\Sigma I_X \bullet W_{IS} \bullet T_{SN}}{\Sigma I_{IS} \bullet V \bullet 0.001\ (mL/L) \bullet RRF}$$

ΣI_X = Sum of the intensities of the noise levels of the characteristic ions in the region of analyte elution. (IPPR – Columns "Height1" and "Height2", Row {mass} 188, Sub-Row "Noise").

W_{IS} = Mass in ng of the Internal Standard. (IPSR – Column "Std Amt", Row "13C12-PCB 1").

T_{SN} = Minimum Signal-to-Noise threshold. = 2.5. A constant, specified by the method.

ΣI_{IS} = Intensity of the corresponding ^{13}C ions. (IPSR – Column "Height", Row "13C12-PCB 9")

V = Volume of sample extracted in mL. (IPSR – Header Column 2, Row "Initial Wt/Vol")

RRF = Native analyte mean relative response factor from the initial calibration or daily standard as appropriate. (IPSR – Column "RF", Row "PCB 1")

Substituting typical values $\frac{79 \bullet 2000\ (pg) \bullet 2.5}{334600 \bullet 2200\ (mL) \bullet 0.001\ (mL/L) \bullet 1.136}$ = 0.466 pg/L

In sample data, peaks must have an intensity of 2.5 times the height of the background noise in order to be considered. Careful examination of the two equations above, and a bit of algebra reveals that for the concentration of the smallest peak detectable (per the EDL equation) to exactly equal the smallest peaks that are calculated, requires that the average height to area ratio obtained during the calibration must equal the area to height ratio for every peak obtained near 2.5 times the noise. When the area to height ratio on a peak in a sample is less than the average obtained during calibration, the calculated result will correspond to a peak that would have been less than 2.5 X the noise on the calibration. This is the result of normal variability. Because the source method for the EDL (EPA 1668) does not provide for censoring of results by any other magnitude standard than being 2.5 times the noise, the laboratory does not censor at the calculated EDL. Hence, detections may be reported below the estimated detection limits.

Table 1							
Concentration of PCBs in Calibration Solutions							
		CS 0.5	CS 1	CS 2	CS 3[2]	CS 4	CS 5
Analyte Type	BZ/IUPAC[1]	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL
Congeners							
2-MoCB	1	0.5	1.0	5.0	50	400	2000
4-MoCB	3	0.5	1.0	5.0	50	400	2000
2,2'-DiCB	4	0.5	1.0	5.0	50	400	2000
4,4'-DiCB	15	0.5	1.0	5.0	50	400	2000
2,2',6'-TrCB	19	0.5	1.0	5.0	50	400	2000
3,4,4'-TrCB	37	0.5	1.0	5.0	50	400	2000
2,2',6,6'-TeCB	54	0.5	1.0	5.0	50	400	2000
3,3',4,4'-TeCB	77	0.5	1.0	5.0	50	400	2000
3,4,4',5-TeCB	81	0.5	1.0	5.0	50	400	2000
2,2',4,6,6'-PeCB	104	0.5	1.0	5.0	50	400	2000
2,3,3',4,4'-PeCB	105	0.5	1.0	5.0	50	400	2000
2,3,4,4',5-PeCB	114	0.5	1.0	5.0	50	400	2000
2,3',4,4',5-PeCB	118	0.5	1.0	5.0	50	400	2000
2',3,4,4',5-PeCB	123	0.5	1.0	5.0	50	400	2000
3,3',4,4',5-PeCB	126	0.5	1.0	5.0	50	400	2000
2,2',4,4',6,6'-HxCB	155	0.5	1.0	5.0	50	400	2000
2,3,3',4,4',5-HxCB	156	0.5	1.0	5.0	50	400	2000
2,3,3',4,4',5'-HxCB	157	0.5	1.0	5.0	50	400	2000
2,3',4,4',5,5'-HxCB	167	0.5	1.0	5.0	50	400	2000
3,3',4,4',5,5'-HxCB	169	0.5	1.0	5.0	50	400	2000
2,2',3,4',5,6,6'-HpCB	188	0.5	1.0	5.0	50	400	2000
2,3,3',4,4',5,5'-HpCB	189	0.5	1.0	5.0	50	400	2000
2,2',3,3',5,5',6,6'-OcCB	202	0.5	1.0	5.0	50	400	2000
2,3,3',4,4',5,5',6-OcCB	205	0.5	1.0	5.0	50	400	2000
2,2',3,3',4,4',5,5',6-NoCB	206	0.5	1.0	5.0	50	400	2000
2,2',3,3',4',5,5',6,6'-NoCB	208	0.5	1.0	5.0	50	400	2000
DeCB	209	0.5	1.0	5.0	50	400	2000
All other CB congeners		0.5	1.0	5.0	50	400	2000
Labeled Congeners							
$^{13}C_{12}$-2-MoCB	1L	100	100	100	100	100	100
$^{13}C_{12}$-4-MoCB	3L	100	100	100	100	100	100
$^{13}C_{12}$-2,2'-DiCB	4L	100	100	100	100	100	100
$^{13}C_{12}$-4,4'-DiCB	15L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',6-TrCB	19L	100	100	100	100	100	100
$^{13}C_{12}$-3,4,4'-TrCB	37L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',6,6'-TeCB	54L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4'-TeCB	77L	100	100	100	100	100	100
$^{13}C_{12}$-3,4,4',5-TeCB	81L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',4,6,6'-PeCB	104L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4'-PeCB	105L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,4,4',5-PeCB	114L	100	100	100	100	100	100
$^{13}C_{12}$-2,3',4,4',5-PeCB	118L	100	100	100	100	100	100
$^{13}C_{12}$-2',3,4,4',5-PeCB	123L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4',5-PeCB	126L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',4,4',6,6'-HxCB	155L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5-HxCB	156L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5'-HxCB	157L	100	100	100	100	100	100
$^{13}C_{12}$-2,3',4,4',5,5'-HxCB	167L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4',5,5'-HxCB	169L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,4',5-HpCB	170L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,4',5,6,6'-HpCB	188L	100	100	100	100	100	100

Table 1							
Concentration of PCBs in Calibration Solutions							
		CS 0.5	CS 1	CS 2	CS 3[2]	CS 4	CS 5
Analyte Type	BZ/IUPAC[1]	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL
$^{13}C_{12}$-2,3,3',4,4',5,5'-HpCB	189L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB	202L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5,5',6-OcCB	205L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NoCB	206L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4',5,5',6,6'-NoCB	208L	100	100	100	100	100	100
$^{13}C_{12}$-DeCB	209L	100	100	100	100	100	100
Cleanup Standards							
$^{13}C_{12}$-2,4,4'-TriCB	28L	0.5	1.0	5.0	50	400	--
$^{13}C_{12}$-2,3,3',5,5'-PeCB	111L	0.5	1.0	5.0	50	400	--
$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB	178L	0.5	1.0	5.0	50	400	--
Recovery Standards							
$^{13}C_{12}$-2,5-DiCB	9L	100	100	100	100	100	100
$^{13}C_{12}$-2,4',5-TriCB	31L	100	100	100	100	100	100
$^{13}C_{12}$-2,4',6-TriCB	32L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',5,5'-TeCB	52L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',4',5,5'-PeCB	101L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,5,5'-PeCB	127L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3',4,4',5'-HxCB	138L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,4,4',5,5'-HpCB	180L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,4',5,5'-OcCB	194L	100	100	100	100	100	100
Labeled Sampling Surrogates							
$^{13}C_{12}$-2,4'-DiCB	8L	0.5	1.0	5.0	50	400	--
$^{13}C_{12}$-3,3',4,5'-TeCB	79L	0.5	1.0	5.0	50	400	--
$^{13}C_{12}$-2,2',3,5',6-PeCB	95L	0.5	1.0	5.0	50	400	--
$^{13}C_{12}$-2,2',4,4',5,5'-HxCB	153L	0.5	1.0	5.0	50	400	--

1. Suffix "L" indicates labeled compound.
2. Calibration verification solution.

Table 2					
PCB Shorthand Nomenclature[4] Used in this Report					
BZ/IUPAC Number[1].	PCB Chemical Structure Name[2]	CAS Registry[3] Number	BZ/IUPAC Number[1].	PCB Chemical Structure Name[2]	CAS Registry[3] Number
1	2-monochlorobiphenyl	2051-60-7	106	2,3,3',4,5-pentachlorobiphenyl	70424-69-0
2	3-monochlorobiphenyl	2051-61-8	107/109	2,3,3',4',5-pentachlorobiphenyl	70424-68-9
3	4-monochlorobiphenyl	2051-62-9	108/107	2,3,3',4,5'-pentachlorobiphenyl	70362-41-3
4	2,2'-dichlorobiphenyl	13029-08-8	109/108	2,3,3',4,6-pentachlorobiphenyl	74472-35-8
5	2,3-dichlorobiphenyl	16605-91-7	110	2,3,3',4',6-pentachlorobiphenyl	38380-03-9
6	2,3'-dichlorobiphenyl	25569-80-6	111	2,3,3',5,5'-pentachlorobiphenyl	39635-32-0
7	2,4-dichlorobiphenyl	33284-50-3	112	2,3,3',5,6-pentachlorobiphenyl	74472-36-9
8	2,4'-dichlorobiphenyl	34883-43-7	113	2,3,3',5',6-pentachlorobiphenyl	68194-10-5
9	2,5-dichlorobiphenyl	34883-39-1	114	2,3,4,4',5-pentachlorobiphenyl	74472-37-0
10	2,6-dichlorobiphenyl	33146-45-1	115	2,3,4,4',6-pentachlorobiphenyl	74472-38-1
11	3,3'-dichlorobiphenyl	2050-67-1	116	2,3,4,5,6-pentachlorobiphenyl	18259-05-7
12	3,4-dichlorobiphenyl	2974-92-7	117	2,3,4',5,6-pentachlorobiphenyl	68194-11-6
13	3,4'-dichlorobiphenyl	2974-90-5	118	2,3',4,4',5-pentachlorobiphenyl	31508-00-6
14	3,5-dichlorobiphenyl	34883-41-5	119	2,3',4,4',6-pentachlorobiphenyl	56558-17-9
15	4,4'-dichlorobiphenyl	2050-68-2	120	2,3',4,5,5'-pentachlorobiphenyl	68194-12-7
16	2,2',3-trichlorobiphenyl	38444-78-9	121	2,3',4,5',6-pentachlorobiphenyl	56558-18-0
17	2,2',4-trichlorobiphenyl	37680-66-3	122	2',3,3',4,5-pentachlorobiphenyl (2,3,3',4',5'-pentachlorobiphenyl)	76842-07-4

Table 2					
PCB Shorthand Nomenclature[4] Used in this Report					
BZ/IUPAC Number[1].	PCB Chemical Structure Name[2]	CAS Registry[3] Number	BZ/IUPAC Number[1].	PCB Chemical Structure Name[2]	CAS Registry[3] Number
18	2,2',5-trichlorobiphenyl	37680-65-2	123	2',3,4,4',5-pentachlorobiphenyl (2,3',4,4',5'-pentachlorobiphenyl)	65510-44-3
19	2,2',6-trichlorobiphenyl	38444-73-4	124	2',3,4,5,5'-pentachlorobiphenyl (2,3',4',5',5-pentachlorobiphenyl)	70424-70-3
20	2,3,3'-trichlorobiphenyl	38444-84-7	125	2',3,4,5,6'-pentachlorobiphenyl (2,3',4',5',6-pentachlorobiphenyl)	74472-39-2
21	2,3,4-trichlorobiphenyl	55702-46-0	126	3,3',4,4',5-pentachlorobiphenyl	57465-28-8
22	2,3,4'-trichlorobiphenyl	38444-85-8	127	3,3',4,5,5'-pentachlorobiphenyl	39635-33-1
23	2,3,5-trichlorobiphenyl	55720-44-0	128	2,2',3,3',4,4'-hexachlorobiphenyl	38380-07-3
24	2,3,6-trichlorobiphenyl	55702-45-9	129	2,2',3,3',4,5-hexachlorobiphenyl	55215-18-4
25	2,3',4-trichlorobiphenyl	55712-37-3	130	2,2',3,3',4,5'-hexachlorobiphenyl	52663-66-8
26	2,3',5-trichlorobiphenyl	38444-81-4	131	2,2',3,3',4,6-hexachlorobiphenyl	61798-70-7
27	2,3',6-trichlorobiphenyl	38444-76-7	132	2,2',3,3',4,6'-hexachlorobiphenyl	38380-05-1
28	2,4,4'-trichlorobiphenyl	7012-37-5	133	2,2',3,3',5,5'-hexachlorobiphenyl	35694-04-3
29	2,4,5-trichlorobiphenyl	15862-07-4	134	2,2',3,3',5,6-hexachlorobiphenyl	52704-70-8
30	2,4,6-trichlorobiphenyl	35693-92-6	135	2,2',3,3',5,6'-hexachlorobiphenyl	52744-13-5
31	2,4',5-trichlorobiphenyl	16606-02-3	136	2,2',3,3',6,6'-hexachlorobiphenyl	38411-22-2
32	2,4',6-trichlorobiphenyl	38444-77-8	137	2,2',3,4,4',5-hexachlorobiphenyl	35694-06-5
33	2',3,4-trichlorobiphenyl (2,3',4'-trichlorobiphenyl)	38444-86-9	138	2,2',3,4,4',5'-hexachlorobiphenyl	35065-28-2
34	2',3,5-trichlorobiphenyl (2,3',5'-trichlorobiphenyl)	37680-68-5	139	2,2',3,4,4',6-hexachlorobiphenyl	56030-56-9
35	3,3',4-trichlorobiphenyl	37680-69-6	140	2,2',3,4,4',6'-hexachlorobiphenyl	59291-64-4
36	3,3',5-trichlorobiphenyl	38444-87-0	141	2,2',3,4,5,5'-hexachlorobiphenyl	52712-04-6
37	3,4,4'-trichlorobiphenyl	38444-90-5	142	2,2',3,4,5,6-hexachlorobiphenyl	41411-61-4
38	3,4,5-trichlorobiphenyl	53555-66-1	143	2,2',3,4,5,6'-hexachlorobiphenyl	68194-15-0
39	3,4',5-trichlorobiphenyl	38444-88-1	144	2,2',3,4,5',6-hexachlorobiphenyl	68194-14-9
40	2,2',3,3'-tetrachlorobiphenyl	38444-93-8	145	2,2',3,4,6,6'-hexachlorobiphenyl	74472-40-5
41	2,2',3,4-tetrachlorobiphenyl	52663-59-9	146	2,2',3,4',5,5'-hexachlorobiphenyl	51908-16-8
42	2,2',3,4'-tetrachlorobiphenyl	36559-22-5	147	2,2',3,4',5,6-hexachlorobiphenyl	68194-13-8
43	2,2',3,5-tetrachlorobiphenyl	70362-46-8	148	2,2',3,4',5,6'-hexachlorobiphenyl	74472-41-6
44	2,2',3,5'-tetrachlorobiphenyl	41464-39-5	149	2,2',3,4',5',6-hexachlorobiphenyl	38380-04-0
45	2,2',3,6-tetrachlorobiphenyl	70362-45-7	150	2,2',3,4',6,6'-hexachlorobiphenyl	68194-08-1
46	2,2',3,6'-tetrachlorobiphenyl	41464-47-5	151	2,2',3,5,5',6-hexachlorobiphenyl	52663-63-5
47	2,2',4,4'-tetrachlorobiphenyl	2437-79-8	152	2,2',3,5,6,6'-hexachlorobiphenyl	68194-09-2
48	2,2',4,5-tetrachlorobiphenyl	70362-47-9	153	2,2',4,4',5,5'-hexachlorobiphenyl	35065-27-1
49	2,2',4,5'-tetrachlorobiphenyl	41464-40-8	154	2,2',4,4',5,6'-hexachlorobiphenyl	60145-22-4
50	2,2',4,6-tetrachlorobiphenyl	62796-65-0	155	2,2',4,4',6,6'-hexachlorobiphenyl	33979-03-2
51	2,2',4,6'-tetrachlorobiphenyl	68194-04-7	156	2,3,3',4,4',5-hexachlorobiphenyl	38380-08-4
52	2,2',5,5'-tetrachlorobiphenyl	35693-99-3	157	2,3,3',4,4',5'-hexachlorobiphenyl	69782-90-7
53	2,2',5,6'-tetrachlorobiphenyl	41464-41-9	158	2,3,3',4,4',6-hexachlorobiphenyl	74472-42-7
54	2,2',6,6'-tetrachlorobiphenyl	15968-05-5	159	2,3,3',4,5,5'-hexachlorobiphenyl	39635-35-3
55	2,3,3',4-tetrachlorobiphenyl	74338-24-2	160	2,3,3',4,5,6-hexachlorobiphenyl	41411-62-5
56	2,3,3',4'-tetrachlorobiphenyl	41464-43-1	161	2,3,3',4,5',6-hexachlorobiphenyl	74472-43-8
57	2,3,3',5-tetrachlorobiphenyl	70424-67-8	162	2,3,3',4',5,5'-hexachlorobiphenyl	39635-34-2
58	2,3,3',5'-tetrachlorobiphenyl	41464-49-7	163	2,3,3',4',5,6-hexachlorobiphenyl	74472-44-9
59	2,3,3',6-tetrachlorobiphenyl	74472-33-6	164	2,3,3',4',5',6-hexachlorobiphenyl	74472-45-0
60	2,3,4,4'-tetrachlorobiphenyl	33025-41-1	165	2,3,3',5,5',6-hexachlorobiphenyl	74472-46-1
61	2,3,4,5-tetrachlorobiphenyl	33284-53-6	166	2,3,4,4',5,6-hexachlorobiphenyl	41411-63-6
62	2,3,4,6-tetrachlorobiphenyl	54230-22-7	167	2,3',4,4',5,5'-hexachlorobiphenyl	52663-72-6

Table 2

PCB Shorthand Nomenclature[4] Used in this Report

BZ/IUPAC Number[1].	PCB Chemical Structure Name[2]	CAS Registry[3] Number	BZ/IUPAC Number[1].	PCB Chemical Structure Name[2]	CAS Registry[3] Number
63	2,3,4',5-tetrachlorobiphenyl	74472-34-7	168	2,3',4,4',5',6-hexachlorobiphenyl	59291-65-5
64	2,3,4',6-tetrachlorobiphenyl	52663-58-8	169	3,3',4,4',5,5'-hexachlorobiphenyl	32774-16-6
65	2,3,5,6-tetrachlorobiphenyl	33284-54-7	170	2,2',3,3',4,4',5-heptachlorobiphenyl	35065-30-6
66	2,3',4,4'-tetrachlorobiphenyl	32598-10-0	171	2,2',3,3',4,4',6-heptachlorobiphenyl	52663-71-5
67	2,3',4,5-tetrachlorobiphenyl	73575-53-8	172	2,2',3,3',4,5,5'-heptachlorobiphenyl	52663-74-8
68	2,3',4,5'-tetrachlorobiphenyl	73575-52-7	173	2,2',3,3',4,5,6-heptachlorobiphenyl	68194-16-1
69	2,3',4,6-tetrachlorobiphenyl	60233-24-1	174	2,2',3,3',4,5,6'-heptachlorobiphenyl	38411-25-5
70	2,3',4',5-tetrachlorobiphenyl	32598-11-1	175	2,2',3,3',4,5',6-heptachlorobiphenyl	40186-70-7
71	2,3',4',6-tetrachlorobiphenyl	41464-46-4	176	2,2',3,3',4,6,6'-heptachlorobiphenyl	52663-65-7
72	2,3',5,5'-tetrachlorobiphenyl	41464-42-0	177	2,2',3,3',4',5,6-heptachlorobiphenyl (2,2',3,3',4,5',6'-heptachlorobiphenyl)	52663-70-4
73	2,3',5',6-tetrachlorobiphenyl	74338-23-1	178	2,2',3,3',5,5',6-heptachlorobiphenyl	52663-67-9
74	2,4,4',5-tetrachlorobiphenyl	32690-93-0	179	2,2',3,3',5,6,6'-heptachlorobiphenyl	52663-64-6
75	2,4,4',6-tetrachlorobiphenyl	32598-12-2	180	2,2',3,4,4',5,5'-heptachlorobiphenyl	35065-29-3
76	2',3,4,5-tetrachlorobiphenyl (2,3',4',5'-tetrachlorobiphenyl)	70362-48-0	181	2,2',3,4,4',5,6-heptachlorobiphenyl	74472-47-2
77	3,3',4,4'-tetrachlorobiphenyl	32598-13-3	182	2,2',3,4,4',5,6'-heptachlorobiphenyl	60145-23-5
78	3,3',4,5-tetrachlorobiphenyl	70362-49-1	183	2,2',3,4,4',5',6-heptachlorobiphenyl	52663-69-1
79	3,3',4,5'-tetrachlorobiphenyl	41464-48-6	184	2,2',3,4,4',6,6'-heptachlorobiphenyl	74472-48-3
80	3,3',5,5'-tetrachlorobiphenyl	33284-52-5	185	2,2',3,4,5,5',6-heptachlorobiphenyl	52712-05-7
81	3,4,4',5-tetrachlorobiphenyl	70362-50-4	186	2,2',3,4,5,6,6'-heptachlorobiphenyl	74472-49-4
82	2,2',3,3',4-pentachlorobiphenyl	52663-62-4	187	2,2',3,4',5,5',6-heptachlorobiphenyl	52663-68-0
83	2,2',3,3',5-pentachlorobiphenyl	60145-20-2	188	2,2',3,4',5,6,6'-heptachlorobiphenyl	74487-85-7
84	2,2',3,3',6-pentachlorobiphenyl	52663-60-2	189	2,3,3',4,4',5,5'-heptachlorobiphenyl	39635-31-9
85	2,2',3,4,4'-pentachlorobiphenyl	65510-45-4	190	2,3,3',4,4',5,6-heptachlorobiphenyl	41411-64-7
86	2,2',3,4,5-pentachlorobiphenyl	55312-69-1	191	2,3,3',4,4',5',6-heptachlorobiphenyl	74472-50-7
87	2,2',3,4,5'-pentachlorobiphenyl	38380-02-8	192	2,3,3',4,5,5',6-heptachlorobiphenyl	74472-51-8
88	2,2',3,4,6-pentachlorobiphenyl	55215-17-3	193	2,3,3',4',5,5',6-heptachlorobiphenyl	69782-91-8
89	2,2',3,4,6'-pentachlorobiphenyl	73575-57-2	194	2,2',3,3',4,4',5,5'-octachlorobiphenyl	35694-08-7
90	2,2',3,4',5-pentachlorobiphenyl	68194-07-0	195	2,2',3,3',4,4',5,6-octachlorobiphenyl	52663-78-2
91	2,2',3,4',6-pentachlorobiphenyl	68194-05-8	196	2,2',3,3',4,4',5,6'-octachlorobiphenyl	42740-50-1
92	2,2',3,5,5'-pentachlorobiphenyl	52663-61-3	197	2,2',3,3',4,4',6,6'-octachlorobiphenyl	33091-17-7
93	2,2',3,5,6-pentachlorobiphenyl	73575-56-1	198	2,2',3,3',4,5,5',6-octachlorobiphenyl	68194-17-2
94	2,2',3,5,6'-pentachlorobiphenyl	73575-55-0	199/200	2,2',3,3',4,5,6,6'-octachlorobiphenyl	52663-73-7
95	2,2',3,5',6-pentachlorobiphenyl	38379-99-6	200/201	2,2',3,3',4,5',6,6'-octachlorobiphenyl	40186-71-8
96	2,2',3,6,6'-pentachlorobiphenyl	73575-54-9	201/199	2,2',3,3',4,5,5',6'-octachlorobiphenyl	52663-75-9
97	2,2',3',4,5-pentachlorobiphenyl (2,2',3,4',5'-pentachlorobiphenyl)	41464-51-1	202	2,2',3,3',5,5',6,6'-octachlorobiphenyl	2136-99-4
98	2,2',3',4,6-pentachlorobiphenyl (2,2',3,4',6'-pentachlorobiphenyl)	60233-25-2	203	2,2',3,4,4',5,5',6-octachlorobiphenyl	52663-76-0
99	2,2',4,4',5-pentachlorobiphenyl	38380-01-7	204	2,2',3,4,4',5,6,6'-octachlorobiphenyl	74472-52-9
100	2,2',4,4',6-pentachlorobiphenyl	39485-83-1	205	2,3,3',4,4',5,5',6-octachlorobiphenyl	74472-53-0
101	2,2',4,5,5'-pentachlorobiphenyl	37680-73-2	206	2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	40186-72-9
102	2,2',4,5,6-pentachlorobiphenyl	68194-06-9	207	2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl	52663-79-3
103	2,2',4,5',6-pentachlorobiphenyl	60145-21-3	208	2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	52663-77-1
104	2,2',4,6,6'-pentachlorobiphenyl	56558-16-8	209	2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	2051-24-3

Table 2					
PCB Shorthand Nomenclature[4] Used in this Report					
BZ/IUPAC Number[1].	PCB Chemical Structure Name[2]	CAS Registry[3] Number	BZ/IUPAC Number[1].	PCB Chemical Structure Name[2]	CAS Registry[3] Number
105	2,3,3',4,4'-pentachlorobiphenyl	32598-14-4			

1. The BZ number is from Ballschmiter and Zell (1980). The IUPAC number, when different from the BZ, follows the recommended changes to the BZ number per Schulte and Malisch (1983) and Guitart et al. (1993).
2. The chemical structure names are from Ballschmiter and Zell (1980). IUPAC nomenclature structure names are listed in parenthesis when different from the BZ name (source CAS Registry).
3. Chemical Abstract Service Registry number (source CAS Registry and 1668 Table 1).
4. A complete discussion of PCB Nomenclature may be found in Mills III, S.A. et al., A summary of the 209 PCB congener nomenclature, Chemosphere (2007), doi:10.1016/j.chemosphere.2007.03.052.

Case Narrative:
Dioxins/Furans - 40 CFR Part 60, Appendix A-7 to Part 60 – Test Method 23
Polychlorinated Biphenyls - USEPA Method 1668A
Polycyclic Aromatic Hydrocarbons - KNOX-ID-0016
Semi-volatile Organic Compounds – SW846 8270C

Night

TestAmerica Laboratories, Inc.

PROJECT NARRATIVE
H6E040410

The results reported herein are applicable to the samples submitted for analysis only. If you have questions regarding this report, please call (865) 291-3000 and ask to speak with the TestAmerica project manager listed on the cover page of this report.

This report shall not be reproduced except in full, without the written approval of the laboratory.

The original chain of custody documentation is included with this laboratory report.

Sample Receipt

Custody seals were not present on the sample shipments upon arrival at the laboratory.

Quality Control and Data Interpretation

Unless otherwise noted, all holding times and QC criteria were met and the test results shown in this report meet all applicable NELAC requirements.

Combined Method 0010 Sampling Train With Method 23 Sampling Train Laboratory Processing

The field sample collection tasks included the use of a Method 0010 sampling train combined with a Method 23 sampling train. The Method 0010 / 23 sampling objectives included stack gas evaluations for the following classes of analytes:

- Semi-volatile compounds analyzed by SW-846 Method 8270 (Full Scan + TICs)
- PAHs analyzed by Low-level Selective Ion Monitoring (SIM) High Res GC/MS
- PCBs analyzed by EPA Method 1668A
- And dioxins and furans analyzed by SW-846 Method 8290.

The field sampling tasks included the collection of the standard sampling train fractions according to the requirements of SW-846 Method 3542 in addition to the additional fractions required for the collection of dioxin and furan samples. This standard sampling train breakdown renders six (6) sample fractions and two (2) toluene rinse fractions that are submitted to the laboratory for processing. The fractions are as follows:

- The particulate filter (collected in a Petri dish)
- The front-half nozzle, probe, and front-half of the filter holder acetone and methylene chloride solvent rinses,
- A separate front-half nozzle, probe, and front-half of the filter holder toluene solvent rinse (for D/Fs, only)
- An XAD-2 resin module
- The back-half of the filter holder and connecting glassware acetone and methylene chloride solvent rinses,
- A separate back-half of the filter holder and connecting glassware toluene solvent rinses,
- The condensate and impinger contents composite,

- And an acetone and methylene chloride solvent rinse of the connecting glassware behind the XAD-2 module and glassware connecting the impingers.

The Front-half fractions were composited in the laboratory for extraction in a Soxhlet apparatus. Extraction was conducted using methylene chloride and a second extraction was conducted using toluene. The sample process was followed for the Back-half fractions. The Condensate portions underwent extraction with methylene chloride, only.

Extracts from the Soxhlet process were combined in such a way as to acquire representative composites for each Front-half or Back-half fraction for the analyte types being determined by these sampling trains. Four (4) separate extract portions were then divided off of the final extract composites for each analyte type outlined above. Since the Condensate fraction composites are analyzed for only three (3) analyte types, and not analyzed for dioxins and furans, only three extract portions were divided off of the final extract composites for them.

A relatively low level contamination was introduced into the sampling train extracts by the Method 8270 surrogate spiking materials used. Biphenyl was determined to be a low level contaminate in the Method 8270 surrogate spiking material because it appears on the PAH SIM Low Level Method as a target analyte. The actual train XAD-2 resin fractions had large biphenyl hits in them which render the low levels introduced by the spiking program inconsequential in comparison. The contamination level in LCS, media blanks, and train blank samples can be used to evaluate the level of biphenyl contributed by the surrogate spikes.

Each analyte class can be summarized for a general analytical laboratory process understanding. The summaries are as follows:

PAHs by Low Level Selective Ion Monitoring (SIM) High Resolution GC/MS

The method 0010 sampling train components were extracted and analyzed for polyaromatic hydrocarbons (PAHs) using TestAmerica Knoxville standard operating procedures KNOX-OP-0009 and KNOX-ID-0016, based on the following extraction method:

SW-846 3542, "Extraction of Semivolatile Analytes Collected Using Method 0010 (Modified Method 5 Sampling Train)"

The sampling trains are prepared as three analytical fractions:

- The particulate filter and front half of the filter holder, nozzle and probe solvent rinses are combined as one sample.
- The XAD-2 resin trap and back half of the filter holder, coil condenser and connecting glassware solvent rinses are combined as a separate sample.
- The condensate, impinger contents and their related glassware solvent rinses make up a third sample.

The condensate fraction extracts were split three ways and the particulate filters and XAD-2 resin fractions were split four ways to accommodate the required analysis. The filters and XAD components are spiked with the appropriate amount of SIM PAH internal standards and the components are Soxhlet extracted with methylene chloride. The condensate portion for this

analyses were spiked with the appropriate levels of internal standards and extracted using a continuous liquid-liquid extractor. The condensate extracts were final concentrated to 0.5 mL while the Front- half and Back-half are final concentrated to 0.25mL and analyzed by by SIM-HRGC/LRMS.

A field QC sampling surrogate was added to the XAD-2 resin by the laboratory prior to the field sampling campaign. The results for the sampling surrogate recoveries appear with the "Internal Standard" percent recovery data.

Note that the labeled internal standards added prior to extraction serve both as a measurement of the extraction efficiency of the method as well as a measure of cleanup recovery efficiency.

The dilution factor reported on the sample result form represents a combination of factors (such as dilution, sample weight/volume adjustment, split ratio, etc.) used to adjust the reporting limits and method detection limits.

Due to the combined extraction where each sampling train composite fraction is split for the different required analysis, each sample was spiked with the necessary internal standards and surrogates before the extractions are commenced. Consequently, one of the target analytes was detected as a background contaminate in all the samples, method blanks, trip blanks and media checks above the reporting limit during the SIM-PAH analysis. A “Spike Interference Check”, which contains all the necessary internal standards and surrogates required for each analysis, was analyzed and confirmed the presence of biphenyl in the spikes. When the concentration of biphenyl in the samples is approximately the same concentration found in the associated method blank, trip blank, and media check, the result should be considered to have been derived from the spiking program. However, high concentrations of biphenyl in the samples appear to be from the small amount in the spike plus the amount collected during the sampling event.

Several of the back-half samples were reported with elevated reporting limits for all PAH analytes. Dilution of the samples because of high analyte levels was necessary prior to analysis and the reporting limits were adjusted accordingly.

Note that the concentration of one or more target compounds in several of these samples exceeded the calibration range even at the maximum fifty-fold dilution allowed by this isotope dilution method. Since some compounds saturated the detector or were extremely high in concentration, the samples were analyzed at a further dilution by using a post-dilution spike technique to bring the concentration of the compound into the instrument calibration range. Due to the addition of the internal standards after extraction, isotope dilution technique correction does not apply to the affected samples. The reporting limits have been adjusted accordingly.

Several samples have one or more internal standard recoveries outside QC limits (high) due to apparent matrix interferences. Under these conditions an apparent low bias of the analytes associated with these internal standards will be incurred.

Several samples have one or more internal standard recoveries outside QC limits (low). Even though the recoveries were below limits, the signal-to-noise ratio was greater than 10:1. The

results are reported in accordance with our standard operating procedure and as indicated by the referenced method, isotope dilution techniques produce results that are corrected for the internal standard recovery and should be usable for their intended purposes.

On the analysis of the "Front Half" samples M23-0010 RUN 1 FH and M23-0010 RUN 4 FH had several internal standards outside QC limits on the original analysis and the diluted analysis. Sample M23-0010 RUN 1 FH, had the coeluting pair benzo(b)fluoranthene and benzo(k)fluoranthene reported from the diluted analysis. The interference that hindered the internal standard recoveries on the original analysis was removed on the dilution analysis. The other native analytes associated with an elevated internal standard recovery outside QC limits that were still reported from the original analysis; the dilution did not minimize the interference effect on the internal standard recoveries. These compounds associated with the high internal standards will have a low bias. Sample M23-0010 RUN 4 FH had internal standard recoveries outside QC limits. The diluted analysis removed the effects of the interferences on these internal standards. The native analytes associated with these internal standards were reported from the dilution analysis.

On the analysis of the 'Back Half" samples, it was noticed that there was a difference in chromatography and concentration between the maximum bench dilution analysis and the post-dilution spike analysis for benzo(a)pyrene; there appears to be a co-elution in the maximum bench dilution. The results from the maximum bench dilution are reported to give a maximum possible concentration, and are qualified with a "CI" to indicate that there is reason to suspect these may have a high bias.

On the analysis of the "Back Half" samples, matrix interferences were observed for several internal standards; the associated analytes were reported from the post-dilution spike analysis. In some cases, even if the recoveries were within acceptable range on the original analysis, the interferences were still present, so the analytes associated with these internal standards were reported from the post dilution spike.

On review of the data, it was noticed that in several samples, the peaks identified by the data system for multiple target analytes exhibited very slight retention time shift or a shoulder on the peak that could not be resolved. Therefore, these compounds have been flagged with "CI" to indicate that although they met the qualitative criteria of the method, there is reason to suspect these may be biased high.

Some benzo(b)fluoranthene and benzo(k)fluoranthene results were qualified with an "EST" flag to indicate that the value is estimated due to a co-eluting peak. These two compounds could not be resolved due to the difficult sample matrix.

<u>Semivolatile Full Scan Analyses Including TICs - (Method SW846 8270C)</u>

The semivolatile organic sampling train components were extracted and analyzed using TestAmerica Knoxville standard operating procedures KNOX-OP-0009 and KNOX-MS-0016, based on the following methods:

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- SW-846 3542, "Extraction of Semivolatile Analytes Collected Using Method 0010 (Modified Method 5 Sampling Train)"
- SW-846 8270C, "Semivolatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS)".

The sampling trains are prepared as three analytical fractions: The particulate filter and front half of the filter holder, nozzle and probe solvent rinses are combined as one sample. The XAD-2 resin trap and back half of the filter holder, coil condenser and connecting glassware solvent rinses are combined as a separate sample. The condensate, impinger contents and their related glassware solvent rinses make up a third sample.

The particulate filter and XAD-2 components are spiked with the method 8270C surrogates and the components are Soxhlet extracted with methylene chloride. The condensates are spiked with the surrogates and extracted using a separatory funnel. The extracts are concentrated to 1 mL and analyzed by GCMS.
Sample results were calculated using the following equation:

$$\text{Result, ug} = (\text{On column concentration, ng/uL}) \text{x} \left(\frac{\text{Volume final extract, uL}}{\text{1 Sample}} \right) \text{x} \left(\frac{\text{1ug}}{\text{1000 ng}} \right) \text{x DF x SF}$$

Where: DF = Bench Dilution Factor
SF = Extraction Split Factor

One or more surrogate recoveries for sample M23-0010 RUN 1 BH were outside QC limits. Since the recoveries were elevated above the laboratory QC limits, the results for the sample may be biased high.

The laboratory control sample and laboratory control sample duplicate results for batches 6118026, 6118027, and 6118028 were outside control limits for several analytes.

Several samples were reported with elevated reporting limits for all analytes due to required sample dilution. Based on screening results, a dilution was necessary prior to analysis and the reporting limits were adjusted accordingly.

Note that a dilution factor reported on the sample result form represents a combination of factors (such as dilution, sample weight/volume adjustment, split ratio, etc.) used to adjust the reporting limits and method detection limits.

Laboratory control sample/laboratory control sample duplicates are performed instead of a matrix spike/matrix spike duplicates for Method 0010 sampling trains in batches 6118026, 6118027, and 6118028.

Dioxin and Furan Analyses Analyzed by Method 8290

All positive 2378-TCDF results at or above the minimum level were confirmed on a DB-225 column. The raw data for the DB-225 analyses is included in the data package directly following the primary column analyses.

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Samples M23-0010 RUN 1 COMBINED, M23-0010 RUN 2 COMBINED, M23-0010 RUN 3 COMBINED, M23-0010 RUN 4 COMBINED, and M23-0010 RUN 5 COMBINED exhibited total TCDD above the calibration range. Samples M23-0010 RUN 3 COMBINED, M23-0010 RUN 4 COMBINED, and M23-0010 RUN 5 COMBINED also exhibited total TCDF above the calibration range. The method does not require further action be taken. The results were reported as is with an "E" qualifier.

The following flags are used to qualify results for chlorinated dioxin and furan results:

J – The reported result is an estimate. The amount reported is below the Minimum Level (ML). The qualitative definition of the ML is "the lowest level at which the analytical system must give a reliable signal and an acceptable calibration point". The ML was introduced in EPA Methods 1624 and 1625 in 1980 and was promulgated in these methods in 1984 at 40 CFR Part 136, Appendix A. For the purposes of this report, the ML is qualitatively defined as described above, and quantitatively defined as follows:

Minimum Level: The concentration or mass of analyte in the sample that corresponds to the lowest calibration level in the initial calibration. It represents a concentration (in the sample extract) equivalent to that of the lowest calibration standard, after corrections for method-specified sample weights, volumes and cleanup procedures has been employed.

Example: The lowest calibration level for TCDD in the initial calibration is 0.5 pg/uL. A mass of 10 pg of 2,3,7,8-TCDD in the sample would result in a concentration of 0.5 pg/uL in the sample extract (at a final volume of 20 uL). Since the concentration in the sample extract corresponds to the concentration in the lowest calibration standard, the 10 pg mass in the sample components is the ML. If the sample extract is further diluted, the ML will increase by the dilution factor.

Example: A 1/10 dilution is performed on the sample extract described above. The ML for 2,3,7,8-TCDD becomes 100 pg rather than the default of 10 pg.

E – The reported result is an estimate. The amount reported is above the Upper Calibration Level (UCL) described below. The quantitative definition of the UCL is listed below:

Upper Calibration Level: The concentration or mass of analyte in the sample that corresponds to the highest calibration level in the initial calibration. It is equivalent to the concentration of the highest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

Example: The maximum calibration level for TCDD in the initial calibration is 200 pg/uL. A mass of 4000 pg of 2,3,7,8-TCDD in the sampling components would result in a concentration of 200 pg/uL in the sample extract (at a final volume of 20 uL). Since the concentration in the sample extract corresponds to the concentration in the highest calibration standard, the 4000 pg mass in the sample components is the UCL. If the sample extract is further diluted, the ML will increase by the dilution factor.

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Example: A 1/10 dilution is performed on the sample extract described above. The UCL for 2,3,7,8-TCDD becomes 40,000 pg rather than the default of 4000 pg. In this example, all positive 2,3,7,8-TCDD results above 40,000 pg are flagged with an E.

B – The analyte is present in the associated method blank at a detectable level. For this analysis, there is no method specified reporting level other than the qualitative criterion that peaks must exhibit a signal-to-noise ratio of ≥2.5 to 1. Therefore, the presence of any reportable amount of the analyte in the blank will result in a B qualifier on all associated samples.

Q – Estimated maximum possible concentration. This qualifier is used when the result is generated from chromatographic data that does not meet all the qualitative criteria for a positive identification given in the method. These may include one or more of the following:

- Ion abundance ratios must be within specified limits (+/-15% of theoretical ion abundance ratio).
- Retention time criteria (relative to the method-specified isotope labeled retention time standard).
- Co-maximization criterion. The two quantitation ion peaks must reach their maxima within 2 seconds of each other.
- 2,3,7,8-TCDF result is reported from the non-isomer specific Rtx-5 column.
- Polychlorinated dibenzofuran purity. An interference may be present on the indicated polychlorinated dibenzofuran when a polychlorinated diphenyl ether peak is present and maximizes within +/- 3 seconds of the dibenzofuran candidate.

S – Ion suppression evident. The trace indicating the signal from the lock mass of the calibration compound shows a deflection at the retention time of the analyte. This may indicate a temporary suppression of the instrument sensitivity due to a matrix-borne interference.

C – Coeluting Isomer. The isomer is known to coelute with another member of its homologue group, or the peak shape is shouldered, indicating the likelihood of a coeluting isomer.

X – Other. See explanation in narrative.

Laboratory studies supporting risk assessment and Total Maximum Daily Load (TMDL) evaluations, frequently use qualified data reported as low as the Method Detection Limit (MDL), or the Estimated Detection Limit (EDL). Several of EPA's isotope dilution methods employ the EDL.[1,2,3] The EDL is based on a direct measurement of the signal-to-noise (S/N) ratio acquired during sample analysis. This S/N measurement is used to calculate the concentration in the sample corresponding to the minimum intensity of the smallest quantifiable peak. The EDL reflects the amount of the particular analyte which would be required to cause a positive result for the particular analysis. Because the S/N obtained covaries with recovery, instrument sensitivity and sample-specific cleanup efficacy, the EDL is a more valid measure of the sensitivity of the entire analytical process for the specific sample than is an MDL run periodically on a reference matrix.

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The EDL is typically calculated according to the following equation:

$$\text{Estimated Detection Limit} = \frac{N \times 2.5 \times Qis}{His \times RRF \times W \times S}$$

Where:

N	=	peak to peak noise of quantitation ion signal in the region of the ion chromatogram where the compound of interest is expected to elute
His	=	peak height of quantitation ion for appropriate internal standard
Qis	=	ng of internal standard added to sample
RRF	=	mean relative response factor of compound obtained during initial calibration
W	=	amount of sample extracted (grams or liters)
S	=	percent solids (optional, if results are requested to be reported on dry weight basis)

(The area of the internal standard is sometimes used instead of height, along with an area-to-height conversion factor.)

This method of estimating the detection limit differs from the MDL in that it does not carry the requirement that the sample be statistically distinguished as being from a contaminated population. As results approach the EDL, the risk of false positives and the analytical uncertainty increase significantly. However, a low false positive well below the ML or MDL is often closer to the true value than an assumption that the target analyte is present at the detection or reporting limits. For relatively clean samples, MDL studies may give an elevated estimate of the detection limit. Additionally, on contaminated samples, the MDL may give a falsely low estimate of the detection limit.

$$\text{Analyte Concentration} = \frac{As \times Qis}{Ais \times RRF \times W \times S}$$

Where:

As	=	Sum of areas of the target peaks
Qis	=	ng of internal standard added to sample
Ais	=	Sum of areas of the internal standard peaks
RRF	=	mean relative response factor of compound obtained during initial calibration
W	=	amount of sample extracted (grams or liters)
S	=	percent solids (optional, if results are requested to be reported on dry weight basis)

In sample data, peaks must have an intensity of $\geq$2.5 times the height of the background noise in order to be considered. Careful examination of the two equations above reveals that for the concentration of the smallest peak detectable (per the EDL equation) to exactly equal the smallest peaks that are calculated, requires that the average height to area ratio obtained during the calibration must equal the area to height ratio for every peak obtained near 2.5 times the noise. When the area to height ratio on a peak in a sample is less than the average obtained during calibration, the calculated result will correspond to a peak that would have been less than 2.5 times the noise on the calibration. This is the result of normal variability. Because

the source methods for the EDL (SW-846 8290 and 8280A) do not provide for censoring of results by any other magnitude standard than being 2.5 times the noise, the laboratory does not censor at the calculated EDL. Hence, detections may be reported below the estimated detection limits.

Footnotes:

1. Code of Federal Regulations, Part 136, Chapter 1, Appendix 1, October 1994: Method 1613 Tetra- Through Octa-Chlorinated Dioxins and Furans by Isotope Dilution High Resolution Gas Chromatography/High Resolution Mass Spectrometry.
2. U.S. EPA. Test Methods for Evaluating Solid Waste, Volume II, SW-846, Update III, December 1996. Method 8280A: The Analysis of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans by High Resolution Gas Chromatography/Low Resolution Mass Spectrometry.
3. U.S. EPA. Test Methods for Evaluating Solid Waste, SW-846. Third Edition. March 1995 Method 8290: Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans by High Resolution Gas Chromatography/High Resolution Mass Spectrometry.

PCBs Analyzed by Method 1668A

Due to the extraction technique where each sample is split for different analysis before extraction, each sample was spiked with the necessary internal standards and surrogates required for each analysis. Consequently, a target analyte, PCB 1, was detected in all method blanks above the minimum level (ML). A "Spike Interference Check", which contains all the necessary internal standards and surrogates required for each analysis, was analyzed and confirmed the presence of PCB 1 in the spikes. When the concentration of PCB 1 in the samples is approximately the same concentration found in the associated method blank the result may be considered attributed to the spike. Higher concentration in the samples may be considered attributed to the spike plus the amount collected during the sampling event.

For sample M23-0010 RUN 4 BH the recovery of internal standard 13C12-PCB 1 was 24%, which is below the lower acceptance criterion (30%). The minimum required signal-to-noise ratio was present, and the target estimated detection limit for associated analytes was met. The results are reported in accordance with the standard operating procedure. As indicated by the referenced method, isotope dilution techniques produce results that are independent of internal standard recovery.

For samples M23-0010 RUN 4 CONDENSATE and M23-0010 RUN 5 CONDENSATE the recovery of internal standard 13C13-PCB 54 was slightly above the upper acceptance criterion (140%) at 141%. The results are reported in accordance with the standard operating procedure. As indicated by the referenced method, isotope dilution techniques produce results that are independent of internal standard recovery.

For sample M23-0010 RUN 1 BH the recovery of surrogate standard 13C12-PCB 8 was 49%, which is below the lower acceptance criterion (50%). The minimum required signal-to-noise ratio was present. All other surrogates were within limits.

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Sample M23-0010 RUN 1 BH exhibited PCB 3 above the upper calibration level (UCL) at the maximum 10-fold dilution. No sample was available for re-extraction; therefore, the result was reported as is with an "E" qualifier.

Several samples were diluted 10-fold due to native PCB levels and/or severe ion suppression.

Nomenclature – The standardization strategy described in this report uses the naming convention of SW-846 Method 8290. This convention differs from Method 1668 in the following manner:

Standard Addition Occurs Prior to:	Method 1668	SW-846 Conventions Used in this Report
Sampling	None	Sampling Surrogate
Extraction	Labeled Toxics/LOC/Window Defining	Internal Standard
Cleanups	Labeled Cleanup Standard	Cleanup Standard*
Injection	Labeled Injection Internal Standard	Recovery Standard

* Cleanup Standard is also referred to as Surrogate Standard on report.

The shorthand notation used for congeners in this report is summarized in Table 2.

Qualifiers – The following flags are used to qualify results for HRMS PCB results:

J – The reported result is an estimate. The amount reported is below the Estimated Minimum Level (EML). EML is defined by the method as the lowest concentration at which an analyte can be measured reliably with common laboratory interferences present. This value has been determined for each congener by MDL and laboratory method blank studies. The value is adjusted to reflect sample specific initial and final volumes.

E – The reported result is an estimate. The amount reported is above the UCL described below.

The E qualifier is applied on the basis of the **Upper Calibration Level (UCL)**. The quantitative definition of the UCL is listed below:

Upper Calibration Level: The concentration or mass of analyte in the sample that corresponds to the highest calibration level in the initial calibration. It is equivalent to the concentration of the highest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

B – The analyte is present in the associated method blank at a reportable level. For this analysis, there is no method specified reporting level, other than the qualitative criterion that peaks must exhibit a signal-to-noise ratio of 2.5-to-1. Therefore, the presence of any

amount of the analyte present in the blank will result a B qualifier on all associated samples.

Note: Some laboratories do not report contamination in the blank unless it is above their lower calibration limit, or an established percentage of the level in the samples, or an established percentage of the regulatory limit. Likewise, some laboratories set a reporting limit at one half the lower calibration limit.

Q – Estimated maximum possible concentration. This qualifier is used when the result is generated from chromatographic data that does not meet all the qualitative criteria for a positive identification given in the method. The criteria include the following areas:

- Ion abundance ratios must be within specified limits (+/-15% of theoretical ion abundance ratio.)
- Retention time criteria (relative to the method-specified isotope labeled retention time standard).
- Co-maximization criterion. The two quantitation ion peaks must reach their maxima within 2 seconds of each other.

S – Ion suppression evident. The trace indicating the signal from the lock mass of the calibration compound shows a deflection at the retention time of the analyte. This may indicate a temporary suppression of the instrument sensitivity, due to a matrix-borne interference.

C – Coeluting Isomer. The isomer is known to coelute with another member of its homologue group, or the peak shape is shouldered, indicating the likelihood of a coeluting isomer. When the C flag is followed by a number, the number indicates the lowest numbered congener among the coelution set. For example, if 100 pg/L is detected at the retention time of PCB 156, and PCB 157 is known to coelute with PCB 156, the results will be flagged as follows:

PCB 156 100 pg/L C

PCB 157 100 pg/L C156

In certain electronic deliverables the result field for PCB 157 will be null, with "C156" appearing in the qualifier field in accordance with the CARP EDD specification.

X – Other. See explanation in narrative.

Results – The results for the analyses are summarized in the following pages. Please see comments regarding qualifiers, above. Additional information regarding qualifiers is explained in the legends at the end of each result summary. A summary of the shorthand conventions used in this report is provided in Table 2.

Detection Limits – For all analyte results a sample specific detection limit is calculated for that analyte. This is done by first determining the GC/MS peak height of the noise or interferent in the expected region of the analyte signal. This value is multiplied by the number 2.5, which serves as a safety factor. The 2.5 safety factor is disregarded if the noise present in the analyte region is a result of chemical interferences. The resulting signal response value is then used to estimate the minimum detectable analyte amount. The result is the estimated sample detection limit.

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When an analyte is not detected, an ND appears in place of the result. The value in the detection limit column is the estimated detection limit for the analyte in that particular sample.

EXAMPLE CALCULATIONS

The following formulas were used for sample calculations. Examples are given for calculating the percent recovery for internal standard $^{13}C_{12}$-PCB 1, the concentration of native PCB 1 and the EDL for PCB 1. All values used in the calculations below are typical (i.e. not extracted from a particular sample). Actual values are found on the IsoCalc Preliminary Sample Report (IPSR) at the position indicated (in parentheses, below):

INTERNAL STANDARD RECOVERY ($^{13}C_{12}$-PCB 1)

$$\text{Percent Recovery} = \frac{\Sigma A_{IS} \bullet W_{RS} \bullet 100\%}{\Sigma A_{RS} \bullet W_{IS} \bullet RRF}$$

ΣA_{IS} = Sum of areas for the Internal Standard quantitation ions. (IPSR – Column "Area", Row "13C12-PCB 1")

W_{RS} = Mass in ng of the Recovery Standard. (IPSR – Column "Std Amt", Row "13C12-PCB 9")

ΣA_{RS} = Sum of areas for the Recovery Standard quantitation ions. (IPSR – Column "Area", Row "13C12-PCB 9")

W_{IS} = Mass in ng of the Internal Standard. (IPSR – Column "Std Amt", Row "13C12-PCB 1")

RRF = Internal Standard mean relative response factor from the initial multipoint calibration. (IPSR - Column "RF", Row "13C12-PCB 1".)

Substituting typical values ,

$$\frac{1106275 \bullet 2.000\,(ng) \bullet 100\%}{1205581 \bullet 2.000\,(ng) \bullet 1.412} = 65\%\ \text{Recovery}$$

NATIVE ANALYTE QUANTITATION (PCB 1)

$$\text{Conc} = \frac{\Sigma A_X \bullet W_{IS}}{\Sigma A_{IS} \bullet V \bullet 0.001\,(mL/L) \bullet RRF}$$

ΣA_X = Sum of areas for analyte quantitation ions. (IPSR – Area Column "Area", Row "PCB 1")

W_{IS} = Mass in ng of Internal Standard. (IPSR – Column "Std Amt", Row "13C12-PCB 1")

ΣA_{IS} = Sum areas for the Internal Standard. (IPSR – Column "Area", Row 13C12-PCB 1)

V = Volume of sample extracted in mL. (IPSR – Header Column 2, Row "Initial Wt/Vol")

RRF = Native analyte mean relative response factor from the initial calibration, or daily response factor as appropriate. (IPSR – Column "RF", Row "PCB 1")

Substituting typical values, $\dfrac{8951 \bullet 2.000\ (ng)}{1106275 \bullet 2200\ (mL) \bullet 0.001\ (mL/L) \bullet 1.136} = 0.00647\ ng/L = 6.47\ pg/L$

CALCULATION OF SAMPLE SPECIFIC ESTIMATED DETECTION LIMIT

This calculation uses the noise values found on the IsoCalc Preliminary Peak Report (IPPR), which follows the IPSR. All the other values used in the equation are found on the IPSR.)

$$\frac{\Sigma I_X \bullet W_{IS} \bullet T_{SN}}{\Sigma I_{IS} \bullet V \bullet 0.001\ (mL/L) \bullet RRF}$$

ΣI_X = Sum of the intensities of the noise levels of the characteristic ions in the region of analyte elution. (IPPR – Columns “Height1” and “Height2”, Row {mass} 188, Sub-Row “Noise”).

W_{IS} = Mass in ng of the Internal Standard. (IPSR – Column “Std Amt”, Row “13C12-PCB 1”).

T_{SN} = Minimum Signal-to-Noise threshold. = 2.5. A constant, specified by the method.

ΣI_{IS} = Intensity of the corresponding ^{13}C ions. (IPSR – Column “Height”, Row “13C12-PCB 9”)

V = Volume of sample extracted in mL. (IPSR – Header Column 2, Row “Initial Wt/Vol”)

RRF = Native analyte mean relative response factor from the initial calibration or daily standard as appropriate. (IPSR – Column “RF”, Row “PCB 1”)

Substituting typical values $\dfrac{79 \bullet 2000\ (pg) \bullet 2.5}{334600 \bullet 2200\ (mL) \bullet 0.001\ (mL/L) \bullet 1.136} = 0.466\ pg/L$

In sample data, peaks must have an intensity of 2.5 times the height of the background noise in order to be considered. Careful examination of the two equations above, and a bit of algebra reveals that for the concentration of the smallest peak detectable (per the EDL equation) to exactly equal the smallest peaks that are calculated, requires that the average height to area ratio obtained during the calibration must equal the area to height ratio for every peak obtained near 2.5 times the noise. When the area to height ratio on a peak in a sample is less than the average obtained during calibration, the calculated result will correspond to a peak that would have been less than 2.5 X the noise on the calibration. This is the result of normal variability. Because the source method for the EDL (EPA 1668) does not provide for censoring of results by any other magnitude standard than being 2.5 times the noise, the laboratory does not censor at the calculated EDL. Hence, detections may be reported below the estimated detection limits.

Table 1							
Concentration of PCBs in Calibration Solutions							
		CS 0.5	CS 1	CS 2	CS 3[2]	CS 4	CS 5
Analyte Type	BZ/IUPAC[1]	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL
Congeners							
2-MoCB	1	0.5	1.0	5.0	50	400	2000
4-MoCB	3	0.5	1.0	5.0	50	400	2000
2,2'-DiCB	4	0.5	1.0	5.0	50	400	2000
4,4'-DiCB	15	0.5	1.0	5.0	50	400	2000
2,2',6'-TrCB	19	0.5	1.0	5.0	50	400	2000
3,4,4'-TrCB	37	0.5	1.0	5.0	50	400	2000
2,2',6,6'-TeCB	54	0.5	1.0	5.0	50	400	2000
3,3',4,4'-TeCB	77	0.5	1.0	5.0	50	400	2000
3,4,4',5-TeCB	81	0.5	1.0	5.0	50	400	2000
2,2',4,6,6'-PeCB	104	0.5	1.0	5.0	50	400	2000
2,3,3',4,4'-PeCB	105	0.5	1.0	5.0	50	400	2000
2,3,4,4',5-PeCB	114	0.5	1.0	5.0	50	400	2000
2,3',4,4',5-PeCB	118	0.5	1.0	5.0	50	400	2000
2',3,4,4',5-PeCB	123	0.5	1.0	5.0	50	400	2000
3,3',4,4',5-PeCB	126	0.5	1.0	5.0	50	400	2000
2,2',4,4',6,6'-HxCB	155	0.5	1.0	5.0	50	400	2000
2,3,3',4,4',5-HxCB	156	0.5	1.0	5.0	50	400	2000
2,3,3',4,4',5'-HxCB	157	0.5	1.0	5.0	50	400	2000
2,3',4,4',5,5'-HxCB	167	0.5	1.0	5.0	50	400	2000
3,3',4,4',5,5'-HxCB	169	0.5	1.0	5.0	50	400	2000
2,2',3,4',5,6,6'-HpCB	188	0.5	1.0	5.0	50	400	2000
2,3,3',4,4',5,5'-HpCB	189	0.5	1.0	5.0	50	400	2000
2,2',3,3',5,5',6,6'-OcCB	202	0.5	1.0	5.0	50	400	2000
2,3,3',4,4',5,5',6-OcCB	205	0.5	1.0	5.0	50	400	2000
2,2',3,3',4,4',5,5',6-NoCB	206	0.5	1.0	5.0	50	400	2000
2,2',3,3',4',5,5',6,6'-NoCB	208	0.5	1.0	5.0	50	400	2000
DeCB	209	0.5	1.0	5.0	50	400	2000
All other CB congeners		0.5	1.0	5.0	50	400	2000
Labeled Congeners							
$^{13}C_{12}$-2-MoCB	1L	100	100	100	100	100	100
$^{13}C_{12}$-4-MoCB	3L	100	100	100	100	100	100
$^{13}C_{12}$-2,2'-DiCB	4L	100	100	100	100	100	100
$^{13}C_{12}$-4,4'-DiCB	15L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',6-TrCB	19L	100	100	100	100	100	100
$^{13}C_{12}$-3,4,4'-TrCB	37L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',6,6'-TeCB	54L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4'-TeCB	77L	100	100	100	100	100	100
$^{13}C_{12}$-3,4,4',5-TeCB	81L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',4,6,6'-PeCB	104L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4'-PeCB	105L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,4,4',5-PeCB	114L	100	100	100	100	100	100
$^{13}C_{12}$-2,3',4,4',5-PeCB	118L	100	100	100	100	100	100
$^{13}C_{12}$-2',3,4,4',5-PeCB	123L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4',5-PeCB	126L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',4,4',6,6'-HxCB	155L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5-HxCB	156L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5'-HxCB	157L	100	100	100	100	100	100
$^{13}C_{12}$-2,3',4,4',5,5'-HxCB	167L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,4',5,5'-HxCB	169L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,4',5-HpCB	170L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,4',5,6,6'-HpCB	188L	100	100	100	100	100	100

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Table 1							
Concentration of PCBs in Calibration Solutions							
		CS 0.5	CS 1	CS 2	CS 3[2]	CS 4	CS 5
Analyte Type	BZ/IUPAC[1]	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL	ng/mL
$^{13}C_{12}$-2,3,3',4,4',5,5'-HpCB	189L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-OcCB	202L	100	100	100	100	100	100
$^{13}C_{12}$-2,3,3',4,4',5,5',6-OcCB	205L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,4',5,5',6-NoCB	206L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4',5,5',6,6'-NoCB	208L	100	100	100	100	100	100
$^{13}C_{12}$-DeCB	209L	100	100	100	100	100	100
Cleanup Standards							
$^{13}C_{12}$-2,4,4'-TriCB	28L	0.5	1.0	5.0	50	400	--
$^{13}C_{12}$-2,3,3',5,5'-PeCB	111L	0.5	1.0	5.0	50	400	--
$^{13}C_{12}$-2,2',3,3',5,5',6-HpCB	178L	0.5	1.0	5.0	50	400	--
Recovery Standards							
$^{13}C_{12}$-2,5-DiCB	9L	100	100	100	100	100	100
$^{13}C_{12}$-2,4',5-TriCB	31L	100	100	100	100	100	100
$^{13}C_{12}$-2,4',6-TriCB	32L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',5,5'-TeCB	52L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',4',5,5'-PeCB	101L	100	100	100	100	100	100
$^{13}C_{12}$-3,3',4,5,5'-PeCB	127L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3',4,4',5'-HxCB	138L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,4,4',5,5'-HpCB	180L	100	100	100	100	100	100
$^{13}C_{12}$-2,2',3,3',4,4',5,5'-OcCB	194L	100	100	100	100	100	100
Labeled Sampling Surrogates							
$^{13}C_{12}$-2,4'-DiCB	8L	0.5	1.0	5.0	50	400	--
$^{13}C_{12}$-3,3',4,5'-TeCB	79L	0.5	1.0	5.0	50	400	--
$^{13}C_{12}$-2,2',3,5',6-PeCB	95L	0.5	1.0	5.0	50	400	--
$^{13}C_{12}$-2,2',4,4',5,5'-HxCB	153L	0.5	1.0	5.0	50	400	--

1. Suffix "L" indicates labeled compound.
2. Calibration verification solution.

Table 2					
PCB Shorthand Nomenclature[4] Used in this Report					
BZ/IUPAC Number[1].	PCB Chemical Structure Name[2]	CAS Registry[3] Number	BZ/IUPAC Number[1].	PCB Chemical Structure Name[2]	CAS Registry[3] Number
1	2-monochlorobiphenyl	2051-60-7	106	2,3,3',4,5-pentachlorobiphenyl	70424-69-0
2	3-monochlorobiphenyl	2051-61-8	107/109	2,3,3',4',5-pentachlorobiphenyl	70424-68-9
3	4-monochlorobiphenyl	2051-62-9	108/107	2,3,3',4,5'-pentachlorobiphenyl	70362-41-3
4	2,2'-dichlorobiphenyl	13029-08-8	109/108	2,3,3',4,6-pentachlorobiphenyl	74472-35-8
5	2,3-dichlorobiphenyl	16605-91-7	110	2,3,3',4',6-pentachlorobiphenyl	38380-03-9
6	2,3'-dichlorobiphenyl	25569-80-6	111	2,3,3',5,5'-pentachlorobiphenyl	39635-32-0
7	2,4-dichlorobiphenyl	33284-50-3	112	2,3,3',5,6-pentachlorobiphenyl	74472-36-9
8	2,4'-dichlorobiphenyl	34883-43-7	113	2,3,3',5',6-pentachlorobiphenyl	68194-10-5
9	2,5-dichlorobiphenyl	34883-39-1	114	2,3,4,4',5-pentachlorobiphenyl	74472-37-0
10	2,6-dichlorobiphenyl	33146-45-1	115	2,3,4,4',6-pentachlorobiphenyl	74472-38-1
11	3,3'-dichlorobiphenyl	2050-67-1	116	2,3,4,5,6-pentachlorobiphenyl	18259-05-7
12	3,4-dichlorobiphenyl	2974-92-7	117	2,3,4',5,6-pentachlorobiphenyl	68194-11-6
13	3,4'-dichlorobiphenyl	2974-90-5	118	2,3',4,4',5-pentachlorobiphenyl	31508-00-6
14	3,5-dichlorobiphenyl	34883-41-5	119	2,3',4,4',6-pentachlorobiphenyl	56558-17-9
15	4,4'-dichlorobiphenyl	2050-68-2	120	2,3',4,5,5'-pentachlorobiphenyl	68194-12-7
16	2,2',3-trichlorobiphenyl	38444-78-9	121	2,3',4,5',6-pentachlorobiphenyl	56558-18-0
17	2,2',4-trichlorobiphenyl	37680-66-3	122	2',3,3',4,5-pentachlorobiphenyl (2,3,3',4',5'-pentachlorobiphenyl)	76842-07-4

Table 2

PCB Shorthand Nomenclature[4] Used in this Report

BZ/IUPAC Number[1].	PCB Chemical Structure Name[2]	CAS Registry[3] Number	BZ/IUPAC Number[1].	PCB Chemical Structure Name[2]	CAS Registry[3] Number
18	2,2',5-trichlorobiphenyl	37680-65-2	123	2',3,4,4',5-pentachlorobiphenyl (2,3',4,4',5'-pentachlorobiphenyl)	65510-44-3
19	2,2',6-trichlorobiphenyl	38444-73-4	124	2',3,4,5,5'-pentachlorobiphenyl (2,3',4',5',5-pentachlorobiphenyl)	70424-70-3
20	2,3,3'-trichlorobiphenyl	38444-84-7	125	2',3,4,5,6'-pentachlorobiphenyl (2,3',4',5',6-pentachlorobiphenyl)	74472-39-2
21	2,3,4-trichlorobiphenyl	55702-46-0	126	3,3',4,4',5-pentachlorobiphenyl	57465-28-8
22	2,3,4'-trichlorobiphenyl	38444-85-8	127	3,3',4,5,5'-pentachlorobiphenyl	39635-33-1
23	2,3,5-trichlorobiphenyl	55720-44-0	128	2,2',3,3',4,4'-hexachlorobiphenyl	38380-07-3
24	2,3,6-trichlorobiphenyl	55702-45-9	129	2,2',3,3',4,5-hexachlorobiphenyl	55215-18-4
25	2,3',4-trichlorobiphenyl	55712-37-3	130	2,2',3,3',4,5'-hexachlorobiphenyl	52663-66-8
26	2,3',5-trichlorobiphenyl	38444-81-4	131	2,2',3,3',4,6-hexachlorobiphenyl	61798-70-7
27	2,3',6-trichlorobiphenyl	38444-76-7	132	2,2',3,3',4,6'-hexachlorobiphenyl	38380-05-1
28	2,4,4'-trichlorobiphenyl	7012-37-5	133	2,2',3,3',5,5'-hexachlorobiphenyl	35694-04-3
29	2,4,5-trichlorobiphenyl	15862-07-4	134	2,2',3,3',5,6-hexachlorobiphenyl	52704-70-8
30	2,4,6-trichlorobiphenyl	35693-92-6	135	2,2',3,3',5,6'-hexachlorobiphenyl	52744-13-5
31	2,4',5-trichlorobiphenyl	16606-02-3	136	2,2',3,3',6,6'-hexachlorobiphenyl	38411-22-2
32	2,4',6-trichlorobiphenyl	38444-77-8	137	2,2',3,4,4',5-hexachlorobiphenyl	35694-06-5
33	2',3,4-trichlorobiphenyl (2,3',4'-trichlorobiphenyl)	38444-86-9	138	2,2',3,4,4',5'-hexachlorobiphenyl	35065-28-2
34	2',3,5-trichlorobiphenyl (2,3',5'-trichlorobiphenyl)	37680-68-5	139	2,2',3,4,4',6-hexachlorobiphenyl	56030-56-9
35	3,3',4-trichlorobiphenyl	37680-69-6	140	2,2',3,4,4',6'-hexachlorobiphenyl	59291-64-4
36	3,3',5-trichlorobiphenyl	38444-87-0	141	2,2',3,4,5,5'-hexachlorobiphenyl	52712-04-6
37	3,4,4'-trichlorobiphenyl	38444-90-5	142	2,2',3,4,5,6-hexachlorobiphenyl	41411-61-4
38	3,4,5-trichlorobiphenyl	53555-66-1	143	2,2',3,4,5,6'-hexachlorobiphenyl	68194-15-0
39	3,4',5-trichlorobiphenyl	38444-88-1	144	2,2',3,4,5',6-hexachlorobiphenyl	68194-14-9
40	2,2',3,3'-tetrachlorobiphenyl	38444-93-8	145	2,2',3,4,6,6'-hexachlorobiphenyl	74472-40-5
41	2,2',3,4-tetrachlorobiphenyl	52663-59-9	146	2,2',3,4',5,5'-hexachlorobiphenyl	51908-16-8
42	2,2',3,4'-tetrachlorobiphenyl	36559-22-5	147	2,2',3,4',5,6-hexachlorobiphenyl	68194-13-8
43	2,2',3,5-tetrachlorobiphenyl	70362-46-8	148	2,2',3,4',5,6'-hexachlorobiphenyl	74472-41-6
44	2,2',3,5'-tetrachlorobiphenyl	41464-39-5	149	2,2',3,4',5',6-hexachlorobiphenyl	38380-04-0
45	2,2',3,6-tetrachlorobiphenyl	70362-45-7	150	2,2',3,4',6,6'-hexachlorobiphenyl	68194-08-1
46	2,2',3,6'-tetrachlorobiphenyl	41464-47-5	151	2,2',3,5,5',6-hexachlorobiphenyl	52663-63-5
47	2,2',4,4'-tetrachlorobiphenyl	2437-79-8	152	2,2',3,5,6,6'-hexachlorobiphenyl	68194-09-2
48	2,2',4,5-tetrachlorobiphenyl	70362-47-9	153	2,2',4,4',5,5'-hexachlorobiphenyl	35065-27-1
49	2,2',4,5'-tetrachlorobiphenyl	41464-40-8	154	2,2',4,4',5,6'-hexachlorobiphenyl	60145-22-4
50	2,2',4,6-tetrachlorobiphenyl	62796-65-0	155	2,2',4,4',6,6'-hexachlorobiphenyl	33979-03-2
51	2,2',4,6'-tetrachlorobiphenyl	68194-04-7	156	2,3,3',4,4',5-hexachlorobiphenyl	38380-08-4
52	2,2',5,5'-tetrachlorobiphenyl	35693-99-3	157	2,3,3',4,4',5'-hexachlorobiphenyl	69782-90-7
53	2,2',5,6'-tetrachlorobiphenyl	41464-41-9	158	2,3,3',4,4',6-hexachlorobiphenyl	74472-42-7
54	2,2',6,6'-tetrachlorobiphenyl	15968-05-5	159	2,3,3',4,5,5'-hexachlorobiphenyl	39635-35-3
55	2,3,3',4-tetrachlorobiphenyl	74338-24-2	160	2,3,3',4,5,6-hexachlorobiphenyl	41411-62-5
56	2,3,3',4'-tetrachlorobiphenyl	41464-43-1	161	2,3,3',4,5',6-hexachlorobiphenyl	74472-43-8
57	2,3,3',5-tetrachlorobiphenyl	70424-67-8	162	2,3,3',4',5,5'-hexachlorobiphenyl	39635-34-2
58	2,3,3',5'-tetrachlorobiphenyl	41464-49-7	163	2,3,3',4',5,6-hexachlorobiphenyl	74472-44-9
59	2,3,3',6-tetrachlorobiphenyl	74472-33-6	164	2,3,3',4',5',6-hexachlorobiphenyl	74472-45-0
60	2,3,4,4'-tetrachlorobiphenyl	33025-41-1	165	2,3,3',5,5',6-hexachlorobiphenyl	74472-46-1
61	2,3,4,5-tetrachlorobiphenyl	33284-53-6	166	2,3,4,4',5,6-hexachlorobiphenyl	41411-63-6
62	2,3,4,6-tetrachlorobiphenyl	54230-22-7	167	2,3',4,4',5,5'-hexachlorobiphenyl	52663-72-6

Table 2					
PCB Shorthand Nomenclature[4] Used in this Report					
BZ/IUPAC Number[1].	PCB Chemical Structure Name[2]	CAS Registry[3] Number	BZ/IUPAC Number[1].	PCB Chemical Structure Name[2]	CAS Registry[3] Number
63	2,3,4',5-tetrachlorobiphenyl	74472-34-7	168	2,3',4,4',5',6-hexachlorobiphenyl	59291-65-5
64	2,3,4',6-tetrachlorobiphenyl	52663-58-8	169	3,3',4,4',5,5'-hexachlorobiphenyl	32774-16-6
65	2,3,5,6-tetrachlorobiphenyl	33284-54-7	170	2,2',3,3',4,4',5-heptachlorobiphenyl	35065-30-6
66	2,3',4,4'-tetrachlorobiphenyl	32598-10-0	171	2,2',3,3',4,4',6-heptachlorobiphenyl	52663-71-5
67	2,3',4,5-tetrachlorobiphenyl	73575-53-8	172	2,2',3,3',4,5,5'-heptachlorobiphenyl	52663-74-8
68	2,3',4,5'-tetrachlorobiphenyl	73575-52-7	173	2,2',3,3',4,5,6-heptachlorobiphenyl	68194-16-1
69	2,3',4,6-tetrachlorobiphenyl	60233-24-1	174	2,2',3,3',4,5,6'-heptachlorobiphenyl	38411-25-5
70	2,3',4',5-tetrachlorobiphenyl	32598-11-1	175	2,2',3,3',4,5',6-heptachlorobiphenyl	40186-70-7
71	2,3',4',6-tetrachlorobiphenyl	41464-46-4	176	2,2',3,3',4,6,6'-heptachlorobiphenyl	52663-65-7
72	2,3',5,5'-tetrachlorobiphenyl	41464-42-0	177	2,2',3,3',4',5,6-heptachlorobiphenyl (2,2',3,3',4,5',6'-heptachlorobiphenyl)	52663-70-4
73	2,3',5',6-tetrachlorobiphenyl	74338-23-1	178	2,2',3,3',5,5',6-heptachlorobiphenyl	52663-67-9
74	2,4,4',5-tetrachlorobiphenyl	32690-93-0	179	2,2',3,3',5,6,6'-heptachlorobiphenyl	52663-64-6
75	2,4,4',6-tetrachlorobiphenyl	32598-12-2	180	2,2',3,4,4',5,5'-heptachlorobiphenyl	35065-29-3
76	2',3,4,5-tetrachlorobiphenyl (2,3',4',5'-tetrachlorobiphenyl)	70362-48-0	181	2,2',3,4,4',5,6-heptachlorobiphenyl	74472-47-2
77	3,3',4,4'-tetrachlorobiphenyl	32598-13-3	182	2,2',3,4,4',5,6'-heptachlorobiphenyl	60145-23-5
78	3,3',4,5-tetrachlorobiphenyl	70362-49-1	183	2,2',3,4,4',5',6-heptachlorobiphenyl	52663-69-1
79	3,3',4,5'-tetrachlorobiphenyl	41464-48-6	184	2,2',3,4,4',6,6'-heptachlorobiphenyl	74472-48-3
80	3,3',5,5'-tetrachlorobiphenyl	33284-52-5	185	2,2',3,4,5,5',6-heptachlorobiphenyl	52712-05-7
81	3,4,4',5-tetrachlorobiphenyl	70362-50-4	186	2,2',3,4,5,6,6'-heptachlorobiphenyl	74472-49-4
82	2,2',3,3',4-pentachlorobiphenyl	52663-62-4	187	2,2',3,4',5,5',6-heptachlorobiphenyl	52663-68-0
83	2,2',3,3',5-pentachlorobiphenyl	60145-20-2	188	2,2',3,4',5,6,6'-heptachlorobiphenyl	74487-85-7
84	2,2',3,3',6-pentachlorobiphenyl	52663-60-2	189	2,3,3',4,4',5,5'-heptachlorobiphenyl	39635-31-9
85	2,2',3,4,4'-pentachlorobiphenyl	65510-45-4	190	2,3,3',4,4',5,6-heptachlorobiphenyl	41411-64-7
86	2,2',3,4,5-pentachlorobiphenyl	55312-69-1	191	2,3,3',4,4',5',6-heptachlorobiphenyl	74472-50-7
87	2,2',3,4,5'-pentachlorobiphenyl	38380-02-8	192	2,3,3',4,5,5',6-heptachlorobiphenyl	74472-51-8
88	2,2',3,4,6-pentachlorobiphenyl	55215-17-3	193	2,3,3',4',5,5',6-heptachlorobiphenyl	69782-91-8
89	2,2',3,4,6'-pentachlorobiphenyl	73575-57-2	194	2,2',3,3',4,4',5,5'-octachlorobiphenyl	35694-08-7
90	2,2',3,4',5-pentachlorobiphenyl	68194-07-0	195	2,2',3,3',4,4',5,6-octachlorobiphenyl	52663-78-2
91	2,2',3,4',6-pentachlorobiphenyl	68194-05-8	196	2,2',3,3',4,4',5,6'-octachlorobiphenyl	42740-50-1
92	2,2',3,5,5'-pentachlorobiphenyl	52663-61-3	197	2,2',3,3',4,4',6,6'-octachlorobiphenyl	33091-17-7
93	2,2',3,5,6-pentachlorobiphenyl	73575-56-1	198	2,2',3,3',4,5,5',6-octachlorobiphenyl	68194-17-2
94	2,2',3,5,6'-pentachlorobiphenyl	73575-55-0	199/200	2,2',3,3',4,5,6,6'-octachlorobiphenyl	52663-73-7
95	2,2',3,5',6-pentachlorobiphenyl	38379-99-6	200/201	2,2',3,3',4,5',6,6'-octachlorobiphenyl	40186-71-8
96	2,2',3,6,6'-pentachlorobiphenyl	73575-54-9	201/199	2,2',3,3',4,5,5',6'-octachlorobiphenyl	52663-75-9
97	2,2',3',4,5-pentachlorobiphenyl (2,2',3,4',5'-pentachlorobiphenyl)	41464-51-1	202	2,2',3,3',5,5',6,6'-octachlorobiphenyl	2136-99-4
98	2,2',3',4,6-pentachlorobiphenyl (2,2',3,4',6'-pentachlorobiphenyl)	60233-25-2	203	2,2',3,4,4',5,5',6-octachlorobiphenyl	52663-76-0
99	2,2',4,4',5-pentachlorobiphenyl	38380-01-7	204	2,2',3,4,4',5,6,6'-octachlorobiphenyl	74472-52-9
100	2,2',4,4',6-pentachlorobiphenyl	39485-83-1	205	2,3,3',4,4',5,5',6-octachlorobiphenyl	74472-53-0
101	2,2',4,5,5'-pentachlorobiphenyl	37680-73-2	206	2,2',3,3',4,4',5,5',6-nonachlorobiphenyl	40186-72-9
102	2,2',4,5,6-pentachlorobiphenyl	68194-06-9	207	2,2',3,3',4,4',5,6,6'-nonachlorobiphenyl	52663-79-3
103	2,2',4,5',6-pentachlorobiphenyl	60145-21-3	208	2,2',3,3',4,5,5',6,6'-nonachlorobiphenyl	52663-77-1
104	2,2',4,6,6'-pentachlorobiphenyl	56558-16-8	209	2,2',3,3',4,4',5,5',6,6'-decachlorobiphenyl	2051-24-3

Table 2					
PCB Shorthand Nomenclature[4] Used in this Report					
BZ/IUPAC Number[1].	PCB Chemical Structure Name[2]	CAS Registry[3] Number	BZ/IUPAC Number[1].	PCB Chemical Structure Name[2]	CAS Registry[3] Number
105	2,3,3',4,4'-pentachlorobiphenyl	32598-14-4			

1. The BZ number is from Ballschmiter and Zell (1980). The IUPAC number, when different from the BZ, follows the recommended changes to the BZ number per Schulte and Malisch (1983) and Guitart et al. (1993).
2. The chemical structure names are from Ballschmiter and Zell (1980). IUPAC nomenclature structure names are listed in parenthesis when different from the BZ name (source CAS Registry).
3. Chemical Abstract Service Registry number (source CAS Registry and 1668 Table 1).
4. A complete discussion of PCB Nomenclature may be found in Mills III, S.A. et al., A summary of the 209 PCB congener nomenclature, Chemosphere (2007), doi:10.1016/j.chemosphere.2007.03.052.

Case Narrative:
Volatile Organic Compounds – SW846 5041A, SW846 8260B

Day

TestAmerica Laboratories, Inc.

PROJECT NARRATIVE
H6D260410

The results reported herein are applicable to the samples submitted for analysis only. If you have any questions about this report, please call (865) 291-3000 to speak with the TestAmerica project manager listed on the cover page.

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Sample Receipt

The temperature blank container was outside of temperature specifications at 12.3 °C.

Custody seals were not present.

Quality Control and Data Interpretation

Unless otherwise noted, all holding times and QC criteria were met and the test results shown in this report meet all applicable NELAC requirements.

VOST tubes and condensate samples were analyzed for the volatile organic target analytes by purge and trap GCMS using TestAmerica Knoxville standard operating procedures KNOX-MS-0011 and KNOX-MS-0015, based on the following methods:

- SW-846 5041A, "Analysis for Desorption of Sorbent Cartridges from Volatile Organic Sampling Train (VOST)"
- SW-846 8260B, "Volatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS)"

Samples were received as SW-846 method 0031 trains. Each Tenax/Tenax tube pair and Tenax/Charcoal tube was separately prepared by spiking a known amount of surrogate onto the media using a flash vaporization device. Volatile compounds are introduced into the gas chromatograph by thermal desorption of the analytes from the VOST tube using a clamshell oven and a purge and trap device. VOST condensates are spiked with surrogates and purged directly. The components are separated using the chromatograph and detected using a mass spectrometer, which provides both qualitative and quantitative information.

Sample results were calculated using the following equations:

$$\text{VOST Result, ug} = (\text{On column concentration, ug/L}) * (\text{Purge Volume, L})$$

$$\text{Condensate Result, ug/L} = (\text{On column concentration, ug/L}) * \text{Dilution Factor}$$

Due to the nature of the VOST analysis, and limited sample volume, a laboratory control sample/laboratory control sample duplicate was performed instead of a matrix spike/matrix spike duplicate for all samples.

PROJECT NARRATIVE
H6D260410

The laboratory control sample results for batch 6118020 were outside control limits for 1,2,3-trichloropropane and naphthalene. However, the LCS results met the marginal exceedence acceptance criterion, which allows for three analytes to be within marginal exceedence limits.

The laboratory control sample/laboratory control sample duplicate RPD results for batch 6124011 were acceptable for all analytes except tert-butylbenzene. However, the laboratory control samples showed acceptable recoveries.

The following condensate samples were received at the corresponding volumes:

Client ID	Volume (mL)
R1 CONDENSATE	42.9
R2 CONDENSATE	43.4
R3 CONDENSATE	43.3
R4 CONDENSATE	43.1
R5 CONDENSATE	42.9
FB CONDENSATE	42.9

The concentrations of acetone and/or methylene chloride were greater than the calibration range for all condensate samples. Reanalysis at a dilution was not possible because the entire sample was consumed during analysis.

Due to the high level of organics in the samples, all VOST tubes with a dilution factor of 1X that were thermally desorbed directly to the mass spectrometry instrument had their TIC search intensity raised to greater than or equal to the height of the internal standard.

The following samples were not reported because of extremely high levels of organics in the samples which interfered with the internal standards.

A030844/A032578 R1 SET 3 TUBE 1+2,
A032666 R1 SET 3 TUBE 3
A033210/A033235 R1 SET 4 TUBE 1+2,
A033195 R1 SET 4 TUBE 3

Due to the high concentration of organics in the samples, the following samples were desorbed into a methanol impinger using the standard operating procedure "Tenax Resin Volatile Sample Thermal Desorption/Methanol Micro-Trap Preparation(KNOX-MS-0026) and analyzed by GCMS by the standard operating procedure KNOX-MS-0015 with the client's permission. The desorption procedure resulted in at least a 20X dilution of the VOST tube.

A033192/A031573 R2 SET 1 TUBE 1+2
A032766 R2 SET 1 TUBE 3
A033031/A032603 R2 SET 2 TUBE 1+2
A032807 R2 SET 2 TUBE 3
A031073/A030548 R3 SET 1 TUBE 1+2
A033272 R3 SET 1 TUBE 3
A032779/A032775 R4 SET 2 TUBE 1+2
A030542 R4 SET 2 TUBE 3

PROJECT NARRATIVE
H6D260410

A031125/A033141 R4 SET 3 TUBE 1+2
A033144 R4 SET 3 TUBE 3
A033163/A033149 R4 SET 4 TUBE 1+2
A030924 R4 SET4 TUBE 3
A033151/A032778 R5 SET 2 TUBE 1+2
A011502 R5 SET 2 TUBE 3
A011553/A033086 R5 SET 3 TUBE 1+2
A031290 R5 SET 3 TUBE 3
A033159/A033126 R5 SET 4 TUBE 1+2
A030517 R5 SET 4 TUBE 3

Due to the high level of benzene in samples, the surrogate of 1,2-dichloroethane-d4 could not be quantitated and therefore not reported in several samples. The result is flagged with "NC".

Surrogate 1,2-dichloroethane d-4 percent recovery for samples A032743/A032797 R1 SET 1 TUBE 1+2 and A032739/A033206 R1 SET 2 TUBE 1+2 were outside control limits due to obvious matrix interferences.

Surrogate percent recoveries of dibromofluoromethane and 1,2-dichloroethane-d4 for sample A033163/A033149 R4 SET 4 TUBE 1+2 were below QC limits. However, reanalysis of the associated sample was not possible since the entire sample was consumed during analysis.

Due to mass spectrometer saturation, the results for benzene, ethylbenzene, styrene and toluene in several samples are estimated. Please note that the extrapolation of results above the quantitation range can lead to significant quantitative error, especially when peak saturation is observed.

Due to the high level of benzene in several samples, there is a significant contribution from benzene's minor ions to the quantization of 1,2-dichloroethane. Therefore, the 1,2-dichloroethane results are biased high and should be considered estimated. The results are flagged with "EST".

There is a significant contribution from an interfering target analyte of styrene to the quantitation of o-xylene in several samples Therefore, the o-xylene results are biased high and should be considered estimated. The result is flagged with "EST".

Case Narrative:
Volatile Organic Compounds – SW846 5041A, SW846 8260B

Night

TestAmerica Laboratories, Inc.

PROJECT NARRATIVE
H6E040405

The results reported herein are applicable to the samples submitted for analysis only. If you have any questions about this report, please call (865) 291-3000 to speak with the TestAmerica project manager listed on the cover page.

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Sample Receipt

Custody seals were not present.

Sample A030523 Tube 2 was labeled as A030923.

Quality Control and Data Interpretation

Unless otherwise noted, all holding times and QC criteria were met and the test results shown in this report meet all applicable NELAC requirements.

VOST tubes and condensate samples were analyzed for the volatile organic target analytes by purge and trap GCMS using TestAmerica Knoxville standard operating procedures KNOX-MS-0015 and KNOX-MS-0026. Due to the high concentration of organics in the samples, the VOST samples were desorbed into a methanol impinger using the standard operating procedure "Tenax Resin Volatile Sample Thermal Desorption/Methanol Micro-Trap Preparation(KNOX-MS-0026) and analyzed by GCMS by the standard operating procedure KNOX-MS-0015 with the client's permission. The desorption procedure resulted in at least a 20X dilution of the VOST tube. Due to the lack of historical data for this extraction procedure, control limits have not been established for laboratory control analytes or surrogates; limits on the report are considered advisory.

The analytical procedures are based on the following methods:

- SW-846 5041A, "Analysis for Desorption of Sorbent Cartridges from Volatile Organic Sampling Train (VOST)"
- SW-846 8260B, "Volatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS)"

Samples were received as SW-846 method 0031 trains. Each Tenax/ Tenax tube pair and Tenax/charcoal tube was separately prepared by spiking a known amount of surrogate onto the media using a flash vaporization device. Volatile compounds are introduced into the gas chromatograph by a methanol extract obtained from the thermal desorption of the analytes from the VOST tube using a clamshell oven. A portion of methanol extract is then injected into a sparge vessel and analyzed by a purge and trap device in conjunction of a GC/MS. VOST condensates are spiked with surrogates and purged directly. The components are separated using the chromatograph and detected using a mass spectrometer, which provides both qualitative and quantitative information.

PROJECT NARRATIVE
H6E040405

Sample results were calculated using the following equations:

$$\text{VOST Result, ug} = (\text{On column concentration, ug/L}) * (\text{Purge Volume, L})$$

$$\text{Condensate Result, ug/L} = (\text{On column concentration, ug/L}) * \text{Dilution Factor}$$

Due to limited sample volume, a laboratory control sample/laboratory control sample duplicate was performed instead of a matrix spike/matrix spike duplicate for all samples.

The laboratory control sample duplicate results for batch 6125063 were outside control limits for trans-1,3-dichloropropene. In addition, laboratory control sample results for batch 6131013 were outside control limits for vinyl chloride. However, the LCS results met the marginal exceedence acceptance criterion, which allows for three analytes being within marginal exceedence limits.

One or more surrogate recoveries for several samples and laboratory control sample duplicate M8LNK1AD were outside QC limits. However, reanalysis of the associated samples was not possible since the entire sample was consumed during analysis.

The following water samples were received at the corresponding volumes:

Client ID	Volume (mL)
R1 CONDENSATE	42.4
R2 CONDENSATE	43.8
R3 CONDENSATE	42.7
R4 CONDENSATE	43.5
R5 CONDENSATE	43.3
R6 CONDENSATE	42.7
FB DI WATER CONDENSATE	42.7

Samples R1 CONDENSATE and R2 CONDENSATE were analyzed at a dilution due to high levels of isopropyl alcohol.

The following samples were received damaged and could not be analyzed:

A033108/A033202 R3 SET 4 TUBE 1+2
A031523 R3 SET 4 TUBE 3
A033155/A032672 R4 SET 4 TUBE 1+2
A033252 R4 SET 4 TUBE 3
A032646/A033113 R6 SET 2 TUBE 1+2
A032586 R6 SET 2 TUBE 3

The following samples were damaged during sample preparation and could not be analyzed:

A033026/A033044 R4 SET 2 TUBE 1+2
A032810 R4 SET 2 TUBE 3
A033028/A033168 R6 SET 4 TUBE 1+2
A030829 R6 SET 4 TUBE 3

Case Narrative:
Hydrogen Chloride - KNOX 0050/26A

Day

TestAmerica Laboratories, Inc.

PROJECT NARRATIVE
H6D280405

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Sample Receipt

Custody seals were not present.

Quality Control and Data Interpretation

Unless otherwise noted, all holding times and QC criteria were met and the test results shown in this report meet all applicable NELAC requirements.

Samples were analyzed for chloride (Cl^-) by ion chromatography using SOP number KNOX-WC-005 (based on EPA methods 9056, 9057 and 26A). All sample results were reported as total µg hydrogen chloride (HCl). Results were calculated using the following equation:

$$\text{HCl, ug} = \left(\text{Cl}^-,\text{ug/mL}\right) * \left(\text{Sample Volume,mL}\right) * \left(\frac{\text{Molecular Weight HCl}}{\text{Molecular Weight Cl}^-}\right) * \text{Bench Dilution}$$

Note: A sample volume of 100 mL was used to convert the results to total µg for the method blanks, laboratory control samples, and client reagent blanks.

For demonstration of analytical method performance on these samples, TestAmerica Knoxville analyzed matrix spikes (MS) and matrix spike duplicates (MSD). Acceptable recoveries of these spikes demonstrate that quantitation from this particular stack gas matrix is accurate and acceptable. Impinger samples containing 0.1N H_2SO_4 often display matrix interference effects causing poor method performance and possibly giving unreliable data unless the interference is dealt with. Therefore, the samples were diluted in the lab to reduce the interference for a more accurate anion response. The samples may be analyzed at increasing dilutions along with matrix spikes until matrix spikes display acceptable recoveries. The ion chromatograph calibration range used to quantitate the sample results permits a standard ten-fold sample dilution while supporting the reporting limit with the low calibration standard.

The dilution factor reported on the sample result form **does not** represent the bench dilution factor. It is actually the combination of factors required by the method to convert the anion reporting limit and method detection limit from µg/mL to total µg. It appears to be elevated since it includes the total sample impinger volume in mL in order to calculate total µg in the sample.

Case Narrative:
Hydrogen Chloride - KNOX 0050/26A

Night

TestAmerica Laboratories, Inc.

PROJECT NARRATIVE
H6E040411

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Sample Receipt

Custody seals were not present.

Quality Control and Data Interpretation

Unless otherwise noted, all holding times and QC criteria were met and the test results shown in this report meet all applicable NELAC requirements.

Samples were analyzed for chloride (Cl^-) by ion chromatography using SOP number KNOX-WC-005 (based on EPA methods 9056, 9057 and 26A). All sample results were reported as total µg hydrogen chloride (HCl). Results were calculated using the following equation:

$$\text{HCl, ug} = \left(\text{Cl}^-, \text{ug/mL}\right) * \left(\text{Sample Volume, mL}\right) * \left(\frac{\text{Molecular Weight HCl}}{\text{Molecular Weight Cl}^-}\right) * \text{Bench Dilution}$$

Note: A sample volume of 100 mL was used to convert the results to total µg for the method blanks, laboratory control samples, and client reagent blanks.

For demonstration of analytical method performance on these samples, TestAmerica Knoxville analyzed matrix spikes (MS) and matrix spike duplicates (MSD). Acceptable recoveries of these spikes demonstrate that quantitation from this particular stack gas matrix is accurate and acceptable. Impinger samples containing 0.1N H_2SO_4 often display matrix interference effects causing poor method performance and possibly giving unreliable data unless the interference is dealt with. Therefore, the samples were diluted in the lab to reduce the interference for a more accurate anion response. The samples may be analyzed at increasing dilutions along with matrix spikes until matrix spikes display acceptable recoveries. The ion chromatograph calibration range used to quantitate the sample results permits a standard ten-fold sample dilution while supporting the reporting limit with the low calibration standard.

The dilution factor reported on the sample result form **does not** represent the bench dilution factor. It is actually the combination of factors required by the method to convert the anion reporting limit and method detection limit from µg/mL to total µg. It appears to be elevated since it includes the total sample impinger volume in mL in order to calculate total µg in the sample.

Case Narrative:
Hydrogen Cyanide – USEPA Method 9014

Day

TestAmerica Laboratories, Inc.

PROJECT NARRATIVE
H6D280404

The results reported herein are applicable to the samples submitted for analysis only. If you have any questions about this report, please call (865) 291-3000 to speak with the TestAmerica project manager listed on the cover page.

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Sample Receipt

Custody seals were not present.

Subcontract

The following analyses were performed by the TestAmerica Pittsburgh Laboratory (NELAP Accrediting Authority: PADEP; Lab ID 02-00416), 301 Alpha Drive, Pittsburgh, PA 15238, (412)963-7058, Debbie Lowe, Laboratory Director: Cyanide (SW846 9014

Field Spike Recovery

To provide an accuracy demonstration of the field sampling procedures, the client performed a field spike using 1.0 mL of a 500 µg/L spike concentration solution spiked onto 100mL of a 0.5N NaOH solution. The percent recovery was determined by the following equation:

% Recovery = (Measured Value/True Value) x 100

The results are presented below:

Client Sample ID / Lab ID	Measured Value (µg/L)	True Value (µg/L)	Percent Recovery (%)
Spike / 180-54287-12	410	500	82

Quality Control and Data Interpretation

Unless otherwise noted, all holding times and QC criteria were met and the test results shown in this report meet all applicable NELAC requirements.

Case Narrative:
Hydrogen Cyanide – USEPA Method 9014

Night

TestAmerica Laboratories, Inc.

PROJECT NARRATIVE
H6E040412

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The original chain of custody documentation is included with this report.

Sample Receipt

Custody seals were not present.

Subcontract

The following analyses were performed by the TestAmerica Pittsburgh Laboratory (NELAP Accrediting Authority: PADEP; Lab ID 02-00416), 301 Alpha Drive, Pittsburgh, PA 15238, (412)963-7058, Debbie Lowe, Laboratory Director: Cyanide (SW846 9014).

Quality Control and Data Interpretation

Unless otherwise noted, all holding times and QC criteria were met and the test results shown in this report meet all applicable NELAC requirements.

Case Narrative:
Particle Size Distribution – MVA Method 316

Day/Night

MVA Scientific Consultants

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Fluorescence Microscopy

Ion Milling & Ultramicrotomy

Accreditations

cGMP Compliant

ISO/IEC 17025
A2LA Certificate #2096.01

FDA Registered

Report of Results: MVA11688

Particle Size Distribution Measurement

Prepared for:

Ambient Air Services
106 Ambient Airway
Starke, FL 32091

Respectfully Submitted by:

EXECUTED BY ELECTRONIC SIGNATURE

Tim B. Vander Wood, Ph.D.
Executive Director

29 September 2016

Report of Results: MVA11688

Particle Size Distribution Measurement

Introduction

This report includes the results of the requested particle size analysis to 0.5μm minimum diameter of ten Method 5 filter samples received on 9 September 2016. Upon receipt, the samples were assigned unique MVA Scientific Consultants laboratory identification numbers as shown in Table 1. Analyses were performed at MVA Scientific Consultants during the period of 15 September through 29 September 2016.

Methods

Samples were prepared for analysis in accordance with MVA SOP 310, "Sample Preparation Methods for Total Particle Sizing Using Microscopical Techniques."

The analyses were performed using a JEOL JSM-6500F field emission scanning electron microscope operating in automated mode under the control of a Thermo Scientific Noran System 7 x-ray analysis system, utilizing MVA SOP 316, "Automated Particle Size Analysis Using the JEOL JSM-6500F FESEM and Thermo Scientific Noran System 7." The particle size data are presented in terms of particle number and in terms of estimated mass. The assumption has been made that the particles are all of similar density and therefore the particle volume distribution is equivalent to the particle mass distribution.

Results

The size distributions of the particles down to 0.5 micrometer are shown in Tables 1 and 2.

Table 1. MVA 11688. Percentages of Particles in Various Diameter Ranges by Number of Particles

MVA#	AB1362	AB1363	AB1364	AB1365	AB1366	AB1367	AB1368	AB1369	AB1370	AB1371
Client ID	4924 - Run D5	5357 - Run D1	5359 - Run N5	5361 - Run N3	5362 - Run D2	5363 - Run D4	5364 - Run N4	5365 - Run N2	5367 - Run N1	5368 - Run D3
Diameter Range (µm)	Number %	Number %	Number %	Number %	Number %	Number %	Number %	Number %	Number %	Number %
0.5-≤1.0	56.2	57.1	51.3	53.8	60.9	63.8	56.2	46.8	45.1	52.8
>1.0-≤2.5	33.1	31.4	39.1	40.0	34.9	27.0	36.1	41.4	39.6	39.0
>2.5-≤5.0	8.7	8.0	7.4	5.2	3.7	5.9	5.8	9.8	10.7	6.9
>5.0-≤7.5	1.3	2.1	1.8	0.7	0.4	1.6	1.3	1.4	2.5	0.9
>7.5-≤10.0	0.4	0.8	0.2	0.1	0.1	0.9	0.3	0.4	1.1	0.3
>10.0	0.3	0.6	0.2	0.2	0.1	0.9	0.3	0.1	1.0	0.1
Total Particles	19302	19394	2590	18465	38801	14301	10422	9691	11445	12810

Table 2. MVA 11688. Percentages of Particles in Various Diameter Ranges by Mass of Particles

MVA#	AB1362	AB1363	AB1364	AB1365	AB1366	AB1367	AB1368	AB1369	AB1370	AB1371
Client ID	4924 - Run D5	5357 - Run D1	5359 - Run N5	5361 - Run N3	5362 - Run D2	5363 - Run D4	5364 - Run N4	5365 - Run N2	5367 - Run N1	5368 - Run D3
Diameter Range (µm)	Mass %	Mass %	Mass %	Mass %	Mass %	Mass %	Mass %	Mass %	Mass %	Mass %
0.5-≤1.0	1.3	0.9	1.0	3.0	5.6	0.6	2.2	2.0	0.6	2.7
>1.0-≤2.5	8.2	4.2	6.6	16.6	22.7	2.7	11.0	16.0	5.2	17.0
>2.5-≤5.0	17.8	13.5	10.3	17.2	24.5	5.9	17.0	30.3	13.3	27.4
>5.0-≤7.5	12.6	17.0	14.8	10.8	15.8	7.3	17.7	19.6	12.9	17.1
>7.5-≤10.0	10.0	19.2	2.4	7.4	7.0	12.2	11.2	17.2	16.9	11.7
>10.0	50.2	45.2	64.9	45.0	24.5	71.3	41.0	15.0	51.1	24.2

MVA SCIENTIFIC CONSULTANTS
Full Service Analytical Microscopy Laboratory

APPENDIX N

OPERATIONS DATA

Note: Information in this Appendix supplied by MultiMac JV.

Daily Log

Site Photos

DAYBOOK NSGB AIR CURTAIN INCINERATOR SAMPLING

DATE	Arrival TIME	EVENT	Personnel Onsite	Departure TIME
Apr-16	8:30	Recon trip to site, equipment delivery and setup. Met with Landfill Operations.	Amec FW (Rafael DePaz, Justin Knoll) KMEA (Bill Basta) AASI (Abram Lafferty, Will Garabrandt, Mike Hinkle, Matt Hamilton) NAVFAC (Matt Cookingham, Donald Hommeland).	14:50
Apr-17	10:00	Additional site reconnaissance. Pre sample planning.	Amec FW (Rafael DePaz, Justin Knoll) KMEA (Bill Basta) AASI (Abram Lafferty) NAVFAC (Matt Cookingham, Donald Hommeland).	11:45
Apr-18	8:23	Daytime Sampling #1, Processed 22.64 tons of Household Garbage ~ 50% of which was added to Air Curtain Incinerator under test. Monday is the busiest day of the week. Weather Clear, Dry and Windy ~15 mph, primarily out of the North and North West.	Amec FW (Rafael DePaz, Justin Knoll) KMEA (Bill Basta) AASI (Abram Lafferty, Will Garabrandt, Mike Hinkle, Matt Hamilton) NAVFAC (Matt Cookingham, Donald Hommeland) Navy Marine Corps Public Health (Dr. Paul Gillooly) Pioneer Technologies (Chris Waldron)	19:05
Apr-19	6:58	Daytime Sampling #2, Processed 14.5 tons of Household Garbage ~ 60% of which was added to Air Curtain Incinerator under test. Weather Clear, Dry and Breesy 5- 10 mph from north in morning, turning windy after noon ~ 15-20 mph from south and SE.	Amec FW (Justin Knoll) KMEA (Bill Basta) AASI (Abram Lafferty, Will Garabrandt, Mike Hinkle, Matt Hamilton) NAVFAC (Matt Cookingham, Donald Hommeland, Arnie Olsen).	17:05
Apr-20	6:58	Daytime Sampling #3 processed 13.74 tons of Household Garbage ~ 70% of which was added to Air Curtain Incinerator under test. . Weather Clear, Dry and Breezy, winds started out of North, switched from South and finally out of the East in mid afternoon.	Amec FW (Justin Knoll) KMEA (Bill Basta) AASI (Abram Lafferty, Will Garabrandt, Mike Hinkle, Matt Hamilton) NAVFAC (Matt Cookingham, Donald Hommeland).	17:10
Apr-21	7:10	Daytime Sampling #4, Processed 7.17 tons of Household Garbage ~ 90% of which was added to Air Curtain Incinerator under test. Weather Cloudy, Dry and Breezy ~5-10 mph, primarily out of the North and North West.	Amec FW (Justin Knoll) KMEA (Bill Basta) AASI (Abram Lafferty, Will Garabrandt, Mike Hinkle, Matt Hamilton) NAVFAC (Matt Cookingham, Donald Hommeland).	16:33
Apr-22	7:30	Daytime Sampling #5, Processed 15.08 tons of Household Garbage ~ 66% of which was added to Air Curtain Incinerator under test. Weather Cloudy and Breezy ~5 mph, primarily out of the North and North West. Afternoon sprinkles and rain showers.	Amec FW (Justin Knoll, Pete Yanczyk) AASI (Abram Lafferty, Will Garabrandt, Mike Hinkle, Matt Hamilton) NAVFAC (Matt Cookingham, Donald Hommeland).	17:30
Apr-23	9:00	AASI personnel onsite to perform field blanks and prepare for night time testing	Amec FW (Justin Knoll, Pete Yanczyk) AASI (Abram Lafferty, Will Garabrandt, Mike Hinkle, Matt Hamilton) NAVFAC (Matt Cookingham, Donald Hommeland) Pioneer Technologies (Chris Waldron)	13:30

DATE	Arrival TIME	EVENT	Personnel Onsite	Departure TIME
Apr-24	20:30	Onsite to check lighting towers under night time conditions in preperation for night time sampling.	Amec FW (Justin Knoll) AASI (Abram Lafferty, Will Garabrandt) NAVFAC (Matt Cookingham)	21:00
Apr-25	15:30	Night Sampling #1, Processed 22.8 tons of Household Garbage, unsure how much was added to ACI under test. Hot, Dry and Windy, wind started from East @~10-15mph, shifted to winds from North @ ~5-10 mph around sunset.	Amec FW (Justin Knoll, Pete Yanczyk) AASI (Abram Lafferty, Will Garabrandt, Mike Hinkle, Matt Hamilton) NAVFAC (Matt Cookingham, Donald Hommeland).	1:51
Apr-26	16:30	Night Sampling #2, Processed 11.0 tons of Household Garbage, unsure how much was added to ACI under test. Hot, Dry and Breezy, wind started from East @~10 mph, from North @ ~5-10 mph around sunset.	Amec FW (Justin Knoll, Pete Yanczyk) AASI (Abram Lafferty, Will Garabrandt, Mike Hinkle, Matt Hamilton) NAVFAC (Matt Cookingham, Donald Hommeland).	1:35
Apr-27	16:30	Night Sampling #3, Processed 15.65 tons of Household Garbage, unsure how much was added to ACI under test. Admiral Iverson and group from the hospital onsite to view sampling operations. Hot, Dry and Windy, wind started from East @~10-15mph, shifting to winds from North @ ~5-10 mph around sunset.	Amec FW (Justin Knoll, Pete Yanczyk) AASI (Abram Lafferty, Will Garabrandt, Mike Hinkle, Matt Hamilton) NAVFAC (Matt Cookingham, Donald Hommeland).	1:10
Apr-28	16:30	Night Sampling #4, Processed 12.23 tons of Household Garbage, unsure how much was added to ACI under test. Hot, Dry and Breezy, wind started from East @~10 mph, from North East @ ~5-10 mph around sunset.	Amec FW (Justin Knoll, Pete Yanczyk) AASI (Abram Lafferty, Will Garabrandt, Mike Hinkle, Matt Hamilton) NAVFAC (Matt Cookingham, Donald Hommeland).	1:10
Apr-29	10:00	Dioxin/Furan Day 1 retest due to breakage during shipment and Night Sampling #5, Processed 11.45 tons of Household Garbage, unsure how much was added to ACI under test. Hot, Dry and Breezy, wind started from South East @~5-10mph, shifted to winds from North, NNE @ ~5-10 mph around sunset. AASI prepared for demobilization.	Amec FW (Justin Knoll) AASI (Abram Lafferty, Will Garabrandt, Mike Hinkle, Matt Hamilton) NAVFAC (Matt Cookingham, Donald Hommeland).	1:10
Apr-30	10:00	Went to site to make sure everything was packed up and ready for demobilization.	Amec FW (Justin Knoll) AASI (Abram Lafferty) NAVFAC (Donald Hommeland).	10:30

AASI