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>>>> This article, FR94, is divided into five files. This is File B: Technical Amendments of Appendix IX to Part 266, Section 3.3 to Section 4.0. <<<<

3.3 Measurement of HCl and Cl_2

3.3.1 Isokinetic HCl/Cl_2 Emission Sampling Train (Method 0050)

3.3.1.1 Scope and Application.

3.3.1.1.1 This method describes the collection of hydrogen chloride (HCl. CAS Registry Number 7647-01-0) and chlorine (Cl_2, CAS Registry Number 7782-50-5) in stack gas emission samples from hazardous waste incinerators' municipal waste combustors, and boilers and industrial furnaces. The collected ed samples are analyzed using Method 9057. This method collects the emission sample isokinetically and is therefore particularly suited for sampling at sources, such as those controlled by wet scrubbers, emitting acid particulate matter (e.g., HCl dissolved in water droplets). A midget impinger train sampling method designed for sampling sources of HCl/Cl_2 emissions not in particulate form is presented in method 0051.

3.3.1.1.2 This method is not acceptable for demonstrating compliance with HCl emission standards less than 20 ppm.

3.3.1.1.3 This method may also be used to collect samples for subsequent determination of particulate emissions (by EPA method 5, reference 1) following the additional sampling procedures described.

3.3.1.2 Summary of Method.

3.3.1.2.1 Gaseous and particulate pollutants are withdrawn from an emission source and are collected in an optional cyclone, on a filter, and in absorbing solutions. The cyclone collects any liquid droplets and is not necessary if the source emissions do not contain liquid droplets. The Teflon mat or quartz-fiber filter collects other particulate matter including chloride salts. Acidic and alkaline absorbing solutions collect gaseous HCl and Cl_2, respectively. Following sampling of emissions containing liquid droplets, any HCl/Cl_2 dissolved in the liquid in the cyclone and/or on the filter is vaporized and ultimately collected in the impingers by pulling Ascarite II^R conditioned ambient air through the sampling train. In the acidified water absorbing solution, the HCl gas is solubilized and forms chloride (Cl^-) ions. The Cl_2 gas present in the emissions has a very low solubility in acidified water and passes through to the alkaline absorbing solution where it undergoes hydrolysis to form a proton (H^+), Cl^-, and hypochlorous acid (HClO). The Cl^- ions in the separate solutions are measured by ion chromatography (method 9057). If desired, the particulate matter recovered from the filter and the probe is analyzed following the procedures in EPA Method 5 (reference 1).

3.3.1.3 Interferences.

3.3.1.3.1 Volatile materials which produce chloride ions upon dissolution during sampling are obvious interferences in the measurement of HCl. One interferant for HCl is diatomic chlorine (Cl_2) gas which disproportionates to HCl and hypochlorous acid (HClO) upon dissolution in water. Cl_2 gas exhibits a low solubility in water, however, and the use of acidic rather than neutral or basic solutions for collection of hydrogen chloride gas greatly reduces the dissolution of any chlorine present.

3.3.1.4 Apparatus and Materials.

3.3.1.4.1 Sampling Train.

3.3.1.4.1.1 A schematic of the sampling train used in this method is shown in Figure 3.3-1. This sampling train configuration is adapted from EPA method 5 procedures, and, as such, the majority of the required equipment is

identical to that used in EPA Method 5 determinations. The new components required are a glass nozzle and probe, a Teflon union, a quartz-fiber or Teflon mat filter (see section 3.3.1.5.5), a Teflon frit, and acidic and alkaline absorbing solutions.

3.3.1.4.1.2 Construction details for the basic train components are provided in section 3.4 of EPA's Quality Assurance Handbook, Volume III (reference 2); commercial models of this equipment are also available.

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Additionally, the following subsections identify allowable train configuration modifications.

3.3.1.4.1.3 Basic operating and maintenance procedures for the sampling train are also described in Reference 2. As correct usage is important in obtaining valid results, all users should refer to Reference 2 and adopt the operating and maintenance procedures outlined therein unless otherwise specified. The sampling train consists of the components detailed below.

3.3.1.4.1.3.1 Probe nozzle. 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. The nozzle should be coupled to the probe liner using a Teflon union. It is recommended that a stainless steel nut be used on this union. In cases where the stack temperature exceeds 210 °C (410 °F), a one-piece glass nozzle/liner assembly must be used. A range of nozzle sizes suitable for isokinetic sampling should be available. Each nozzle shall be calibrated according to the procedures outlined in EPA Method 5 (see References 1 and 2).

3.3.1.4.1.3.2 Probe liner. Borosilicate or quartz-glass tubing with a heated system capable of maintaining a 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 and calibrated according to the procedure in Reference 2 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 is 1500 °C (2732 °F).) Water-cooling of the stainless steel sheath will be necessary at temperatures approaching and exceeding 500 °C.

3.3.1.4.1.3.3 Pitot tube. Type S, as described in section 2.1 of EPA Method 2 (Reference 1). 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 section 3.1.1 of Reference 2) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in section 3.1.1 of Reference 2.

3.3.1.4.1.3.4 Differential pressure gauge. Inclined manometer or equivalent device as described in section 2.2 of EPA method 2 (Reference 1). One manometer shall be used for velocity-head (delta P) readings and the other for orifice differential pressure (delta H) readings.

3.3.1.4.1.3.5 Cyclone (optional). Glass.

3.3.1.4.1.3.6 Filter holder. Borosilicate glass, with a Teflon frit filter support and a sealing gasket. The sealing gasket shall be constructed of Teflon or equivalent materials. 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.

3.3.1.4.1.3.7 Filter heating system. Any heating system capable of maintaining a temperature of 120 ± 14 °C (248 ± 25 °F) around the filter and cyclone during sampling. 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.

3.3.1.4.1.3.8 Impinger train. The following system shall be used to determine the stack gas moisture content and to collect HCl and Cl_2: five or six impingers connected in series with leak-free ground glass fittings or any similar leak-free non-contaminating fittings. The first impinger shown in Figure 1 (knockout or condensate impinger) is optional

and is recommended as a water knockout trap for use under test conditions which require such a trap. If used, this impinger should be constructed as described below for the alkaline impingers, but with a shortened stem, and should contain 50 ml of 0.1 N H_2SO_4. The following two impingers (acid impingers which each contain 100 ml of 0.1 N H_2SO_4) shall be of the Greenburg-Smith design with the standard tip (see method 5, paragraph 2.1.7). The next two impingers (alkaline impingers which each contain 100 ml of 0.1 N NaOH) and the last impinger (containing silica gel) 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 impinger (see method 5, paragraph 2.1.7). The condensate, acid, and alkaline impingers shall contain known quantities of the appropriate absorbing reagents. The last impinger shall contain a known weight of silica gel or equivalent desiccant.

3.3.1.4.1.3.9 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 percent, an orifice meter, (rate meter). 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 percent of isokineticity and of determining sample volumes to within 2 percent may be used. The metering system should be used in conjunction with a pitot tube to enable checks of isokinetic sampling rates.

3.3.1.4.1.3.10 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 300-m (100 ft) elevation increase (vice versa for elevation decrease).

3.3.1.4.1.3.11 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, Reference 1). The temperature sensor ideally should be permanently attached to the pitot tube or sampling probe in a fixed configuration such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just 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 the stack gas is saturated, the stack temperature may be measured at a single point near the center of the stack.

3.3.1.4.1.3.12 Ascarite tube for conditioning ambient air. Tube tightly packed with approximately 150 g of fresh 8 to 20 mesh Ascarite II® sodium hydroxide coated silica, or equivalent, to dry and remove acid gases from the ambient air used to remove moisture from the filter and optional cyclone. The inlet and outlet ends of the tube should be packed with at least 1 cm thickness of glass wood or filter material suitable to prevent escape of Ascarite II fines. Fit one end with flexible tubing. etc. to allow connection to probe nozzle.

3.3.1.4.2 Sample Recovery.

3.3.1.4.2.1 Probe liner. Probe and nozzle 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 and the probe nozzle.

3.3.1.4.2.2 Wash bottles. Two. Polyethylene or glass, 500 ml or larger.

3.3.1.4.2.3 Glass sample storage containers. Glass, 500- or 1000-ml. Screw-cap liners shall be Teflon and constructed so as to be leak-free. Narrow-mouth glass bottles have been found to exhibit less tendency toward leakage.

3.3.1.4.2.4 Petri dishes. Glass or plastic, sealed around the circumference with Teflon tape, for storage and transport of filter samples.

3.3.1.4.2.5 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.

3.3.1.4.2 6 Plastic storage containers. Screw-cap polypropylene or polyethylene containers to store silica gel.

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

3.3.1.4.2.8 Funnels. Glass, to aid in sample recovery.

3.3.1.5 Reagents

3.3.1.5.1 Reagent grade 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 higher purity to permit its use without lessening the accuracy of the determination.

3.3.1.5.2 ASTM Type II water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified. It is advisable to analyze a blank sample of this reagent prior to sampling, since the reagent blank values obtained during the field sample analysis must be less than 10 percent of the sample values (see method 9057).

3.3.1.5.3 Sulfuric acid (0.1 N), H_2SO_4. Used as the HCl absorbing reagent in the impinger train. To prepare 1 L, slowly add 2.80 ml of concentrated H_2SO_4 to about 900 ml of water while stirring, and adjust the final volume to 1 L using additional water. Shake well to mix the solution. It is advisable to analyze a blank sample of this reagent prior to sampling, since the reagent blank values obtained during the field sample analysis must be less than 10 percent of the sample values (see method 9057).

3.3.1.5.4 Sodium hydroxide (0.1 N). NaOH. Used as the Cl_2 absorbing reagent in the impinger train. To prepare 1 L, dissolve 4.00 g of solid NaOH in about 900 ml of water and adjust the final volume of 1 L using additional water. Shake well to mix the solution. It is advisable to analyze a blank sample of this reagent prior to sampling, since the reagent blank values obtained during the field sample analysis must be less than 10 percent of the sample values (see Method 9057).

3.3.1.5.5 Filter. Quartz-fiber or Teflon mat (e.g., Pallflex® TX40HI45) filter.

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

3.3.1.5.7 Acetone. When using this train for determination of particulate emissions, reagent grade acetone, <0.001 percent residue, in glass bottles is required. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks shall be run prior to field use and only acetone with low blank values (<0.001 percent) shall be used. In no case shall a blank value greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight.

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

3.3.1.5.9 Stopcock grease. Acetone-insoluble, heat-stable silicone grease may be used, if needed. Silicone grease usage is not necessary if screw-on connectors or Teflon sleeves on ground-glass joints are used.

3.3.1.6 Sample Collection, Preservation, and Handling.

3.3.1.6.1 Sample collection is described in this method. The analytical procedures for HCl and Cl_2 are described in method 9057 and for particulate matter in EPA method 5 (Reference 1).

3.3.1.6.2 Samples should be stored in clearly labeled, tightly sealed containers between sample recovery and analysis. They may be analyzed up to four weeks after collection.

3.3.1.7 Procedure.

3.3.1.7.1 Preparation for Field Test.

3.3.1.7.1.1 All sampling equipment shall be maintained and calibrated according to the procedures described in section 3.4.2 of EPA's Quality Assurance Handbook, Volume III (Reference 2).

3.3.1.7.1.2 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 just prior to train assembly.

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

3.3.1.7.1.4 If a particulate determination will be conducted, desiccate the filters at 20 ± 5.6°C (68 ± 10°F) and ambient pressure for at least 24 hours, and weigh at intervals of at least 6 hours 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 percent. Alternatively (unless otherwise specified by the Administrator), the filters may be oven-dried at 105°C (220°F) for 2-3 hours, desiccated for 2 hours, and weighed.

3.3.1.7.2 Preliminary Field Determinations.

3.3.1.7.2.1 Select the sampling site and the minimum number of sampling points according to EPA method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and range of velocity heads using EPA method 2. It is recommended that a leak-check of the pitot lines (see EPA method 2, section 3.1) be performed. Determine the stack-gas moisture content using EPA 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 (Reference 1) 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.

3.3.1.7.2.2 Select a nozzle size based on the range of velocity heads so that it is not necessary to change the nozzle size 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).

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

3.3.1.7.2.4 The total sampling time should be two hours. 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. Size the condensate impinger for the expected moisture catch or be prepared to empty it during the run.

3.3.1.7.3 Preparation of Sampling Train.

3.3.1.7.3.1 Add 50 ml of 0.1 N H_2SO_4 to the condensate impinger, if used. Place 100 ml of 0.1 N H_2SO_4 in each of the next two impingers. Place 100 ml of 0.1 N NaOH in each of the following two impingers. Finally, transfer approximately 200-300 g of preweighed silica gel from its container to the last 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 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.

3.3.1.7.3.2 Using a tweezer or clean disposable surgical gloves, place a labeled (identified) filter (weighed, if particulate matter to be determined) 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.

3.3.1.7.3.3 To use glass liners, 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. Other connecting systems utilizing 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 sampling point.

3.3.1.7.3.4 Set up the train as in Figure 3.3-1. A minimal amount of silicone grease may be used on ground glass joints. Connect temperature sensors to the appropriate potentiometer/display unit. Check all temperature sensors at ambient temperature.

3.3.1.7.3.5 Place crushed ice around the impingers.

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

3.3.1.7.4 Leak-Check Procedures.

3.3.1.7.4.1 Pretest leak-check. A pretest leak-check is recommended, but not required. If the tester opts to conduct the pretest leak-check, the following procedure shall be used.

3.3.1.7.4.1.1 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 380-mm Hg (15-in. Hg) vacuum.

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

3.3.1.7.4.1.2 If a woven glass-fiber gasket is used, do not connect the probe to the train during the leak-check. Instead, leak-check the train by first plugging the inlet to the cyclone, if used, or the filter holder and pulling a 380-mm Hg (15-in. Hg) vacuum (see Note above). 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 380-mm Hg (15-in. Hg) vacuum. Leakage rates in excess of 4 percent of the average sampling rate or 0.00057 m^3 /min (0.02 cfm), whichever is less, are unacceptable.

3.3.1.7.4.1.3 The following leak-check instructions for the sampling train may be helpful. Start the pump with bypass valve fully open and coarse adjust valve completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until the desired vacuum is reached. Do not reverse direction of the bypass valve; this will cause water to back up into the filter holder. If the desired volume is exceeded, either leak-check at this higher vacuum or end the leak-check, as shown below, and start over.

3.3.1.7.4.1.4 When the leak-check is completed, first slowly remove the plug from the inlet to the probe, cyclone, or filter holder and immediately turn off the vacuum pump. This prevents the liquid in the impingers from being forced backward into the filter holder and silica gel from being entrained backward into the fifth impinger.

3.3.1.7.4.2 Leak-checks during sample run. If during the sampling run, a component (e.g., filter assembly or impinger) change becomes necessary or a port change is conducted, a leak-check shall be conducted immediately after the interruption of sampling and before the change is made. The leak-check shall be conducted according to the procedure outlined in Section 3.3.1.7.4.1, except that it shall be conducted 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 percent of the average sampling rate (whichever is less), the results are acceptable. If a higher leakage rate is obtained, the tester shall void the sampling run. Immediately after a component change or port change, and before sampling is reinitiated, another leak-check similar to a pre-test leak-check is recommended.

3.3.1.7.4.3 Post-test leak-check. A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done using 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 percent of the average sampling rate (whichever is less), the results are acceptable. If a higher leakage rate is obtained, the tester shall void the sampling run.

3.3.1.7.5 Train Operation.

3.3.1.7.5.1 During the sampling run, maintain an isokinetic sampling rate to within 10 percent of true isokinetic, unless otherwise specified by the Administrator. Maintain a temperature around the filter (and cyclone, if used) of 120 ± 14°C (248 ± 25°F).

3.3.1.7.5.2 For each run, record the data required on a data sheet such as the one shown in Figure 3.3-2. 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 required by Figure 3.3-2 at least once at each sample point during each time increment and additional readings when significant changes (20 percent 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.

3.3.1.7.5.3 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 positioned properly. 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 using a calculator or a nomograph. 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. If the stack gas molecular weight and the pitot tube coefficient are outside the above ranges, do not use the nomographs unless appropriate steps are taken to compensate for the deviations (see Reference 3).

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

3.3.1.7.5.5 When the probe is in position, block off the openings around the probe and stack access port to prevent unrepresentative dilution of the gas stream.

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

3.3.1.7.5.7 During the test run, make periodic adjustments to keep the temperature around the filter holder (and cyclone, if used) at the proper level. 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.

3 3.1.7.5.8 If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, it may be replaced in the midst of a sample run. Using another complete filter holder assembly is recommended, rather than attempting to change the filter itself. After a new filter assembly is installed, conduct a leak-check. If determined, the total particulate weight shall include the summation of all filter assembly catches.

3.3.1.7.5.9 If the condensate impinger becomes too full, it may be emptied, recharged with 50 ml of 0.1 N H_2SO_4, and replaced during the sample run. The condensate emptied must be saved and included in the measurement of the volume of moisture collected and included in the sample for analysis. The additional 50 ml of absorbing reagent must also be considered in calculating the moisture. After the impinger is reinstalled in the train, conduct a leak. check.

3.3.1.7.5.10 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.

3.3.1.7.5.11 Note that when two or more trains are used, separate analyses of the particulate catch (if applicable) and the HCl and Cl_2 impinger catches from each train shall be performed, unless identical nozzle sizes were used on all trains. In that case, the particulate catch and the HCl and Cl_2 impinger catches from the individual trains may be combined, and a single particulate analysis and single HCl and Cl_2 analyses of the impinger contents may be performed.

3.3.1.7.5.12 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, and record the final dry gas meter reading.

3.3.1.7.5.13 If there is any possibility that liquid has collected in the glass cyclone and/or on the filter, connect the Ascarite tube at the probe inlet and operate the train with the filter heating system at 120 ± 14 °C (248 ± 25 °F) at a low flow rate (e.g., H = 1) sufficient to vaporize the liquid and any HCl in the cyclone or on the filter and pull it through the train into the impingers. After 30 minutes, turn off the flow, remove the Ascarite tube, and examine the cyclone and filter for any visible moisture. If moisture is visible, repeat this step for 15 minutes.

3.3.1.7.5.14 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.

3.3.1.7.5.15 If the moisture value is available, calculate percent isokineticity (see section 3.3.1.7.7.10) to determine whether the run was valid or another test run should be conducted.

3.3.1.7.6 Sample Recovery.

3.3.1.7.6.1 Allow the probe to cool. When the probe can be handled safely, wipe off all the external surfaces of the tip of the probe nozzle and place a cap over the tip. 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 holder.

3.3.1.7.6.2 Before moving the sampling train to the cleanup site, remove the probe, wipe off any silicone grease, and cap the open outlet, being careful not to lose any condensate that might be present. Wipe off any silicone grease and cap the filter or cyclone inlet. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger and the filter holder, disconnect it at the filter holder and let any condensed water drain into the first impinger. Wipe off any silicone grease and cap the filter holder outlet and the impinger inlet. Ground glass stoppers, plastic caps, serum caps, Teflon tape, Parafilm®, or aluminum foil may be used to close these openings.

3.3.1.7.6.3 Transfer the probe and filter/impinger assembly to the cleanup area. This area should be clean and protected from the weather to minimize sample contamination or loss.

3.3.1.7.6.4 Save portions of all washing solutions used for cleanup (acetone and Type II water) and the absorbing reagents (0.1 N H_2SO_4 and 0.1 N NaOH) as blanks. Transfer 200 ml of each solution directly from the wash bottle being used (rinse solutions) or the supply container (absorbing reagents) and place each in a separate, prelabeled glass sample container.

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

3.3.1.7.6.6 Container No. 1 (filter catch for particulate determination). Carefully remove the filter from the filter holder and place it in its identified Petri dish container. Use one or more pair 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 Teflon tape around the circumference of the lid.

3.3.1.7.6.7 Container No. 2 (front-half rinse for particulate determination). 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 with acetone into a glass container. Retain an acetone blank and analyze with the samples.

3.3.1.7.6.8 Perform rinses as follows: Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone 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 acetone. Brush and rinse the inside parts of the Swagelok fitting with the acetone in a similar way until no visible particles remain.

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

3.3.1.7.6.10 Follow the acetone rinse with a probe brush. Hold the probe in an inclined position and squirt acetone 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 acetone and particulate matter that is brushed from the probe. Run the brush through the probe three or more times until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. Rinse the brush with acetone and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above. Between sampling runs, keep brushes clean and protected from contamination.

3.3.1.7.6.11 Clean the inside of the front half of the filter holder and cyclone by rubbing the surfaces with a nylon bristle brush and rinsing with acetone. 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 rinses and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone 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.

3.3.1.7.6.12 Container No. 3 (knockout and acid impinger catch for moisture and HCl determination). Disconnect the impingers. Measure the liquid in the acid and knockout 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. Quantitatively transfer this liquid to a leak-free sample storage container. Rinse these impingers, connecting glassware (and tubing, if used); and the back half of the filter holder with water and add these rinses to the storage container. Seal the container, shake to mix, and label. The fluid level should be marked so that if any sample is lost during transport, a correction proportional to the lost volume can be applied. Retain rinse water and acidic absorbing solution blanks and analyze with the samples.

3.3.1.7.6.13 Container No. 4 (alkaline impinger catch for Cl_2 and moisture determination). Measure and record the liquid in the alkaline impingers as described in section 3.3.1.7.6.12. Quantitatively transfer this liquid to a leak-free sample storage container. Rinse these two impingers and connecting glassware with water and add these rinses to the container. Seal the container, shake to mix, and label; mark the fluid level. Retain alkaline absorbing solution blank and analyze with the samples.

3.3.1.7.6.14 Container No. 5 (silica gel for moisture determination). 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 last 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.

3.3.1.7.6.15 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 and all particulate filters with the particulate catch facing upward.

3.3.1.7.7 Calculations. Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

3.3.1.7.7.1 Nomenclature.

A_n = Cross-sectional area of nozzle, m^2 (ft^2).
B_{ws} = Water vapor in the gas stream, proportion by volume.
C_a = Acetone blank residue concentration, mg/mg.
C_d = Type S pitot tube coefficient (nominally 0.84 ± 0.02), dimensionless.
C_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf).
I = Percent of isokinetic sampling.
m_a = Mass of residue of acetone after evaporation, mg.
M_n = Total amount of particulate matter collected, mg.
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, ms 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 2), °K (°R).
T_s = Absolute average stack-gas temperature (see Figure 2), °K (°R).
T_{std} = Standard absolute temperature, 293 °K (528 °R).
V_{lc} = Total volume of liquid collected in the impingers and silica gel, ml.
V_m = Volume of gas sample is 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.
V_a = Volume of acetone blank, ml.
V_{aw} = Volume of acetone used in wash; ml.
Y = Dry-gas-meter calibration factor, dimensionless.
ΔH = Average pressure differential across the orifice meter, mm H_2O (in H_2O).
p_a = Density of acetone, mg/µl (see label on bottle).
p_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.

3.3.1.7.7.2 Average dry gas meter temperature and average orifice pressure drop. See data sheet (Figure 3.3-2).

3.3.1.7.7.3 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:

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

$$= K_1 V_m Y \frac{P_{bar} = \Delta H/13.6}{T_m} \qquad (1)$$

where:

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

3.3.1.7.7.4 Volume of water vapor.

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

where:

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

3.3.1.7.7.5 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 2 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is ± 1 °C (2 °F).

3.3.1.7.7.6 Acetone blank concentration. For particulate determination.

$$C_a = \frac{m_a}{V_a p_a} \qquad (4)$$

3.3.1.7.7.7 Acetone wash blank. For particulate determination.

$$W_a = C_a V_{aw} \Delta_a \qquad (5)$$

3.3.1.7.7.8 Total particulate weight. Determine the total particulate catch from the sum of the weights obtained from Container Nos. 1 and 2 less the acetone blank (W_a).

3.3.1.7.7.9 Particulate concentration.

$$c_s = (0.001\ g/mg)(m_n/V_{m(std)}) \quad (6)$$

3.3.1.7.7.10 Isokinetic variation.

3.3.1.7.7.10.1 Calculation from raw data.

$$I = \frac{100\ T_s[K_3F_{1c} + (V_m/T_m)(P_{bar} + H/13.6)]}{60\ \Theta\ V_sP_sA_n} \quad (7)$$

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.

3.3.1.7.7.10.2 Calculation for intermediate values.

$$I = \frac{T_sV_{m(std)}P_{std}100}{T_{std}V_s\Theta A_nP_s60(1-B_{ws})}$$

$$= K_4 \frac{T_sV_{m(std)}}{P_sV_sA_n\Theta(1-B_{ws})} \quad (8)$$

where:

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

3.3.1.7.7.10.3 Acceptable units. If 90 percent <I <110 percent, 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 percent, the Administrator may opt to accept the results.

3.3.1.8 Quality Control.

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

3.3.1.8.2 Analysis. At the present time, a validated audit material does not exist for this method. Analytical quality control procedures are detailed in Method 9057.

3.3.1.9 Method Performance.

3.3.1.9.1 The in-stack detection limit for the method is approximately 0.02 µg of HCl per liter of stack gas. The method has a negative bias below 20 ppm HCl (Reference 6).

3.3.1.9.2 It is preferable to include the cyclone in the sampling train to protect the filter from any moisture present. There is research in progress regarding the necessity of the cyclone at low moisture sources and the use of Ascarite II in the drying procedure (Section 3.3.1.7.5.12).

References

1. U.S. Environmental Protection Agency, 40 CFR part 60, appendix A, Methods 1-5.

2. U.S. Environmental Protection Agency, "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods," Publication No. EPA-600/4-77-027b, August 1977.

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

4. Steinsberger, S.C. and J.H. Margeson, "Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions from Municipal and Hazardous Waste Incinerators," U.S. Environmental Protection Agency, Office of Research and Development, Report No. EPA 600/3-89/064, NTIS PB89 220586-AS.

5. State of California, Air Resources Board, method 421, "Determination of Hydrochloric Acid emissions from Stationary Sources," March 18, 1987.

6. Entropy Environmentalists, Inc., "Laboratory Evaluation of a Sampling and Analysis Method for Hydrogen Chloride Emissions
from Stationary Sources: Interim Report," EPA Contract No. 68-02-4442, Research Triangle Park, North Carolina, January 22, 1988.

3.3.2 Midget Impinger HCl/Cl_2 Emission Sampling Train (Method 0051)

3.3.2.1 Scope and Application.

3.3.2.1.1 This method describes the collection of hydrogen chloride (HCl, CAS Registry Number 7647-01-0) and chlorine (Cl_2, CAS Registry Number 7782-50-5) in stack gas emission samples from hazardous waste incinerators, municipal waste combustors, and boilers and industrial furnaces. The collected samples are analyzed using method 9057. This method is designed to collect HCl/Cl_2 in their gaseous forms. Sources, such as those controlled by wet scrubbers, that emit acid particulate matter (e.g., HCl dissolved in water droplets) must be sampled using an isokinetic HCl/Cl_2 sampling train (see Method 0050).

3.3.2.2 Summary of Method.

3.3.2.2.1 An integrated gas sample is extracted from the stack and passes through a particulate filter, acidified water, and finally through an alkaline solution. The filter serves to remove particulate matter such as chloride salts which could potentially react and form analyte in the absorbing solutions. In the acidified water absorbing solution, the HCl gas is solubilized and forms chloride ions (Cl^-) as follows:

$$HCl + H_2O = H_3O^+ + Cl^-$$

The Cl_2 gas present in the emissions has a very low solubility in acidified water and passes through to the alkaline absorbing solution where it undergoes hydrolysis to form a proton (H^+), Cl^-, and hypochlorous acid (HClO) as follows:

$$H_2O + Cl_2 = H^+ + Cl^- + HClO$$

The Cl^- ions in the separate solutions are measured by ion chromatography (Method 9057).

3.3.2.3 Interferences.

3.3.2.3.1 Volatile materials which produce chloride ions upon dissolution during sampling are obvious interferences in the measurement of HCl. One interferant for HCl is diatomic chlorine (Cl_2) gas which disproportionates to HCl and hypochlorous acid (HClO) upon dissolution in water. Cl_2 gas exhibits a low solubility in water, however, and the use of acidic rather than neutral or basic solutions for collection of hydrogen chloride gas greatly reduces the dissolution of any chlorine present. Sampling a 400 ppm HCl gas stream containing 50 ppm Cl_2 with this method does not cause a significant bias. Sampling a 220 ppm HCl gas stream containing 180 ppm Cl_2 results in a positive bias of 3.4 percent in the HCl measurement.

3.3.2.3.2 Reducing agents such as SO_2 may cause a positive bias in the Cl_2 measurement by the following reaction:

$$HClO + HSO_3^- = H_2SO_4 + Cl^-$$

3.3.2.4 Apparatus and Materials.

3.3.2.4.1 Sampling Train. The sampling train is shown in Figure 1 and component parts are discussed below.

3.3.2.4.1.1 Probe. Borosilicate glass, approximately 3/8-in (9-mm) inside diameter, with a heating system to prevent condensation. When the concentration of alkaline particulate matter in the emissions is high, a 3/8-in (9-mm) inside diameter Teflon elbow should be attached to the inlet of the probe; a 1-in (25-mm) length of Teflon tubing with a 3/8-in (9-mm) inside diameter should be attached at the open end of the elbow to permit the opening of the probe to be burned away from the gas stream, thus reducing the amount of particulate entering the train. When high concentrations of particulate matter are not present, the Teflon elbow is not necessary, and the probe inlet can be perpendicular to the gas stream. When sampling at locations where gas temperatures are greater than approximately 400°F, such as wet scrubber inlets, glass or quartz elbows must be used. In no case should a glass wool plug be used to remove particulate matter; use of such a filtering device could result in a bias in the data.(1) Instead, a Teflon filter should be used as specified in section 3.3.2.5.5.

3.3.2.4.1.2 Three-way stopcock. A borosilicate, three-way glass stopcock with a heating system to prevent condensation. The heated stopcock should connect directly to the outlet of the probe and filter assembly and the inlet of the first impinger. The heating system should be capable of preventing condensation up to the inlet of the first impinger. Silicone grease may be used, if necessary, to prevent leakage.

3.3.2.4.1.3 Impingers. Five 30-ml midget impingers with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakage. For sampling at high moisture sources or for extended sampling times greater than one hour, a midget impinger with a shortened stem (such that the gas sample does not bubble through the collected condensate) should be used in front of the first impinger.

3.3.2.4.1.4 Mae West impinger or drying tube. Mae West design impinger (or drying tube, if a moisture determination is not to be conducted) filled with silica gel, or equivalent, to dry the gas sample and to protect the dry gas meter and pump.

3.3.2.4.1.5 Sample Line. Leak-free, with compatible fittings to connect the last impinger to the needle valve.

3.3.2.4.1.6 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure 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) shall be requested and an adjustment for the elevation 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 or vice versa for elevation decrease.

3.3.2.4.1.7 Purge pump, purge line, drying tube, needle valve, and rate meter. Pump capable of purging sample probe at 2 liters/min, with drying tube, filled with silica gel or equivalent, to protect pump, and a rate meter, 0 to 5 liters/min.

3.3.2.4.1.8 Metering system. The following items comprise the metering system which is identical to that used for EPA Method 6 (see Reference 5).

3.3.2.4.1.8.1 Valve. Needle valve, to regulate sample gas flow rate.

3.3.2.4.1.8.2 Pump. Leak-free diaphragm pump, or equivalent, to pull gas through train. Install a small surge tank between the pump and the rate meter to eliminate the pulsation effect of the diaphragm pump on the rotameter.

3.3.2.4.1.8.3 Rate meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of selected flow rate of 2 liters/min.

3.3.2.4.1.8.4 Volume meter. Dry gas meter, sufficiently accurate to measure the sample volume within 2 percent, calibrated at the selected flow rate and conditions encountered during sampling, and equipped with a temperature gauge (dial thermometer or equivalent) capable of measuring temperature to within 3°C (5.4°F).

3.3.2.4.1.8.5 Vacuum gauge. At least 760 mm Hg (30 in. Hg) gauge to be used for leak check of the sampling train.

3.3.2.4.2 Sample Recovery.

3.3.2.4.2.1 Wash bottles. Polyethylene or glass, 500 ml or larger, two.

3.3.2.4.2.2 Storage bottles. Glass, with Teflon-lined lids, 100 ml, to store impinger samples (two per sampling run).

3.3.2.5 Reagents.

3.3.2 5.1 Reagent grade 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.

3.3.2.5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified. It is advisable to analyze a blank sample of this reagent prior to sampling, since the reagent blank value obtained during the field sample analysis must be less than 10 percent of the sample values (see method 9057).

3.3.2.5.3 Sulfuric acid (0.1 N), H_2SO_4. Used as the HCl absorbing reagent. To prepare 100 ml, slowly add 0.28 ml of concentrated H_2SO_4 to about 90 ml of water while stirring, and adjust the final volume to 100 ml using additional water. Shake well to mix the solution. It is advisable to analyze a blank sample of this reagent prior to sampling, since the reagent blank value obtained during the field sample analysis must be less than 10 percent of the sample values (see method 9057).

3.3.2.5.4 Sodium hydroxide (0.1 N), NaOH. Used as the Cl_2 absorbing reagent. To prepare 100 ml, dissolve 0.40 g of solid NaOH in about 90 ml of water and adjust the final volume to 100 ml using additional water. Shake well to mix the solution. It is advisable to analyze a blank sample of this reagent prior to sampling, since the reagent blank value obtained during the field sample analysis must be less than 10 percent of the sample values (see method 9057).

3.3.2.5.5 Filter. Teflon mat Pallflex® TX40HI75 or equivalent. Locate in a glass, quartz, or Teflon filter holder with a Teflon filter support in a filter box heated to 250°F.

3.3.2.5.6 Stopcock grease. Acetone-insoluble, heat-stable silicone grease may be used, if necessary.

3.3.2.5.7 Silica gel. Indicating type, 6- to 16-mesh. If the silica gel has been used previously, dry at 175°C (350°F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.

3.3.2.6 Sample Collection, Preservation, and Handling.

3.3.2.6.1 Sample collection is described in this method. The analytical procedures are described in method 9057.

3.3.2.6.2 Samples should be stored in clearly labeled, tightly sealed containers between sample recovery and analysis. They may be analyzed up to four weeks after collection.

3.3.2.7 Procedure.

3.3.2.7.1 Calibration. Section 3.5.2 of EPA's Quality Assurance Handbook, Volume III (Reference 4) may be used as a guide for these operations.

3.3.2.7.1.1 Dry Gas Metering System.

3.3.2.7.1.1.1 Initial calibration. Before its initial use in the field, first leak check the metering system (sample line, drying tube, if used, vacuum gauge, needle valve, pump, rate meter, and dry gas meter) as follows: plug the inlet end of the sampling line, pull a vacuum of 250 mm (10 in) Hg, plug off the outlet of the dry gas meter, and turn off the pump. The vacuum should remain stable for 30 seconds. Carefully release the vacuum from the system by slowly removing the plug from the sample line inlet. Remove the sampling line (and drying tube, if applicable), and connect the dry gas metering system to an appropriately sized wet test meter (e.g.. 1 liter per revolution). Make three independent calibration runs, using at least five revolutions of the dry gas meter per run. Calculate the calibration factor, Y (wet test meter calibration volume divided by the dry gas meter volume, with both volumes adjusted to the same reference temperature and pressure), for each run, and average the results. If any Y value deviates by more than 2 percent from the average, the metering system is unacceptable for use. Otherwise, use the average as the calibration factor for subsequent test runs.

3.3.2.7.1.1.2 Post-test calibration check. After each field test series, conduct a calibration check as in section 3.3.2.7.1.1.1 above, except for the following variations: (a) The leak check is not to be conducted, (b) three or more revolutions of the dry gas meter may be used, (c) only two independent runs need to be made. If the calibration factor does not deviate by more than 5 percent from the initial calibration factor (determined in section 3.3.2.7.1.1.1), the dry gas meter volumes obtained during the test series are acceptable. If the calibration factor deviates by more than 5 percent, recalibrate the metering system as section 3.3.2.7.1.1.1, and for the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

3.3.2.7.1.2 Thermometer(s). Prior to each field test, calibrate against mercury-in-glass thermometers at ambient temperature. If the thermometer being calibrated reads within 2°C (2.6°F) of the mercury-in-glass thermometer, it is acceptable. If not, adjust the thermometer or use an appropriate correction factor.

3.3.2.7.1.3 Rate meter. The rate meter need not be calibrated, but should be cleaned and maintained according to the manufacturer's instructions.

3.3.2.7.1.4 Barometer. Prior to each field test, calibrate against a mercury barometer. The field barometer should agree within 0.1 in. Hg with the mercury barometer. If it does not, the field barometer should be adjusted.

3.3.2.7.2 Sampling.

3.3.2.7.2.1 Preparation of collection train. Prepare the sampling train as follows: The first or knockout impinger should have a shortened stem and be left empty to condense moisture in the gas stream. The next two midget

impingers should each be filled with 15 ml of 0.1 N H_2SO_4, and the fourth and fifth impingers should each be filled with 15 ml of 0.1 N NaOH. Place a fresh charge of silica gel, or equivalent, in the Mae West impinger (or the drying tube). Connect the impingers in series with the knockout impinger first, followed by the two impingers containing the acidified reagent, the two impingers containing the alkaline reagent, and the Mae West impinger containing the silica gel. If the moisture will be determined, weigh the impinger assembly to the nearest ± 0.5 g and record the weight.

3.3.2.7.2.2 Leak check procedures. Leak check the probe and three-way stopcock prior to inserting the probe into the stack. Connect the stopcock to the outlet of the probe, and connect the sample line to the needle valve. Plug the probe inlet, turn on the sample pump, and pull a vacuum of at least 250 mm Hg (10 in. Hg). Turn off the needle valve, and note the vacuum gauge reading. The vacuum should remain stable for at least 30 seconds. Place the probe in the stack at the sampling location, and adjust the filter heating system to 250°F and the probe and stopcock heating systems to a temperature sufficient to prevent water condensation. Connect the first impinger to the stopcock, and connect the sample line to the last impinger and the needle valve. Upon completion of a sampling run, remove the probe from the stack and leak check as described above. If a leak has occurred, the sampling run must be voided. Alternatively, the portion of the train behind the probe may be leak checked between multiple runs at the same site as follows: Close the stopcock to the first impinger (see Figure 3.3-3A), and turn on the sample pump. Pull a vacuum of at least 250 mm Hg (10 in. Hg), turn off the needle valve, and note the vacuum gauge reading. The vacuum should remain stable for at least 30 seconds. Release the vacuum on the impinger train by turning the stopcock to the vent position to permit ambient air to enter (see Figure 3.3-3B). If this procedure is used, the full train leak check described above must be conducted following the final run and all preceding sampling runs voided if a leak has occurred.

>>>> See the accompanying hardcopy volume for non-machine-readable data that appears at this point. <<<<

3.3.2.7.2.3 Purge procedure. Immediately prior to sampling, connect the purge line to the stopcock and turn the stopcock to permit the purge pump to purge the probe (see Figure 3.3-3A). Turn on the purge pump, and adjust the purge rate to 2 liters/min. Purge for at least 5 minutes prior to sampling.

3.3.2.7.2.4 Sample collection. Turn on sample pump, pull a slight vacuum of approximately 25 mm Hg (1 in. Hg) on the impinger train, and turn the stopcock to permit stack gas to be pulled through the impinger train (see Figure 3.3-3C). Adjust the sampling rate to 2 liters/min, as indicated by the rate meter, and maintain this rate within 10 percent during the entire sampling run. Take readings of the dry gas meter, the dry gas meter temperature, rate meter, and vacuum gauge at least once every five minutes during the run. A sampling time of one hour is recommended. However, if the expected condensate catch for this sampling run duration will exceed the capacity of the sampling train, (1) a larger knockout impinger may be used or (2) two sequential half-hour runs may be conducted. At the conclusion of the sampling run, remove the train from the stack, cool, and perform a leak check as described in section 3.3.2.7.2.2.

3.3.2.7.3 Sample recovery. Following sampling, disconnect the impinger train from the remaining sampling equipment at the inlet to the knockout impinger and the outlet to the last impinger. If performing a moisture determination, wipe off any moisture on the outside of the train and any excess silicone grease at the inlet and outlet openings; weigh the train to the nearest 0.5 g and record this weight. Then disconnect the impingers from each other. Quantitatively transfer the contents of the first three impingers (the knockout impinger and the two 0.1 N H_2SO_4 impingers) to a leak-free storage bottle. Add the water rinses of each of these impingers and connecting glassware from the second set of impingers (containing the 0.1 N NaOH) should be recovered in a similar manner if a Cl_2 analysis is desired. The sample bottle should be marked so that if any sample is lost during transport, a correction proportional to the lost volume can be applied. Save portions of the 0.1 N H_2SO_4 and 0.1 N NaOH used as impinger reagents as reagent blanks. Take 50 ml of each and place in separate leak-free storage bottles. Label and mark the fluid levels as previously described.

3.3.2.7.4 Calculations. Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

3.3.2.7.4.1 Nomenclature.

B_{ws} = Water vapor in the gas stream, proportion by volume.
M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_{bar} = Barometric pressure at the exit orifice of the dry gas meter, 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 = Average dry gas meter absolute temperature, °K (°R).
T_{std} = Standard absolute temperature, 293 °K (528 °R).
V_{1c} = Total volume of liquid collected in impingers and silica gel, ml (equivalent to the difference in weight of the impinger train before and after sampling, 1 mg = 1 ml).
V_m = Dry gas volume as measured by the dry gas meter, dcm (dcf).
$V_{m(std)}$ = Dry gas volume 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).
Y = Dry gas meter calibration factor.
p_w = Density of water, 0.9982 g/ml (0.002201 lb/ml).

3.3.2.7.4.2 Sample volume, dry basis, corrected to standard conditions. Calculate as described below:

$$V_{m(std)} = V_m Y \left(\frac{+\ T_{std}\ ,}{.\ T_m\ -} \right) \left(\frac{+\ P_{bar}\ ,}{.\ P_{std}\ -} \right)$$

$$= K_1 Y \frac{V_m P_{bar}}{T_m} \qquad (1)$$

where:

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

3.3.2.7.4.3 Volume of water vapor.

$$V_{w(std)} = V_{lc} \frac{P_w}{M_w} \frac{RT_{std}}{P_{std}}$$

$$= K_2 V_{lc} \qquad (2)$$

where:

K_2 = 0.0013333 m^3/ml for metric units.
K_2 = 0.04707 ft^3/ml for English units.

3.3.2.7.4.4 Moisture content.

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

3.3.2.8 Quality Control.

3.3.2.8.1 At the present time, a validated audit material does not exist for this method. Analytical quality control procedures are detailed in Method 9057.

3.3.2.9 Method Performance.

3.3.2.9.1 The in-stack detection limit for the method is approximately 0.08 µg of HCl per liter of stack gas for a 1-hour sample.

3.3.2.9.2 The precision and bias for measurement of HCl using this sampling protocol combined with the analytical protocol of method 9057 have been determined. The within laboratory relative standard deviation is 6.2 percent and 3.2 percent at HCl concentrations of 3.9 and 15.3 ppm, respectively. The method does not exhibit any bias for HCl when sampling at Cl_2 concentrations less than 50 ppm.

References

1. Steinsberger. S.C. and J.H. Margeson, "Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions from Municipal and Hazardous Waste Incinerators," U.S. Environmental Protection Agency, Office of Research and Development, Report No. EPA 600/3- 89/064, NTIS PB 89 220586-AS.

2. State of California, Air Resources Board, Method 421, "Determination of Hydrochloric Acid Emissions from Stationary Sources," March 18, 1987.

3. Entropy Environmentalists, Inc., "Laboratory Evaluation of a Sampling and Analysis Method for Hydrogen Chloride Emissions from Stationary Sources: Interim Report," EPA Contract No. 68-02-4442, Research Triangle Park, North Carolina, January 22, 1988.

4. U.S. Environmental Protection Agency, "Quality Assurance Handbook for Air Pollution Measurement Systems, volume III, Stationary Source Specific Methods," Publication No. EPA-600/4-77-027b, August 1977.

5. U.S. Environmental Protection Agency, 40 CFR part 60, appendix A, method 6.

3.3.3 Protocol for Analysis of Samples from HCl/Cl_2 Emission Sampling Train (Method 9057)

3.3.3.1 Scope and Application.

3.3.3.1.1 This method describes the analytical protocol for determination of hydrogen chloride (HCl, CAS Registry Number 7647-01-0) and chloride (Cl_2, CAS Registry Number 7782-50-5) in stack gas emission samples collected from hazardous waste and municipal waste incinerators using the midget impinger HCl/Cl_2 sampling train (method 0051) or the isokinetic HCl/Cl_2 sampling train (method 0050).

3.3.3.1.2 The lower detection limit is 0.1 µg of chloride (Cl^-) per ml of sample solution. Samples with concentrations which exceed the linear range of the analytical instrumentation may be diluted.

3.3.3.1.3 This method is recommended for use only by analysts experienced in the use of ion chromatography and in the interpretation of ion chromatograms.

3.3.3.2 Summary of Method.

3.3.3.2.1 The stoichiometry of HCl and Cl_2 collection in the sampling train (see methods 0050 and 0051) is as follows: In the acidified water absorbing solution, the HCl gas is solubilized and forms chloride ions (Cl^-) according to the following formula:

$HCl + H_2O = H_3O^+ + Cl^-$

The Cl_2 gas present in the emissions has a very low solubility in acidified water and passes through to the alkaline absorbing solution where it undergoes hydrolysis to form a proton (H^+), Cl^- , and hypochlorous acid (HClO) as shown:

$H_2O + Cl_2 = H^+ + Cl^- + HClO$

Non-suppressed or suppressed ion chromatography (IC) is used for analysis of the Cl^-.

3.3.3.3 Interferences.

3.3.3.3.1 Volatile materials which produce chloride ions upon dissolution during sampling are obvious interferences in the measurement of HCl. One likely interferant is diatomic chlorine (Cl_2) gas which dispropor-tionates to HCl and hypochlorous acid (HOCl) upon dissolution in water. Cl_2 gas exhibits a low solubility in water, however, and the use of acidic rather than neutral or basic solutions for collection of hydrogen chloride gas greatly reduces the dissolution of any chlorine present. Sampling a 400 ppm HCl gas stream containing 50 ppm Cl_2 with this method does not cause a significant bias. Sampling a 220 ppm HCl gas stream containing 180 ppm Cl_2 results in a positive bias of 3.4 percent in the HCl measurement. Other interferants have not been encountered.

3.3.3.3.2 Reducing agents such as SO_2 may cause a positive bias in the Cl_2 measurement by the following reaction:

$HClO + HSO_3^- = H_2SO_4 + Cl^-$

3.3.3.4 Apparatus and Materials.

3.3.3.4.1 Volumetric Flasks. Class A, various sizes.

3.3.3.4.2 Volumetric Pipettes. Class A, assortment, to dilute samples to calibration range of the IC.

3.3.3.4.3 Ion Chromatograph. Suppressed or non-suppressed, with a conductivity detector and electronic integrator operating in the peak area mode. Other detectors, a strip chart recorder, and peak heights may be used provided the 5 percent repeatability criteria for sample analysis and the linearity criteria for the calibration curve can be met.

3.3.3.5 Reagents.

3.3.3.5.1 Reagent grade 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.

3.3.3.5.2 ASTM Type II Water (ASTM D1193-77 (1983)). All references to water in the method refer to ASTM Type II unless otherwise specified.

3.3.3.5.3 Sulfuric acid (0.1 N), H_2SO_4. To prepare 100 ml, slowly add 0.28 ml of concentrated H_2SO_4 to about 90 ml of water while stirring, and adjust the final volume to 100 ml using additional water. Shake well to mix the solution.

3.3.3.5.4 Sodium hydroxide (0.1 N), NaOH. To prepare 100 ml, dissolve 0.40 g of solid NaOH in about 90 ml of water and adjust the final volume to 100 ml using additional water. Shake well to mix the solution.

3.3.3.5.5 Reagent blank solutions. A separate blank solution of each sampling train reagent used and collected in the field (0.1 N H_2SO_4 and 0.1 N NaOH) should be prepared for analysis with the field samples. For midget impinger train sample analysis, dilute 30 ml of each reagent with rinse water collected in the field as a blank to the final volume of the samples; for isokinetic train sample analysis, dilute 200 ml to the same final volume as the field samples also using the blank sample of rinse water.

3.3.3.5.6 Sodium chloride, NaCl, stock standard solution. Solutions containing a nominal certified concentration of 1000 mg/L NaCl are commercially available as convenient stock solutions from which working standards can be made by appropriate volumetric dilution. Alternately, concentrated stock solutions may be produced from reagent grade NaCl that has been dried at 110 °C for two or more hours and then cooled to room temperature in a desiccator immediately before weighing. Accurately weigh 1.6 to 1.7 g of the dried NaCl to within 0.1 mg, dissolve in water, and dilute to 1 liter. The exact Cl^- concentration can be calculated using the equation:

$\mu g\ Cl^-/ml = g\ of\ NaCl\ X\ 10^3\ X\ 35.453/58.44$

Refrigerate the stock standard solutions and store no longer than one month.

3.3.3.5.7 Chromatographic eluent. Effective eluents for non-suppressed ion chromatography using a resin- or silica-based weak ion exchange column are a 4 mM potassium hydrogen phthalate solution, adjusted to a pH of 4.0 using a saturated sodium borate solution, and a mM 4-hydroxy benzoate solution, adjusted to a pH of 8.6 using 1 N sodium hydroxide. An effective eluent for suppressed ion chromatography is a solution containing 3 mM sodium bicarbonate and 2.4 mM sodium carbonate. Other dilute solutions buffered to a similar pH that contain no ions interfering with the chromatographic analysis may be used. If, using suppressed ion chromatography, the "water dip" resulting from sample injection is interfering with the chlorine peak, use a 2 mM sodium hydroxide/2.4 mM sodium bicarbonate eluent.

3.3.3.6 Sample Collection, Preservation, and Handling.

3.3.3.6.1 Sample collection using the midget impinger HCl/Cl_2 train or the isokinetic HCl/Cl_2 train is described in Method 0051 or 0050, respectively.

3.3.3.6.2 Samples should be stored in clearly labeled, tightly sealed containers between sample recovery and analysis. They may be analyzed up to four weeks after collection.

3.3.3.7 Procedure.

3.3.3.7.1 Sample preparation for analysis. Check the liquid level in each sample, and determine if any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume can be determined from the difference between the initial and final solution levels, and this value can be used to correct the analytical results. For midget impinger train samples, quantitatively transfer each sample solution to a 100 ml volumetric flask and dilute to 100 ml with water. For isokinetic sampling train samples, quantitatively transfer each sample to a volumetric flask or graduated cylinder and dilute with water to a final volume appropriate for all samples.

3.3.3.7.2 Calibration of Ion Chromatograph.

3.3.3.7.2.1 The ion chromatographic conditions will depend on the type of analytical column used and whether suppressed or non-suppressed ion chromatography is used. Prior to calibration and sample analysis, establish a stable baseline. Next, inject a sample of water, and determine if any Cl^- appears in the chromatogram. If Cl^- is present, repeat the load/injection procedure until no Cl^- is present.

3.3.3.7.2.2 To prepare the calibration standards, dilute given amounts (1.0 ml or greater) of the stock standard solution to convenient volumes, using 0.1 H_2SO_4 or 0.1 NaOH as appropriate. Prepare at least four standards that are within the linear range of the field samples. Inject the calibration standards, starting with the lowest concentration standard first, both before and after injection of the quality control check sample, reagent blank, and field samples. This allows compensation for any instrument drift occurring during sample analysis.

3.3.3.7.2.3 Determine the peak areas, or heights, of the standards and plot individual values versus Cl^- concentrations in µg/ml. Draw a smooth curve through the points. Use linear regression to calculate a formula describing the resulting linear curve.

3.3.3.7.3 Sample analysis. Between injections of the series of calibration standards, inject in duplicate the reagent blanks and the field samples, including a matrix spike sample. Measure the areas or heights (same as done for the calibration standards) of the Cl^- peaks. Use the average response to determine the concentrations of the field samples, matrix spike, and reagent blanks using the linear calibration curve. The results for a reagent blank should not exceed 10 percent of the corresponding value for a field sample.

3.3.3.7.4 Calculations. Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

3.3.3.7.4.1 Total µg HCl per sample. Calculate as described below:

$$^{m}HCl = (S - B) \times V_s \times 36.46/35.453 \quad (1)$$

where:

^{m}HCl = Mass of HCl in sample, µg,
S = Analysis of sample, µg Cl^-/ml,
B = Analysis of reagent blank, µg Cl^-/ml,
V_s = Volume of filtered and diluted sample, ml,
36.46 = Molecular weight of HCl, µg/µg-mole, and
35.45 = Atomic weight of Cl^-, µg/µg-mole.

3.3.3.7.4.2 Total µg Cl_2 per sample. Calculate as described below:

$$^{M}Cl_2 = (S - B) \times V_2 \times 70.91/35.45 \quad (2)$$

where:

$^{M}Cl_2$ = Mass of Cl_2 in sample, µg,
70.91 = Molecular weight of Cl_2, µg/µg-mole, and
35.45 = Atomic weight of Cl^-, µg/µg-mole.

3.3.3.7.4.3 Concentration of HCl in the flue gas. Calculate as described below:

$$C = K \times m/V_{m(std)} \quad (3)$$

where:

C = Concentration of HCl or Cl_2, dry basis, mg/dscm,
K = 10^{-3}mg/µg,
m = Mass of HCl or Cl_2 in sample, µg, and
$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm (from Method 0050 or Method 0051).

3.3.3.8 Quality Control.

3.3.3.8.1 At the present time, a validated audit material does not exist for this method. However, it is strongly recommended that a quality control check sample and a matrix spike sample be used.

3.3.3.8.1.1 Quality control check sample. Chloride solutions of reliably known concentrations are available for purchase from the National Bureau of Standards (SRM 3182). The QC check sample should be prepared in the appropriate absorbing reagent at a concentration approximately equal to the mid range calibration standard. The quality control check sample should be injected in duplicate immediately after the calibration standards have been injected for the first time. The Cl^- value obtained for the check sample using the final calibration curve should be within 10 percent of the known value for the check sample.

3.3.3.8.1.2 Matrix spike sample. A portion of at least one field sample should be used to prepare a matrix spike sample. Spike the sample aliquot in the range of the expected concentration. Analyze the matrix spike sample in duplicate along with the field samples. Based on the matrix spike results, determine the recovery for the spiked material. This should be within 10 percent of the known spike value.

3.3.3.9 Method Performance.

3.3.3.9.1 The lower detection limit of the analytical method is 0.1 μg of Cl^- per ml of sample solution. Samples with concentrations which exceed the linear range of the IC may be diluted.

3.3.3.9.2 The precision and bias for analysis of HCl using this analytical protocol have been measured in combination with the midget impinger HCl/Cl_2 train (method 0051) for sample collection. The within-laboratory relative standard deviation is 6.2 percent and 3.2 percent at HCl concentrations of 3.9 and 15.3 ppm, respectively. The method does not exhibit any bias for HCl when sampling at Cl_2 concentrations less than 50 ppm.

References

1. Steinsberger, S.C. and J.H. Margeson, "Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions from Municipal and Hazardous Waste Incinerators," U.S. Environmental Protection Agency, Office of Research and Development, Report No. EPA 600/3-89/064, NTIS PB89 220586-AS.

2. State of California, Air Resources Board, Method 421, "Determination of Hydrochloric Acid Emissions from Stationary Sources" March 18, 1987.

3. Entropy Environmentalists, Inc., "Laboratory Evaluation of a Sampling and Analysis Method for Hydrogen Chloride emissions from Stationary Sources: Interim Report," EPA Contract No. 68-02-4442, Research Triangle Park, North Carolina, January 22, 1988.

3.4 Determination of Polychlorinated Dibenzo-p-Dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) From Stationary Sources (Method 23)

3.4.1 Applicability and Principle

3.4.1.1 Applicability. This method is applicable to the determination of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) from stationary sources.

3.4.1.2 Principle. A sample is withdrawn from the gas stream isokinetically and collected in the sample probe, on a glass fiber filter, and on a packed column of adsorbent material. The sample cannot be separated into a particle vapor fraction. The PCDDs and PCDFs are extracted from the sample, separated by high resolution gas chromatography, and measured by high resolution mass spectrometry.

3.4.2 Apparatus

3.4.2.1 Sampling. A schematic of the sampling train used in this method is shown in Figure 3.4-1. Sealing greases may not be used in assembling the train. The train is identical to that described in Section 2.1 of Method 5 (40 CFR part 60, appendix A) with the following additions:

3.4.2.1.1 Reagents. Reagent grade 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.

3.4.2.1.2 Nozzle. The nozzle shall be made of nickel, nickel-plated stainless steel, quartz, or borosilicate glass.

>>>> See the accompanying hardcopy volume for non-machine-readable data that appears at this point. <<<<

3.4.2.1.3 Sample Transfer Lines. The sample transfer lines, if needed, shall be heat-traced, heavy walled TFE (1/2 in. OD with 1/8 in. wall) with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases. The line shall be as short as possible and must be maintained at 120 °C.

3.4.2.1.4 Filter Support. Teflon or Teflon-coated wire.

3.4.2.1.5 Condenser. Glass, coil type with compatible fittings. A schematic diagram is shown in Figure 3.4-2.

3.4.2.1.6 Water Bath. Thermostatically controlled to maintain the gas temperature exiting the condenser at <20 °C (68 °F).

3.4.2.1.7 Adsorbent Module. Glass container to hold the solid adsorbent. A schematic diagram is shown in Figure 3.4-2. Other physical configurations of the resin trap/condenser assembly are acceptable. The connecting fittings shall form leak-free, vacuum tight seals. No sealant greases shall be used in the sampling train. A coarse glass frit is included to retain the adsorbent.

>>>> See the accompanying hardcopy volume for non-machine-readable data that appears at this point. <<<<

3.4.2.2 Sample Recovery.

3.4.2.2.1 Fitting Caps. Ground glass, Teflon tape, or aluminum foil (Section 3.4.2.2.6) to cap off the sample-exposed sections of the train.

3.4.2.2.2 Wash Bottles. Teflon, 500-ml.

3.4.2.2.3 Probe-Liner Probe-Nozzle, and Filter-Holder Brushes. Inert bristle brushes with precleaned stainless steel or Teflon handles. The probe brush shall have extensions of stainless steel or Teflon, at least as long as the probe. The brushes shall be properly sized and shaped to brush out the nozzle, probe liner, and transfer line, if used.

3.4.2.2.4 Filter Storage Container. Sealed filter holder, wide-mouth amber glass jar with Teflon-lined cap, or glass petri dish.

3.4.2.2.5 Balance. Triple beam.

3.4.2.2.6 Aluminum Foil. Heavy duty, hexane-rinsed.

3.4.2.2.7 Metal Storage Container. Air-tight container to store silica gel.

3.4.2.2.8 Graduated Cylinder. Glass, 250-ml with 2-ml graduation.

3.4.2.2.9 Glass sample Storage container. Amber glass bottle for sample glassware washes, 500- or 1000-ml, with leak-free Teflon-lined caps.

3.4.2.3 Analysis.

3.4.2.3.1 Sample Container. 125- and 250-ml flint glass bottles with Teflon-lined caps.

3.4.2.3.2 Test Tube. Glass.

3.4.2.3.3 Soxhlet Extraction Apparatus. Capable of holding 43 X 123 mm extraction thimbles.

3.4.2.3.4 Extraction Thimble. Glass, precleaned cellulosic, or glass fiber.

3.4.2.3.5 Pasteur Pipettes. For preparing liquid chromatographic columns.

3.4.2.3.6 Reacti-vials. Amber glass, 2-ml, silanized prior to use.

3.4.2.3.7 Rotary Evaporator. Buchi/Brinkman RF-121 or equivalent.

3.4.2.3.8 Nitrogen Evaporator Concentrator. N-Evap Analytical Evaporator Model III or equivalent.

3.4.2.3.9 Separatory Funnels. Glass, 2-liter.

3.4.2.3.10 Gas Chromatograph. Consisting of the following components:

3.4.2.3.10.1 Oven. Capable of maintaining the separation column at the proper operating temperature ± 1 °C and performing programmed increases in temperature at rates of at least 3 °C/min.

3.4.2.3.10.2 Temperature Gauge. To monitor column, oven, detector, and exhaust temperatures ± 1 °C.

3.4.2.3.10.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

3.4.2.3.10.4 Capillary Columns. A fused silica column, 60 X 0.25 mm inside diameter (ID), coated with DB.5 and a fused silica column, 30 m X 0.25 mm ID coated with DB-225. Other column systems may be used provided that the user is able to demonstrate, using calibration and performance checks, that the column system is able to meet the specifications of section 3.4.6.1.2.2.

3.4.2.3.11 Mass Spectrometer. Capable of routine operation at a resolution of 1:10000 with a stability of ± 5 ppm.

3.4.2.3.12 Data System. Compatible with the mass spectrometer and capable of monitoring at least five groups of 25 ions.

3.4.2.3.13 Analytical Balance. To measure within 0.1 mg.

3.4.3 Reagents

3.4.3.1 Sampling.

3.4.3.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D 2986-71 (Reapproved 1978) (incorporated by reference-see § 60.17).

3.4.3.1.1.1 Precleaning. All filters shall be cleaned before their initial use. Place a glass extraction thimble, 1 g of silica gel, and a plug of glass wool into a Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Place no more than 50 filters in the thimble onto the silica gel bed and top with the cleaned glass wool. Charge the Soxhlet with toluene and reflux for 16 hours. After extraction, allow the Soxhlet to cool, remove the toluene extract, and retain it for analysis. Remove the filters and dry them under a clean N_2 stream. Store the filters in a glass petri dish sealed with Teflon tape.

3.4.3.1.2 Adsorbent Resin. Amberlite XAD-2 resin, thoroughly cleaned before initial use.

3.4.3.1.2.1 Cleaning Procedure. This procedure may be carried out in a giant Soxhlet extractor. An all-glass filter thimble containing an extra-coarse frit is used for extraction of XAD-2. The frit is recessed 10-15 mm above a crenelated 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 a stainless steel ring 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 water, and discard. Fill with water a second time, let stand overnight, and discard.
Water	Extract with water for 8 hours.
Methanol	Extract for 22 hours.
Methylene Chloride	Extract for 22 hours.
Methylene Chloride (fresh)	Extract for 22 hours.

3.4.3.1.2.2 Drying.

3.4.3.1.2.2.1 Drying Column. Pyrex pipe, 10.2 cm ID by 0.6 m long, with suitable retainers.

3.4.3.1.2.2.2 Procedure. The adsorbent must be dried with clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source of large volumes of gas free from organic contaminants. Connect the liquid nitrogen cylinder to the column by a length of cleaned copper tubing, 0.95 cm ID, coiled to pass through a heat source. 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. Continue flowing nitrogen through the adsorbent until all the residual solvent is removed. The flow rate should be sufficient to gently agitate the particles but not so excessive as to cause the particles to fracture.

3.4.3.1.2.3 Quality Control Check. The adsorbent must be checked for residual methylene chloride as well as PCDDs and PCDFs.

3.4.3.1.2.3.1 Extraction. Weigh a 1.0 g sample of dried resin into a small vial, add 3 ml of toluene, cap the vial, and shake it well.

3.4.3.1.2.3.2 Analysis. Inject a 2-µl sample of the extract into a gas chromatograph operated under the following conditions:

Column: 6 ft X 1/8 in. stainless steel containing 10 percent OV-101 on 100/120 Supelcoport.

Carrier Gas: Helium at a rate of 30 ml/min.

Detector: Flame ionization detector operated at a sensitivity of 4×10^{-11} A/mV.

Injection Port Temperature: 250 °C.

Detector Temperature: 305 °C.

Oven Temperature: 30 °C for 4 min; programmed to rise at 40 °C/min until it reaches 250 °C; return to 30 °C after 17 minutes.

Compare the results of the analysis to the results from the reference solution. Prepare the reference solution by injecting 2.5 µl of methylene chloride into 100 ml of toluene. This corresponds to 100 µg of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000 µg/g of adsorbent. If the adsorbent exceeds this level, drying must be continued until the excess methylene chloride is removed.

3.4.3.1.2.3.3 Storage. The adsorbent must be used within 4 weeks of cleaning. After cleaning, it may be stored in a wide mouth amber glass container with a Teflon-lined cap or placed in one of the glass adsorbent modules tightly sealed with glass stoppers. If precleaned adsorbent is purchased in sealed containers, it must be used within 4 weeks after the seal is broken.

3.4.3.1.3 Glass Wool. Cleaned by sequential immersion in three aliquots of methylene chloride, dried in a 110 °C oven. and stored in a methylene chloride-washed glass jar with a Teflon-lined screw cap.

3.4.3.1.4 Water. Deionized distilled and stored in a methylene chloride-rinsed glass container with a Teflon-lined screw cap.

3.4.3.1.5 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for two hours. 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.

3.4.3.1.6 Chromic Acid Cleaning Solution. Dissolve 20 g of sodium dichromate in 15 ml of water, and then carefully add 400 ml of concentrated sulfuric acid.

3.4.3.2 Sample Recovery.

3.4.3.2.1 Acetone. Pesticide quality.

3.4.3.2.2 Methylene Chloride. Pesticide quality.

3.4.3.2.3 Toluene. Pesticide quality.

3.4.3.3 Analysis.

3.4.3.3.1 Potassium Hydroxide. ACS grade, 2-percent (weight/volume) in water.

3.4.3.3.2 Sodium Sulfate. Granulated, reagent grade. Purify prior to use by rinsing with methylene chloride and oven drying. Store the cleaned material in a glass container with a Teflon-lined screw cap.

3.4.3.3.3 Sulfuric Acid. Reagent grade.

3.4.3.3.4 Sodium Hydroxide. 1.0 N. Weigh 40 g of sodium hydroxide into a 1-liter volumetric flask. Dilute to 1 liter with water.

3.4.3.3.5 Hexane. Pesticide grade.

3.4.3.3.6 Methylene Chloride. Pesticide grade.

3.4.3.3.7 Benzene. Pesticide grade.

3.4.3.3.8 Ethyl Acetate.

3.4.3.3.9 Methanol. Pesticide grade.

3.4.3.3.10 Toluene. Pesticide grade.

3.4.3.3.11 Nonane. Pesticide grade.

3.4.3.3.12 Cyclohexane. Pesticide grade.

3.4.3.3.13 Basic Alumina. Activity grade 1, 100-200 mesh. Prior to use, activate the alumina by heating for 16 hours at 130 °C before use. Store in a desiccator. Pre-activated alumina may be purchased from a supplier and may be used as received.

3.4.3.3.14 Silica Gel. Bio-Sil A, 100-200 mesh. Prior to use, activate the silica gel by heating for at least 30 minutes at 180 °C. After cooling, rinse the silica gel sequentially with methanol and methylene chloride. Heat the rinsed silica gel at 50 °C for 10 minutes, and then increase the temperature gradually to 180 °C over 25 minutes and maintain it at this temperature for 90 minutes. Cool at room temperature and store in a glass container with a Teflon-lined screw cap.

3.4.3.3.15 Silica Gel Impregnated with Sulfuric Acid. Combine 100 g of silica gel with 44 g of concentrated sulfuric acid in a screw-capped glass bottle and agitate thoroughly. Disperse the solids with a stirring rod until a uniform mixture is obtained. Store the mixture in a glass container with a Teflon-lined screw cap.

3.4.3.3.16 Silica Gel Impregnated with Sodium Hydroxide. Combine 39 g of 1 N sodium hydroxide with 100 g of silica gel in a screw-capped glass bottle and agitate thoroughly. Disperse solids with a stirring rod until a uniform mixture is obtained. Store the mixture in a glass container with a Teflon-lined screw cap.

3.4.3.3.17 Carbon/Celite. Combine 10.7 g of AX-21 carbon with 124 g of Celite 545 in a 250-ml glass bottle with a Teflon-lined screw cap. Agitate the mixture thoroughly until a uniform mixture is obtained. Store in the glass container.

3.4.3.3.18 Nitrogen. Ultra high purity.

3.4.3.3.19 Hydrogen. Ultra high purity.

3.4.3.3.20 Internal Standard Solution. Prepare a stock standard solution containing the isotopically labeled PCDDs and PCDFs at the concentrations shown in Table 3.4-1 under the heading "Internal Standards" in 10 ml of nonane.

3.4.3.3.21 Surrogate Standard Solution. Prepare a stock standard solution containing the isotopically labeled PCDDs and PCDFs at the concentrations shown in Table 1 under the heading "Surrogate Standards" in 10 ml of nonane.

3.4.3.3.22 Recovery Standard Solution. Prepare a stock standard solution containing the isotopically labeled PCDDs and PCDFs at the concentrations shown in Table 1 under the heading "Recovery Standards" in 10 ml of nonane.

Table 3.4-1.-Composition of the Sample Fortification and Recovery Standards Solutions

Analyte	Concentration (pg/µl)
Internal Standards:	
$^{13}C_{12}$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,7,8-PeCCD	100

$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100
$^{13}C_{12}$-2,3,7,8-TCDF	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100
Surrogate Standards:	
$^{37}Cl_4$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100
Recovery Standards:	
$^{13}C_{12}$-1,2,3,4-TCDD	500
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	500

3.4.4 Procedure

3.4.4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, analysts should be trained and experienced with the analytical procedures.

3.4.4.1.1 Preparation Prior to Analysis.

3.4.4.1.1.1 Cleaning Glassware. All glass components of the train upstream of and including the adsorbent module, shall be cleaned as described in Section 3A of the "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples." Special care shall be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. Any residue shall be removed by soaking the glassware for several hours in a chromic acid cleaning solution prior to cleaning as described above.

3.4.4.1.1.2 Adsorbent Trap. The traps must be loaded in a clean area to avoid contamination. They may not be loaded in the field. Fill a trap with 20 to 40 g of XAD-2. Follow the XAD-2 with glass wool and tightly cap both ends of the trap. Add 100 µl of the surrogate standard solution (Section 3.4.3.3.21) to each trap.

3.4.4.1.1.3 Sample Train. It is suggested that all components be maintained according to the procedure described in APTD-0576.

3.4.4.1.1.4 Silica Gel. Weigh several 200 to 300 g portions of silica gel in an air-tight container to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel may be weighed directly in its impinger or sample holder just prior to sampling.

3.4.4.1.1.5 Filter. Check each filter against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a clean glass container.

3.4.4.1.2 Preliminary Determinations. Same as Section 4.1.2 of Method 5.

3.4.4.1.3 Preparation of Collection Train.

3.4.4.1.3.1 During preparation and assembly of the sampling train, keep all train openings where contamination can enter, sealed until just prior to assembly or until sampling is about to begin.

Note: Do not use sealant grease in assembling the train.

3.4.4.1.3.2 Place approximately 100 ml of water in the second and third impingers, leave the first and fourth impingers empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fifth impinger.

3.4.4.1.3.3 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.

3.4.4.1.3.4 Assemble the train as shown in Figure 3.4-1.

3.4.4.1.3.5 Turn on the adsorbent module and condenser coil recirculating pump and begin monitoring the adsorbent module gas entry temperature. Ensure proper sorbent temperature gas entry temperature before proceeding and before sampling is initiated. It is extremely important that the XAD-2 adsorbent resin temperature never exceed 50 °C because thermal decomposition will occur. During testing, the XAD-2 temperature must not exceed 20 °C for efficient capture of the PCDDs and PCDFs.

3.4.4.1.4 Leak-Check Procedure. Same as method 5, section 4.1.4.

3.4.4.1.5 Sample Train Operation. Same as method 5, section 4.1.5.

3.4.4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Seal the nozzle end of the sampling probe with Teflon tape or aluminum foil.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with aluminum foil. Seal off the inlet to the train with Teflon tape, a ground glass cap, or aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area shall be clean and enclosed so that the chances of losing or contaminating the sample are minimized. Smoking, which could contaminate the sample, shall not be allowed in the cleanup area.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broken filters, colored impinger liquid, etc. Treat the samples as follows:

3.4.4.2.1 Container No. 1. Either seal the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Use a pair of cleaned tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and a sharp-edged blade. Seal the container.

3.4.4.2.2 Adsorbent Module. Remove the module from the train, tightly cap both ends, label it, cover with aluminum foil, and store it on ice for transport to the laboratory.

3.4.4.2.3 Container No. 2. Quantitatively recover material deposited in the nozzle, probe transfer lines, the front half of the filter holder, and the cyclone, if used, first, by brushing while rinsing three times each with acetone, and then by rinsing the probe three times with methylene chloride. Collect all the rinses in Container No. 2.

Rinse the back half of the filter holder three times with acetone. Rinse the connecting line between the filter and the condenser three times with acetone. Soak the connecting line with three separate portions of methylene chloride for 5 minutes each. If using a separate condenser and adsorbent trap, rinse the condenser in the same manner as the connecting line. Collect all the rinses in Container No. 2 and mark the level of the liquid on the container.

3.4.4.2.4 Container No. 3. Repeat the methylene chloride-rinsing described in section 3.4.4.2.3 using toluene as the rinse solvent. Collect the rinses in Container No. 3 and mark the level of the liquid on the container.

3.4.4.2.5 Impinger Water. Measure the liquid in the first three impingers to with ± 1 ml by using a graduated cylinder or by weighing it to within ± 0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Discard the liquid after measuring and recording the volume or weight.

3.4.4.2.6 Silica Gel. Note the color of the indicating silica gel to determine if it has been completely spent and make a mention of its condition. Transfer the silica gel from the fifth impinger to its original container and seal.

3.4.5 Analysis

All glassware shall be cleaned as described in section 3A of the "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples." All samples must be extracted within 30 days of collection and analyzed within 45 days of extraction.

3.4.5.1 Sample Extraction.

3.4.5.1.1 Extraction System. Place an extractable thimble (section 3.4.2.3.4), 1 g of silica gel, and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Remove the extraction thimble from the extraction system and place it in a glass beaker to catch the solvent rinses.

3.4.5.1.2 Container No. 1 (Filter). Transfer the contents of container number 1 directly to the glass thimble of the extraction system and extract them simultaneously with the XAD-2 resin.

3.4.5.1.3 Adsorbent Module. Suspend the adsorbent module directly over the extraction thimble in the beaker (see section 3.4.5.1.1). The glass frit of the module should be in the up position. Using a Teflon squeeze bottle containing toluene, flush the XAD-2 into the thimble onto the bed of cleaned silica gel. Thoroughly rinse the glass module catching the rinsings in the beaker containing the thimble. If the resin is wet, effective extraction can

be accomplished by loosely packing the resin in the thimble. Add the XAD-2 glass wool plug to the thimble.

3.4.5.1.4 Container No. 2 (Acetone and Methylene Chloride Rinse). Concentrate the sample to a volume of about 1-5 ml using the rotary evaporator apparatus, at a temperature of less than 37 °C. Rinse the sample container three times with small portions of methylene chloride and add these to the concentrated solution and concentrate further to near dryness. This residue contains particulate matter removed in the rinse of the train probe and nozzle. Add the concentrate to the filter and the XAD-2 resin in the Soxhlet apparatus described in section 3.4.5.1.1.

3.4.5.1.5 Extraction. Add 100 µl of the internal standard solution (section 3.4.3.3.20) to the extraction thimble containing the contents of the adsorbent cartridge, the contents of Container No. 1, and the concentrate from section 3.4.5.1.3. Cover the contents of the extraction thimble with the cleaned glass wool plug to prevent the XAD-2 resin from floating into the solvent reservoir of the extractor. Place the thimble in the extractor, and add the toluene contained in the beaker to the solvent reservoir. Pour additional toluene to fill the reservoir approximately 2/3 full. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle three times per hour. Extract the sample for 16 hours. After extraction, allow the Soxhlet to cool. Transfer the toluene extract and three 10-ml rinses to the rotary evaporator. Concentrate the extract to approximately 10 ml. At this point the analyst may choose to split the sample in half. If so, split the sample, store one half for future use, and analyze the other according to the procedures in sections 3.4.5.2 and 3.4.5.3. In either case, use a nitrogen evaporative concentrator to reduce the volume of the sample being analyzed to near dryness. Dissolve the residue in 5 ml of hexane.

3.4.5.1.6 Container No. 3 (Toluene Rinse). Add 100 µl of the Internal Standard solution (section 3.4.3.3.20) to the contents of the container. Concentrate the sample to a volume of about 1-5 ml using the rotary evaporator apparatus at a temperature of less than 37 °C. Rinse the sample container three times with small portions of toluene and add these to the concentrated solution and concentrate further to near dryness. Analyze the extract separately according to the procedures in sections 3.4.5.2 and 3.4.5.3, but concentrate the solution in a rotary evaporator apparatus rather than a nitrogen evaporative concentrator.

3.4.5.2 Sample Cleanup and Fractionation.

3.4.5.2.1 Silica Gel Column. Pack one end of a glass column, 20 mm X 230 mm, with glass wool. Add in sequence, 1 g silica gel, 2 g of sodium hydroxide impregnated silica gel, 1 g silica gel, 4 g of acid-modified silica gel, and 1 g of silica gel. Wash the column with 30 ml of hexane and discard it. Add the sample extract, dissolved in 5 ml of hexane to the column with two additional 5-ml rinses. Elute the column with an additional 90 ml of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 ml using the nitrogen evaporative concentrator (section 3.4.2.3.8).

3.4.5.2.2 Basic Alumina Column. Shorten a 25-ml disposable Pasteur pipette to about 16 ml. Pack the lower section with glass wool and 12 g of basic alumina. Transfer the concentrated extract from the silica gel column to the top of the basic alumina column and elute the column sequentially with 120 ml of 0.5 percent methylene chloride in hexane followed by 120 ml of 35 percent methylene chloride in hexane. Discard the first 120 ml of eluate. Collect the second 120 ml of eluate and concentrate it to about 0.5 ml using the nitrogen evaporative concentrator.

3.4.5.2.3 AX-21 Carbon/Celite 545 Column. Remove the bottom 0.5 in. from the tip of a 9-ml disposable Pasteur pipette. Insert a glass fiber filter disk in the top of the pipette 2.5 cm from the constriction. Add sufficient carbon/celite mixture to form a 2 cm column. Top with a glass wool plug. In some cases, AX-21 carbon fines may wash through the glass wool plug and enter the sample. This may be prevented by adding a celite plug to the exit end of the column. Rinse the column in sequence with 2 ml of 50 percent benzene in ethyl acetate, 1 ml of 50 percent methylene chloride in cyclohexane, and 2 ml of hexane. Discard these rinses. Transfer the concentrate in 1 ml of hexane from the basic alumina column to the carbon/celite column along with 1 ml of hexane rinse. Elute the column sequentially with 2 ml of 50 percent methylene chloride in hexane and 2 ml of 50 percent benzene in ethyl acetate and discard these eluates. Invert the column and elute in the reverse direction with 13 ml of toluene. Collect this eluate. Concentrate the eluate in a rotary evaporator at 50 °C to about 1 ml. Transfer the concentrate to a Reacti-vial using a toluene rinse and concentrate to a volume of 200µ1 using a stream of N_2. Store extracts at room temperature, shielded from light, until the analysis is performed.

3.4.5.3 Analysis. Analyze the sample with a gas chromatograph coupled to a mass spectrometer (GC/MS) using the instrumental parameters in sections 3.4.5.3.1 and 3.4.5.3.2. Immediately prior to analysis, add a 20-µl aliquot of the Recovery Standard solution from Table 1 to each sample. A 2-µl aliquot of the extract is injected into the GC. Sample extracts are first analyzed using the DB-5 capillary column to determine the concentration of each isomer of PCDDs and PCDFs (tetra- through octa-). If tetra-chlorinated dibenzofurans are detected in this analysis, then analyze another aliquot of the sample in a separate run, using the DB-225 column to measure the 2.3.7.8-tetrachlorodibenzofuran isomer. Other column systems may be used, provided that the user is able to demonstrate, using calibration and performance checks, that the column system is able to meet the specifications of Section 3.4.6.1.2.2.

3.4.5 3.1 Gas Chromatograph Operating Conditions.

3.4.5.3.1.1 Injector. Configured for capillary column, splitless, 250 °C.

3.4.5.3.1.2 Carrier Gas. Helium, 1-2 ml/min.

3.4.5.3.1.3 Oven. Initially at 150 °C. Raise by at least 40 °C/min to 190 °C and then at 3 °C/min up to 300 °C.

3.4.5.3.2 High Resolution Mass Spectrometer.

3.4.5.3.2.1 Resolution. 10000 m/e.

3.4.5.3.2.2 Ionization Mode. Electron impact.

3.4.5.3.2.3 Source Temperature 250 °C.

3.4.5.3.2.4 Monitoring Mode. Selected ion monitoring. A list of the various ions to be monitored is summarized in Table 3.4-2.

Table 3.4-2.-Elemental Compositions and Exact Masses of the Ions Monitored by High Resolutions Mass Spectrometry for PCDD's and PCDF's

Descriptor no.	Accurate mass[a]	Ion type	Elemental composition	Analyte

1	[Not used]			
2	292.9825	LOCK	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M + 2	$C_{12}H_4{}^{35}Cl^{37}O$	TCDF
	315.9419	M	$^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M + 2	$^{13}C_{12}H_4{}^{35}C13^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}ClO_2$	TCDD
	321.8936	M + 2	$C_{12}H_4{}^{35}Cl_{337}ClO_2$	TCDD
	327.8847	M	$C_{12}H_{437}Cl_4O_2$	TCDD (S)
	330.9792	QC	C_7F_{13}	PFK
	331.9368	M	$_{13}C_{12}H_{435}Cl_4O_2$	TCDD (S)
	333.9339	M + 2	$_{13}C_{12}H_{43}5Cl^{37}ClO_2$	TCDD (S)
	339.8597	M + 2	$C_{12}H_{335}Cl_{437}ClO$	PECDF
	341.8567	M + 4	$C_{12}H_{435}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M + 2	$^{13}C_{12}H_{335}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M + 4	$^{13}C_{12}H_{335}Cl_3{}^{37}Cl_2O$	PeCDF (S)
	355.8546	M + 2	$C_{12}H_{335}Cl_{337}ClO_2$	PeCDD
	357.8516	M + 4	$C_{12}H_{335}Cl_{337}Cl_2O_2$	PeCDD
	367.8949	M + 2	$^{13}C_{12}H_{335}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M + 4	$^{13}C_{12}H_{335}Cl_3{}^{37}ClO_2$	PeCDD (S)
	375.8364	M + 2	$C_{12}H_{435}Cl_{537}ClO$	HxCDPE
	409.7974	M + 2	$C_{12}H_{335}Cl_6{}^{37}ClO$	HpCPDE
3	373.8208	M + 2	$C_{12}H_{235}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M + 4	$C_{12}H_{235}Cl_4{}^{37}Cl_2O$	HxCDF
	383.8639	M	$^{13}C_{12}H_{235}Cl_6O$	HxCDF (S)
	385.8610	M + 2	$^{13}C_{12}H_{235}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8157	M + 2	$C_{12}H_{235}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M + 4	$C_{12}H_{235}Cl_4{}^{37}Cl_2O_2$	HxCDD
	392.9760	LOCK	C_9F_{15}	PFK
	401.8559	M + 2	$^{13}C_{12}H_{235}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M + 4	$^{13}C_{12}H_{235}Cl_4{}^{37}Cl_2O$	HxCDD (S)
	445.7555	M + 4	$C_{12}H_{235}Cl_6{}^{37}Cl_2O$	OCDPE
	430.9729	QC	C_9F_{17}	PFK
4	407.7818	M + 2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF

409.7789	M + 4	$C_{12}H^{35}Cl_5{}^{37}Cl_2O$	HpCDF
417.8253	M	$^{13}C_{12}H_{35}Cl_7O$	HpCDF (S)
419.8220	M + 2	$^{13}C_{12}H_{35}Cl_6{}^{37}ClO$	HpCDF (S)
423.7766	M + 2	$C_{12}H_{35}Cl_6{}^{37}ClO_2$	HpCDD
425.7737	M + 4	$C_{12}H_{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
435.8169	M + 2	$^{13}C_{12}H_{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
437.8140	M + 4	$^{13}C_{12}H_{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
479.7165	M + 4	$C_{12}H_{35}Cl_7{}^{37}Cl_2O$	NCPDE
430.9729	LOCK	C_9F_{17}	PFK
441.7428	M + 2	$C_{1235}Cl_7{}^{37}ClO$	OCDF
443.7399	M + 4	$C_{1235}Cl_6{}^{37}Cl_2O$	OCDF
457.7377	M + 2	$C_{1235}Cl_7{}^{37}ClO_2$	OCDD
459.7348	M + 4	$C_{1235}Cl_6{}^{37}Cl_2O_2$	OCDD
469.7779	M + 2	$^{13}C_{1235}Cl_7{}^{37}ClO_2$	OCDD (S)
471.7750	M + 4	$^{13}C_{1235}Cl_6{}^{37}Cl_2O_2$	OCDD (S)
513.6775	M + 4	$C_{1235}Cl_8{}^{37}Cl_2O_2$	DCDPE
442.9728	QC	$C_{10}F_{17}$	PFK

[a]The following nuclidic masses were used: H = 1.007825, O = 15.994915, C = 12.000000, ^{35}Cl = 34.968853,

^{13}C = 13.003355, $_{37}Cl$ = 36.965903, F = 18.9984, S = Labeled Standard, QC = Ion selected for monitoring
instrument stability during the GC/MS analysis.

Table 3.4-3.-Acceptable Ranges for Ion-Abundance Ratios of PCDD's and PCDF's

			Control limits	
Number of Chlorine atoms	Ion type	Theoretical ratio	Lower	Upper
4	M/M + 2	0.77	0.65	0.89
5	M + 2/M + 4	1.55	1.32	1.78
6	M + 2/M + 4	1.24	1.05	1.43
6[a]	M/M + 2	0.51	0.43	0.59
7[b]	M/M + 2	0.44	0.37	0.51
7	M + 2/M + 4	1.04	0.88	1.20
8	M + 2/M + 4	0.89	0.76	1.02

[a]Used only for ^{13}C-HxCDF

[b]Used only for ^{13}C-HpCDF

3.4.5.3.2.5 Identification Criteria. The following identification criteria shall be used for the characterization of polychlorinated dibenzodioxins and dibenzofurans.

1. The integrated ion-abundance ratio (M/M + 2 or M + 2/M + 4) shall be within 15 percent of the theoretical value. The acceptable ion-abundance ratio ranges for the identification of chlorine-containing compounds are given in Table 3.

2. The retention time for the analytes must be within 3 seconds of the corresponding ^{13}C-labeled internal standard, surrogate or alternate standard.

3. The monitored ions, shown in Table 3.4-2 for a given analyte, shall reach their maximum within 2 seconds of each other.

4. The identification of specific isomers that do not have corresponding ^{13}C-labeled standards is done by comparison of the relative retention time (RRT) of the analyte to the nearest internal standard retention time with reference (i.e., within 0.005 RRT units) to the comparable RRTs found in the continuing calibration.

5. The signal to noise ratio for all monitored ions must be greater than 2.5.

6. The confirmation of 2,3,7,8-TCDD and 2,3,7,8-TCDF shall satisfy all of the above identification criteria.

7. For the identification of PCDFs, no signal may be found in the corresponding PCDPE channels.

3.4.5.3.2.6 Quantitation. The peak areas for the two ions monitored for each analyte are summed to yield the total response for each analyte. Each internal standard is used to quantitate the indigenous PCDDs or PCDFs in its homologous series. For example, the $^{13}C_{12}$-2,3,7,8-tetrachlorodibenzodioxin is used to calculate the concentrations of all other tetrachlorinated isomers. Recoveries of the tetra- and penta-internal standards are calculated using the $^{13}C_{12}$-1,2,3,4-TCDD. Recoveries of the hexa- through octa-internal standards are calculated using $^{13}C_{12}$-1,2,3,7,8,9-HxCDD. Recoveries of the surrogate standards are calculated using the corresponding homolog from the internal standard.

3.4.6 Calibration

Same as Method 5 with the following additions.

3.4.6.1 GC/MS System.

3.4.6.1.1 Initial Calibration. Calibrate the GC/MS system using the set of five standards shown in Table 3.4-4. The relative standard deviation for the mean response factor from each of the unlabeled analytes (Table 4) and of the internal, surrogate, and alternate standards shall be less than or equal to the values in Table 3.4-5. The signal to noise ratio for the GC signal present in every selected ion current profile shall be greater than or equal to 2.5. The ion abundance ratios shall be within the control limits in Table 3.4-3.

3.4.6.1.2 Daily Performance Check.

3.4.6.1.2.1 Calibration Check. Inject one µl of solution Number 3 from table 4. Calculate the relative response factor (RRF) for each compound and compare each RRF to the corresponding mean RRF obtained during the initial calibration. The analyzer performance is acceptable if the measured RRFs for

the labeled and unlabeled compounds for the daily run are within the limits of the mean values shown in Table 3.4-5. In addition, the ion-abundance ratios shall be within the allowable control limits shown in Table 3.4-3.

3.4.6.1.2.2 Column Separation Check. Inject a solution of a mixture of PCDDs and PCDFs that documents resolution between 2,3,7,8-TCDD and other TCDD isomers. Resolution is defined as a valley between peaks that is less than 25 percent of the lower of the two peaks. Identify and record the retention time windows for each homologous series.

Table 3.4-4.-Composition of the Initial Calibration Solutions

		Concentrations (pg/μL)			
Compound	Solution No.	1	2	3	4
Unlabeled Analytes					
2,3,7,8-TCDD	0.5	1	5	50	100
2,3,7,8-TCDF	0.5	1	5	50	100
1,2,3,7,8-PeCDD.	2.5	5	25	250	500
1,2,3,7,8-PeCDF.	2.5	5	25	250	500
2,3,4,7,8-PeCDF.	2.5	5	25	250	500
1,2,3,4,7,8-HxCDD	2.5	5	25	250	500
1,2,3,6,7,8-HxCDD	2.5	5	25	250	500
1,2,3,7,8,9-HxCDD	2.5	5	25	250	500
1,2,3,4,7,8-HxCDF	2.5	5	25	250	500
1,2,3,6,7,8-HxCDF	2.5	5	25	250	500
1,2,3,7,8,9-HxCDF	2.5	5	25	250	500
2,3,4,6,7,8-HxCDD	2.5	5	25	250	500
1,2,3,4,6,7,8-HpCDD	2.5	5	25	250	500
1,2,3,4,6,7,8-HpCDF	2.5	5	25	250	500
1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500
OCDD	5.0	10	50	500	1000
OCDF	5.0	10	50	500	1000
Internal Standards					
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8,-HxCDD	100	100	100	100	100
$^{13}C_{12}$-,2,3,4,6,7,8-HpCDD	100	100	100	100	100

$^{13}C_{12}$-OCDD	200	200	200	200	200
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100
Surrogate Standards					
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	1	5	50	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	2.5	5	25	250	500
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	2.5	5	25	250	500
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	2.5	5	25	250	500
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500
Alternative Standard					
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	2.5	5	25	250	500
Recovery Standards					
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

Table 3.4-5.-Minimum Requirements for Initial and Daily Calibration Response Factors

Compound	Relative Response Factors	
	Initial Calibration RSD	Daily Calibration % Difference
Unlabeled Analytes		
2,3,7,8-TCDD	25	25
2,3,7,8-TCDF	25	25
1,2,3,7,8-PeCDD	25	25
1,2,3,7,8-PeCDF	25	25
2,3,4,7,8-PeCDF	25	25
1,2,4,5,7,8-HxCDD	25	25
1,2,3,6,7,8-HxCDD	25	25
1,2,3,7,8,9-HxCDD	25	25
1,2,3,4,7,8-HxCDF	25	25
1,2,3,6,7,8-HxCDF	25	25

1,2,3,7,8,9-HxCDF	25	25
2,3,4,6,7,8-HxCDF	25	25
1,2,3,4,6,7,8-HpCDD	25	25
1,2,3,4,6,7,8-HpCDF	25	25
OCDD	25	25
OCDF	30	30
Internal Standards		
$^{13}C_{12}$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-1,2,3,7,8-PeCCD	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	30	30
$^{13}C_{12}$-OCDD	30	30
$^{13}C_{12}$-2,3,7,8-TCDF	30	30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	30	30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	30	30
Surrogate Standards		
$^{37}Cl_4$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HXCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	25
Alternate Standard		
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	25	25

Perform a similar resolution check on the confirmation column to document the resolution between 2,3,7,8-TCDF and other TCDF isomers.

3.4.6.2 Lock Channels. Set mass spectrometer lock channels as specified in Table 3.4-3. Monitor the quality control check channels specified in Table 3.4-3 to verify instrument stability during the analysis.

3.4.7 Quality Control

3.4.7.1 Sampling Train Collection Efficiency Check. Add 100 µ1 of the surrogate standards in Table 3.4-1 to the adsorbent cartridge of each train before collecting the field samples.

3.4.7.2 Internal Standard Percent Recoveries. A group of nine carbon-labeled PCDDs and PCDFs representing, the tetra-through octachlorinated homologues, is added to every sample prior to extraction. The role of the

internal standards is to quantitate the native PCDDs and PCDFs present in the sample as well as to determine the overall method efficiency. Recoveries of the internal standards must be between 40 to 130 percent for the tetra- through hexachlorinated compounds while the range is 25 to 130 percent for the higher hepta- and octachlorinated homologues.

3.4.7.3 Surrogate Recoveries. The five surrogate compounds in Table 3.4-4 are added to the resin the adsorbent sampling cartridge before the sample is collected. The surrogate recoveries are measured relative to the internal standards and are a measure of collection efficiency. They are not used to measure native PCDDs and PCDFs. All recoveries shall be between 70 and 130 percent. Poor recoveries for all the surrogates may be an indication of breakthrough in the sampling train. If the recovery of all standards is below 70 percent, the sampling runs must be repeated. As an alternative, the sampling runs do not have to be repeated if the final results are divided by the fraction of surrogate recovery. Poor recoveries of isolated surrogate compounds should not be grounds for rejecting an entire set of samples.

3.4.7.4 Toluene QA Rinse. Report the results of the toluene QA rinse separately from the total sample catch. Do not add it to the total sample.

3.4.8 Quality Assurance

3.4.8.1 Applicability. When the method is used to analyze samples to demonstrate compliance with a source emission regulation, an audit sample must be analyzed, subject to availability.

3.4.8.2 Audit Procedure. Analyze an audit sample with each set of compliance samples. The audit sample contains tetra through octa isomers of PCDD and PCDF. Concurrently, analyze the audit sample and a set of compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation. The same analyst, analytical reagents, and analytical system shall be used both for the compliance samples and the EPA audit sample.

3.4.8.3 Audit Sample Availability. Audit samples will be supplied only to enforcement agencies for compliance tests. The availability of audit samples may be obtained by writing: Source Test Audit Coordinator (MD-77B), Quality Assurance Division, Atmospheric Research and Exposure Assessment Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711. or by calling the Source Test Audit Coordinator (STAC) at (919) 541-7834. The request for the audit sample must be made at least 30 days prior to the scheduled compliance sample analysis.

3.4.8.4 Audit Results. Calculate the audit sample concentration according to the calculation procedure described in the audit instructions included with the audit sample. Fill in the audit sample concentration and the analyst's name on the audit response form included with the audit instructions. Send one copy to the EPA Regional Office or the appropriate enforcement agency and a second copy to the STAC. The EPA Regional Office or the appropriate enforcement agency will report the results of the audit to the laboratory being audited. Include this response with the results of the compliance samples in relevant reports to the EPA Regional Office or the appropriate enforcement agency.

3.4.9 Calculations

Same as method 5, section 6 with the following additions.

3.4.9.1 Nomenclature.

A_{ai} = Integrated ion current of the noise at the retention time of the analyte.
A^*_{ci} = Integrated ion current of the two ions characteristic of the internal standard i in the calibration standard.
A_{cij} = Integrated ion current of the two ions characteristic of compound i in the jth calibration standard.
A^*_{cij} = Integrated ion current of the two ions characteristic of the internal standard i in the jth calibration standard.
A_{csi} = Integrated ion current of the two ions characteristic of surrogate compound i in the calibration standard.
A_i = Integrated ion current of the two ions characteristic of compound in the sample.
A^*_i = Integrated ion current of the two ions characteristic of internal standard i in the sample.
A_{rs} = Integrated ion current of the two ions characteristic of the recovery standard.
A_{si} = Integrated ion current of the two ions characteristic of surrogate compound i in the sample.
C_i = Concentration of PCDD or PCDF i in the sample, pg/M^3.
C_T = Total concentration of PCDDs or PCDFs in the sample, pg/M^3.
m_{ci} = Mass of compound i in the calibration standard injected into the analyzer, pg.
m^*_{ci} = Mass of labeled compound i in the calibration standard injected into the analyzer, pg.
m^*_i = Mass of internal standard i added to the sample, pg.
m_{rs} = Mass of recovery standard in the calibration standard injected into the analyzer, pg.
m_{si} = Mass of surrogate compound i in the calibration standard, pg.
RRF_i = Relative response factor.
RRF_{rs} = Recovery standard response factor.
RRF_s = Surrogate compound response factor.

3.4.9.2 Average Relative Response Factor.

$$RRF_i = 1/n \sum_{j=1}^{n} [A_{cij} m^*_{ci} / (A^*_{cij} m_{ci})] \quad \text{Eq. 23-1}$$

3.4.9.3 Concentration of the PCDDs and PCDFs.

$$C_i = m^*_i A_i / (A^*_i \, RRF_1 \, V_{m(std)}) \quad \text{Eq. 23-2}$$

3.4.9.4 Recovery Standard Response Factor.

$$RRF_{rs} = A^*_{ci} m_{rs} / (A_{rs} \, m^*_{ci}) \quad \text{Eq. 23-3}$$

3.4.9.5 Recovery of Internal Standards (R^*).

$$R^* = (A^*_i \, m_{rs} / A_{rs} \, RF_{rs} m^*_i) \text{ X } 100\% \quad \text{Eq. 23-4}$$

3.4.9.6 Surrogate Compound Response Factor.

$$RRFs = A^*_{ci} \, m_s / (A_{cis} \, m^*_{ci}) \quad \text{Eq. 23-5}$$

3.4.9.7 Recovery of Surrogate Compounds (R_s).

$$R_s = (A_s m^*_i / A^*_i RRF_s m_s) \text{ X } 100\% \quad \text{Eq. 23-6}$$

3.4.9.8 Minimum Detectable Limit (MDL).

$$MDL = 2.5\ A_{ai}\ m^*_i/(A^*_{ci}\ RRF_i) \qquad \text{Eq. 23-7}$$

3.4.9.9 Total Concentration of PCDDs and PCDFs in the Sample.

$$C_T = \sum_{i=1}^{n} C_i \qquad \text{Eq. 23-8}$$

3.4.10 Bibliography

1. American Society of Mechanical Engineers. Sampling for the Determination of Chlorinated Organic Compounds in Stack Emissions. Prepared for U.S. Department of Energy and U.S. Environmental Protection Agency. Washington, DC December 1984. 25 p.

2. American Society of Mechanical Engineers. Analytical Procedures to Assay Stack Effluent Samples and Residual Combustion Products for Polychlorinated Dibenzo-p-Dioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF). Prepared for the U.S. Department of Energy and U.S. Environmental Protection Agency. Washington, DC December 1984. 23 p.

3. Thompson, J.R. (ed.) Analysis of Pesticide Residues in Human and Environmental Samples. U.S. Environmental Protection Agency. Research Triangle Park, NC 1974.

4. Triangle Laboratories. Case Study: Analysis of Samples for the Presence of Tetra Through Octachloro-p-Dibenzodioxins and Dibenzofurans. Research Triangle Park, NC 1988. 26 p.

5. U.S. Environmental Protection Agency. Draft Method 8290-The Analysis of Polychlorinated Dibenzo-p-dioxin and Polychlorinated Dibenzofurans by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry. In: Test Methods for Evaluating Solid Waste. Washington, DC SW-846.

3.5 Sampling for Aldehyde and Ketone Emissions from Stationary Sources (Method 0011)

3.5.1 Scope and Application

This method is applicable to the determination of Destruction and Removal Efficiency (DRE) of formaldehyde, CAS Registry number 50-00-0, and possibly other aldehydes and ketones from stationary sources as specified in the regulations. The methodology has been applied specifically to formaldehyde; however, many laboratories have extended the application to other aldehydes and ketones. Compounds derivatized with 2,4-dinitrophenyl-hydrazine can be detected as low as 6.4×10^{-8} lbs/cu ft (1.8 ppbv) in stack gas over a 1 hr sampling period, sampling approximately 45 cu ft.

3.5.2 Summary of Method

3.5.2.1 Gaseous and particulate pollutants are withdrawn isokinetically from an emission source and are collected in aqueous acidic 2,4-dinitrophenyl-hydrazine. Formaldehyde present in the emissions reacts with the 2,4-dinitrophenyl-hydrazine to form the formaldehyde dinitrophenylhydrazone derivative. The dinitrophenylhydrazone derivative is extracted, solvent-exchanged, concentrated, and then analyzed by high performance liquid chromatography.

3.5.3 Interferences

3.5.3.1 A decomposition product of 2,4-dinitrophenyl-hydrazine, 2,4-dinitroaniline, can be an analytical interferant if concentrations are high. 2,4-Dinitroaniline can coelute with 2,4-dinitrophenylhydrazone of formaldehyde under high performance liquid chromatography conditions, which may be used for the analysis. High concentrations of highly-oxygenated compounds, especially acetone, that have the same retention time or nearly the same retention time as the dinitrophenylhydrazone of formaldehyde, and that also absorb at 360 nm, will interfere with the analysis.

Formaldehyde, acetone, and 2,4-dinitroaniline contamination of the aqueous acidic 2,4-dinitrophenyl-hydrazine (DNPH) reagent is frequently encountered. The reagent must be prepared within five days of use in the field and must be stored in an uncontaminated environment both before and after sampling in order to minimize blank problems. Some concentration of acetone contamination is unavoidable, because acetone is ubiquitous in laboratory and field operations. However, the acetone contamination must be minimized.

3.5.4 Apparatus and Materials

3.5.4.1 A schematic of the sampling train is shown in Figure 3.5-1. This sampling train configuration is adapted from EPA method 4 procedures. The sampling train consists of the following components: Probe Nozzle, Pitot Tube, Differential Pressure Gauge, Metering System, Barometer, and Gas Density Determination Equipment.

3.5.4.1.1 Probe Nozzle: Quartz or glass with sharp, tapered (30° angle) leading edge. The taper shall be on the outside to preserve a constant inner diameter. The nozzle shall be buttonhook or elbow design. A range of nozzle sizes suitable for isokinetic sampling should be available in increments of 0.15 cm(1/16 in), e.g., 0.32 to 1.27 cm (1/8 to 1/2 in), of larger if higher volume sampling trains are used. Each nozzle shall be calibrated according to the procedures outlined in section 3.5.8.1.

3.5.4.1.2 Probe Liner: Borosilicate glass or quartz shall be used for the probe liner. The tester should not allow the temperature in the probe to exceed 120 ± 14 °C (248 ± 25°F).

3.5.4.1.3 Pitot Tube: The Pitot tube shall be Type S, as described in section 2.1 of EPA method 2, or any other appropriate device. 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 plan (see EPA method 2, Figure 26b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in section 4 of EPA method 2.

>>>> See the accompanying hardcopy volume for non-machine-readable data that appears at this point. <<<<

3.5.4.1.4 Differential Pressure Gauge: The differential pressure gauge shall be an inclined manometer or equivalent device as described in section 2.2 of EPA method 2. One manometer shall be used for velocity-head reading and the other for orifice differential pressure readings.

3.5.4.1.5 Impingers: The sampling train requires a minimum of four impingers, connected as shown in Figure 3.5-1, with ground glass (or equivalent) vacuum-tight fittings. For the first, third, and fourth implngers, use the Greenburg-Smith design, modified by replacing the tip with a 1.3 cm inside diameter (1/2 in) glass tube extending to 1.3 cm (1/2 in) from the bottom of the flask. For the second impinger, use a Greenburg-Smith Impinger with the standard tip. Place a thermometer capable of measuring temperature to

within 1 °C (2 °F) at the outlet of the fourth impinger for monitoring purposes.

3.5.4.1.6 Metering System: The necessary components are a vacuum gauge, leak-free pump, thermometers capable of measuring temperature within 3 °C (5.4 °F), dry-gas meter capable of measuring volume to within 1%, and related equipment as shown in Figure 3.5-1. 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 may be used which are capable of maintaining sample volumes to within 2%. The metering system may be used in conjunction with a pitot tube to enable checks of isokinetic sampling rates.

3.5.4.1.7 Barometer: The barometer may be 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 increases (vice versa for elevation decrease).

3.5.4.1.8 Gas Density Determination Equipment: Temperature sensor and pressure gauge (as described in sections 2.3 and 2.3 of EPA method 2), and gas analyzer, if necessary (as described in EPA method 3). The temperature sensor ideally should be permanently attached to the pitot tube or sampling probe in a fixed configuration such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just 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 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.

3.5.4.2 Sample Recovery.

3.5.4.2.1 Probe Liner: Probe nozzle and brushes; Teflon 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 impingers.

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

3.5.4.2.3 Graduate Cylinder and/or Balance: A graduated cylinder or balance is required to measure condensed water to the nearest 1 ml or 1 g. Graduated cylinders shall have division not >2 ml. Laboratory balances capable of weighing to ± 0.5 g are required.

3.5.4.2.4 Amber Glass Storage Containers: One-liter wide-mouth amber flint glass bottles with Teflon-lined caps are required to store impinger water samples. The bottles must be sealed with Teflon tape.

3.5.4.2.5 Rubber Policeman and Funnel: A rubber policeman and funnel are required to aid in the transfer of material into and out of containers in the field.

3.5.4.3 Reagent Preparation.

3.5.4.3.1 Bottles/Caps: Amber 1- or 4-L bottles with Teflon-lined caps are required for storing cleaned DNPH solution. Additional 4-L bottles are required to collect waste organic solvents.

3.5.4.3.2 Large Glass Container: At least one large glass (8 to 16 L) is required for mixing the aqueous acidic DNPH solution.

3.5.4.3.3 Stir Plate/Large Stir Bars/Stir Bar Retriever: A magnetic stir plate and large stir bar are required for the mixing of aqueous acidic DNPH solution. A stir bar retriever is needed for removing the stir bar from the large container holding the DNPH solution.

3.5.4.3.4 Buchner Filter/Filter Flask/Filter Paper: A large filter flask (2-4 L) with a buchner filter, appropriate rubber stopper, filter paper, and connecting tubing are required for filtering the aqueous acidic DNPH solution prior to cleaning.

3.5.4.3.5 Separatory Funnel: At least one large separatory funnel (2 L) is required for cleaning the DNPH prior to use.

3.5.4.3.6 Beakers: Beakers (150 ml, 250 ml, and 400 ml) are useful for holding/measuring organic liquids when cleaning the aqueous acidic DNPH solution and for weighing DNPH crystals.

3.5.4.3.7 Funnels: At least one large funnel is needed for pouring the aqueous acidic DNPH into the separator funnel.

3.5.4.3.8 Graduated Cylinders: At least one large graduated cylinder (1 to 2 L) is required for measuring organic-free reagent water and acid when preparing the DNPH solution.

3.5.4.3.9 Top-Loading Balance: A one-place top loading balance is needed for weighing out the DNPH crystals used to prepare the aqueous acidic DNPH solution.

3.5.4.3.10 Spatulas: Spatulas are needed for weighing out DNPH when preparing the aqueous DNPH solution.

3.5.4.4 Crushed Ice: Quantities ranging from 10-50 lb may be necessary during a sampling run, depending upon ambient temperature. Samples which have been taken must be stored and shipped cold; sufficient ice for this purpose must be allowed.

3.5.5 Reagents

3.5.5.1 Reagent grade 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.

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

3.5.5.3 Silica Gel: Silica gel shall be indicating type, 6-16 mesh. If the silica gel has been used previously, dry at 175°C (350 °F) for 2 hours

before using. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.

3.5.5.4 2,4-dinitrophenylhydrazine (DNPH), [2,4-$(O_2N)_2C_6H_3$] $NHNH_2$-The quantity of water may vary from 10 to 30%.

3.5.5.4.1 The 2,4-dinitrophenylhydrazine reagent must be prepared in the laboratory within five days of sampling use in the field. Preparation of DNPH can also be done in the field, with consideration of appropriate procedures required for safe handling of solvent in the field. When a container of prepared DNPH reagent is opened in the field, the contents of the opened container should be used within 48 hours. All laboratory glassware must be washed with detergent and water and rinsed with water, methanol, and methylene chloride prior to use.

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

3.5.5.4.2 Preparation of Aqueous Acidic DNPH Derivatizing Reagent: Each batch of DNPH reagent should be prepared and purified within five days of sampling, according to the procedures described below.

Note: Reagent bottles for storage of cleaned DNPH derivatizing solution must be rinsed with acetonitrile and dried before use. Baked glassware is not essential for preparation of DNPH reagent. The glassware must not be rinsed with acetone or an unacceptable concentration of acetone contamination will be introduced. If field preparation of DNPH is performed, caution must be exercised in avoiding acetone contamination.

3.5.5.4.2.1 Place an 8 L container under a fume hood on a magnetic stirrer. Add a large stir bar and fill the container half full of organic-free reagent water. Save the empty bottle from the organic-free reagent water. Start the stirring bar and adjust the stir rate to be as fast as possible. Using a graduated cylinder, measure 1.4 ml of concentrated hydrochloric acid. Slowly pour the acid into the stirring water. Fumes may be generated and the water may become warm. Weight the DNPH crystals on a one-place balance (see Table 3.5-1 for approximate amounts) and add to the stirring acid solution. Fill the 8-L container to the 8-L mark with organic-free reagent water and stir overnight. If all of the DNPH crystals have dissolved overnight, add additional DNPH and stir for two more hours. Continue the process of adding DNPH with additional stirring until a saturated solution has been formed. Filter the DNPH solution using vacuum filtration. Gravity filtration may be used, but a much longer time is required. Store the filtered solution in an amber bottle at room temperature.

3.5.5.4.2.2 Within five days of proposed use, place about 1.6 L of the DNPH reagent in a 2-L separatory funnel. Add approximately 200 ml of methylene chloride and stopper the funnel. Wrap the stopper of the funnel with paper towels to absorb any leakage. Invert and vent the funnel. Then shake vigorously for 3 minutes. Initially, the funnel should be vented frequently (every 10-15 sec). After the layers have separated, discard the lower (organic) layer.

3.5.5.4.2.3 Extract the DNPH a second time with methylene chloride and finally with cyclohexane. When the cyclohexane layer has separated from the DNPH reagent, the cyclohexane layer will be the top layer in the separatory funnel. Drain the lower layer (the cleaned extract DNPH reagent solution) into an amber bottle that has been rinsed with acetonitrile and allowed to dry.

3.5.5.4.3 Quality Control: Take two aliquots of the extracted DNPH reagent. The size of the aliquots is dependent upon the exact sampling procedure used, but 100 ml is reasonably representative. To ensure that the background in the reagent is acceptable for field use, analyze one aliquot of the reagent according to the procedure of method 8315. Save the other aliquot of aqueous acidic DNPH for use as a method blank when the analysis is performed.

Table 3.5-1.-Approximate Amount of Crystalline DNPH Used To Prepare a Saturated Solution

Amount of moisture in DNPH	Weight required per 8 L of solution
10 weight percent	31 g
15 weight percent	33 g
30 weight percent	40 g

Table 3.5-2.-Instrument Detection Limits and Reagent Capacity for Formaldehyde Analysis[1]

Analyte	Detection limit, ppb[2]	Reagent capacity ppmv
Formaldehyde	1.8	66
Acetaldehyde	1.7	70
Acrolein	1.5	75
Acetone/Propionaldehyde	1.5	75
Butyraldehyde	1.5	79
Methyl ethyl ketone	1.5	79
Valeraldehyde	1.5	84
Isovaleraldehyde	1.4	84
Hexaldehyde	1.3	88
Benzaldehyde	1.4	84
o-/m-/p-Tolualdehyde	1.3	89
Dimethylbenzaldehyde	1.2	93

[1]Oxygenated compounds in addition to formaldehyde are included for comparison with formaldehyde; extension of the methodology to other compounds is possible.
[2]Detection limits are determined in solvent. These values therefore represent the optimum capability of the methodology.

3.5.5.4.4 Shipment to the Field: Tightly cap the bottle containing extracted DNPH reagent using a Teflon-lined cap. Seal the bottle with Teflon tape. After the bottle is labeled, the bottle may be placed in a friction-top can (paint can or equivalent) containing a 1-2 inch layer of granulated charcoal and stored at ambient temperature until use.

3.5.5.4.4.1 If the DNPH reagent has passed the Quality Control criteria, the reagent may be packaged to meet necessary shipping requirements and sent to the sampling area. If the Quality Control criteria are not met, the reagent solution may be re-extracted or the solution may be re-prepared and the extraction sequence repeated.

3.5.5.4.4.2 If the DNPH reagent is not used in the field within five days of extraction, an aliquot may be taken and analyzed as described in method 0011A. If the reagent meets the Quality Control requirements, the reagent may be used. If the reagent does not meet the Quality Control requirements, the reagent must be discarded and new reagent must be prepared and tested.

3.5.5.4.5 Calculation of Acceptable Concentrations of Impurities in DNPH Reagent: The acceptable impurity concentration (AIC, µg/ml) is calculated from the expected analyte concentration in the sampled gas (EAC, ppbv), the volume of air that will be sampled at standard conditions (SVOL, L), the formula weight of the analyte (FW, g/mol), and the volume of DNPH reagent that will be used in the impingers (RVOL, ml):

AIC = 0.1 X [EAC X SVOL X FW/22.4 X (FW + 180)/FW](RVOL X 1,000)

where:

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

3.5.5.4.6 Disposal of Excess DNPH Reagent: Excess DNPH reagent may be returned to the laboratory and recycled or treated as aqueous waste for disposal purposes. 2,4-dinitrophenylhydrazine is a flammable solid when dry, so water should not be evaporated from the solution of the reagent.

3.5.5.5 Field Spike Standard Preparation: To prepare a formaldehyde field spiking standard at 4.01 mg/ml, use a 500 µl syringe to transfer 0.5 ml to 37% by weight of formaldehyde (401 mg/ml) to a 50 ml volumetric flask containing approximately 50 ml of methanol. Dilute to 50 ml with methanol.

3.5.5.6 Hydrochloric Acid, HCL: Reagent grade hydrochloric acid (approximately 12N) is required for acidifying the aqueous DNPH solution.

3.5.5.7 Methylene Chloride, CH_2Cl_2: Methylene chloride (suitable for residue and pesticide analysis, GC/MS, HPLC, GC, Spectrophotometry or equivalent) is required for cleaning the aqueous acidic DNPH solution, rinsing glassware, and recovery of sample trains.

3.5.5.8 Cyclohexane, C_6H_{12}: Cyclohexane (HPLC grade) is required for cleaning the aqueous acidic DNPH solution.

Note: Do not use spectroanalyzed grades of cyclohexane if this sampling methodology is extended to aldehydes and ketones with four or more carbon atoms.

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

3.5.5.10 Acetonitrile, CH_3CN: Acetonitrile (HPLC grade or equivalent) is required for rinsing glassware.

3.5.5.11 Formaldehyde, HCHO: Analytical grade or equivalent formaldehyde is required for preparation of standards. If other aldehydes or ketones are used, analytical grade or equivalent is required.

3.5.6 Sample Collection, Preservation, and Handling

3.5.6.1 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.

3.5.6.2 Laboratory Preparation:

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

3.5.6.2.2 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.

3.5.6.3 Preliminary Field Determinations:

3.5.6.3.1 Select the sampling site and the minimum number of sampling point according to EPA method 1 or other relevant criteria. Determine the stack pressure, temperature, and range of velocity heads using EPA method 2. A leak-check of the pitot lines according to EPA method 2, section 3.1, must 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.

3.5.6.3.2 Select a nozzle size based on the range of velocity heads so that is not necessary to change the nozzle size in order to maintain isokinetic sampling rates below 28 L/min (1.0 cfm). 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).

3.5.6.3.3 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.

3.5.6.3.4 A minimum of 45 ft^3 of sample volume is required for the determination of the Destruction and Removal Efficiency (DRE) of formaldehyde from incineration systems (45 ft^3 is equivalent to one hour of sampling at 0.75 dscf). Additional sample volume shall be collected as necessitated by the capacity of the DNPH reagent and analytical detection limit constraints. To determine the minimum sample volume required, refer to sample calculations in section 10.

3.5.6.3.5 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 0.5 min.

3.5.6.3.6 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-volume samples. In these cases, careful documentation must be maintained in order to allow accurate calculation of concentrations.

3.5.6.4 Preparation of Collection Train:

3.5.6.4.1 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.

3.5.6.4.2 Place 100 ml of cleaned DNPH solution in each of the first two impingers, and leave the third impinger empty. If additional capacity is required for high expected concentrations of formaldehyde in the stack gas, 200 ml of DNPH per impinger may be used or additional impingers may be used for sampling. Transfer approximately 200 to 300 g of pre-weighed silica gel from its container to the fourth impinger. Care should be taken 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 or 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.

3.5.6.4.3 With a glass or quartz liner, install the selected nozzle using a Viton-A O-ring with 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 connection systems utilizing 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 sampling point.

3.5.6.4.4 Assemble the train as shown in Figure 3.5-1. During assembly, do not use any silicone grease on ground-glass joints upstream of the impingers. Use Teflon tape, if required. A very light coating of silicone grease may be used on ground-glass joints downstream of the impingers, but the silicone grease should be limited to the outer portion (see APTD-0576) of the ground-glass joints to minimize silicone grease contamination. If necessary, Teflon tape may be used to seal leaks. Connect all temperature sensors to an appropriate potentiometer/display unit. Check all temperature sensors at ambient temperatures.

3.5.6.4.5 Place crushed ice all around the impingers.

3.5.6.4.6 Turn on and set the probe heating system at the desired operating temperature. Allow time for the temperature to stabilize.

3.5.6.5 Leak-Check Procedures:

3.5.6.5.1 Pre-test Leak Check.

3.5.6.5.1.1 After the sampling train has been assembled, turn on and set the probe heating system at 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.

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

3.5.6.5.1.2 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 to the inlet and then plugging the Inlet and pulling a 381 mm Hg (15 in Hg) vacuum. (A lower vacuum any be used if this lower vacuum is not exceeded during the test.) Next 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 (a) 4% of the average sampling rate or (b) >0.00057 m^3/min (0.02 cfm), are unacceptable.

3.5.6.5.1.3 The following leak check instructions for the sampling train described In ADPT-0576 and APTD-0581 may be helpful. Start the pump with the fine-adjust valve fully open and coarse-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.

3.5.6.5.1.4 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.

3.5.6.5.2 Leak Checks During Sampling Run:

3.5.6.5.2.1 If, during the sampling run, a component change (i.e., impinger) 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 described in section 3.5.6.5.1, except that is 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. If a higher leakage rate is obtained, the tester must void the sampling run.

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

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

3.5.6.5.3 Post-test Leak Check:

3.5.6.5.3.1 A leak check is mandatory at the conclusion of each sampling run. The leak check shall be done with, the same procedures as 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 (0.02 cfm) or 4% of the average sampling rate (whichever is less), the results are acceptable. If, however, a higher leakage rate is obtained, the tester shall record the leakage rate and void the sampling run.

3.5.6.6 Sampling Train Operation:

3.5.6.6.1 During the sampling run, maintain an isokinetic sampling rate to within 10% of true isokinetic, below 20 L/min (1.0 cfm). Maintain a temperature around the probe of 120 °C (248° ± 25°F).

3.5.6.6.2 For each run, record the data on a data sheet such as the one shown in Figure 3.5-2. 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 required by

Figure 2 at least once at each sample 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.

3.5.6.6.3 Clean the stack access ports prior to the test run to eliminate the change 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 are taken to compensate for the deviations.

>>>> See the accompanying hardcopy volume for non-machine-readable data that appears at this point. <<<<

3.5.6.6.4 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 in order to prevent liquid from backing up through the train. If necessary, the pump may be turned on with the coarse-adjust valve closed.

3.5.6.6.5 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.

3.5.6.6.6 Traverse the stack cross section, as required by EPA Method 1, 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.

3.5.6.6.7 During the test run, make periodic adjustments to keep the temperature around the probe 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.

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

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

3.5.6.6.10 At the end of the sampling 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.

3.5.6.6.11 Calculate percent isokineticity (see method 2) to determine whether the run was valid or another test should be made.

3.5.7 Sample Recovery

3.5.7.1 Preparation.

3.5.7.1.1 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.

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

3.5.7.1.3 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.

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

3.5.7.1.5 Save a portion of all washing solution (methylene chloride, 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 sample container.

3.5.7.2 Sample Containers.

3.5.7.2.1 Container 1: Probe and Impinger Catches. Using a graduated cylinder, measure to the nearest ml, and record the volume of the solution in the first three impingers. Alternatively, the solution may be weighed to the nearest 0.5 g. Include any condensate in the probe in this determination. Transfer the impinger solution from the graduated cylinder into the amber flint glass bottle. Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, clean all surfaces to which the sample is exposed (including the probe nozzle, probe fitting, probe liner, first impinger, and impinger connector) with methylene chloride. Use less than 500 ml for the entire wash (250 ml would be better, if possible). Add the washing to the sample container.

3.5.7.2.1.1 Carefully remove the probe nozzle and rinse the inside surface with methylene chloride from a wash bottle. Brush with a Teflon bristle brush, and rinse until the rinse shows no visible particles or yellow color, after which make a final rinse of the inside surface. Brush and rinse the inside parts of the Swagelok fitting with methylene chloride in a similar way.

3.5.7.2.1.2 Rinse the probe liner with methylene chloride. While squirting the methylene chloride into the upper end of the probe, tilt and

rotate the probe so that all inside surfaces will be wetted with methylene chloride. Let the methylene chloride drain from the lower end into the sample container. The tester may use a funnel (glass or polyethylene) to aid in transferring the liquid washes to the container. Follow the rinse with a Teflon brush. Hold the probe in an inclined position, and squirt methylene chloride into the upper end as the probe brush is being pushed with a twisting action through the probe. Hold the sample container underneath the lower end of the probe, and catch any methylene chloride, water, and particulate matter that is brushed from the probe. Run the brush through the probe three times or more. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since there may be small crevices in which particulate matter can be entrapped. Rinse the brush with methylene chloride or water, and quantitatively collect these washing in the sample container. After the brushing, make a final rinse of the probe as described above.

Note: Two people should clean the probe in order to minimize sample losses. Between sampling runs, brushes must be kept clean and free from contamination.

3.5.7.2.1.3 Rinse the inside surface of each of the first three impingers (and connecting tubing) three separate times. Use a small portion of methylene chloride for each rinse, and brush each surface to which the sample is exposed with a Teflon bristle brush to ensure recovery of fine particulate matter. Water will be required for the recovery of the impingers in addition to the specified quantity of methylene chloride. There will be at least two phases in the impingers. This two-phase mixture does not pour well, and a significant amount of the impinger catch will be left on the walls. The use of water as a rinse makes the recovery quantitative. Make a final rinse of each surface and of the brush, using both methylene chloride and water.

3.5.7.2.1.4 After all methylene chloride and water washing and particulate matter have been collected in the sample container, tighten the lid so the solvent, water, and DNPH reagent will not leak out when the container is shipped to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Seal the container with Teflon tape. Label the container clearly to identify its contents.

3.5.7.2.1.5 If the first two impingers are to be analyzed separately to check for breakthrough, separate the contents and rinses of the two impingers into individual containers. Care must be taken to avoid physical carryover from the first impinger to the second. The formaldehyde hydrazone is a solid which floats and froths on top of the impinger solution. Any physical carryover of collected moisture into the second impinger will invalidate a breakthrough assessment.

3.5.7.2.2 Container 2: Sample Blank. Prepare a blank by using an amber flint glass container and adding a volume of DNPH reagent and methylene chloride equal to the total volume in Container 1. Process the blank in the same manner as Container 1.

3.5.7.2.3 Container 3: Silica Gel. Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. The impinger containing the silica gel may be used as a sample transport container with both ends sealed with tightly fitting caps or plugs. Ground-glass stoppers or Teflon caps may be used. The silica gel impinger should then be labeled, covered with aluminum foil, and packaged on ice for transport to the laboratory. If the silica gel is removed from the impinger, the tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. It is not necessary to remove the small amount of 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 water or other liquids to transfer the silica gel. If a balance is available in the field, the spent silica gel (or silica gel plus impinger) may be weighed to the nearest 0.5 g.

3.5.7.2.4 Sample containers should be placed in a cooler, cooled by (although not in contact with) ice. Sample containers must be placed vertically and, since they are glass, protected from breakage during shipment. Samples should be cooled during shipment so they will be received cold at the laboratory.

3.5.8 Calibration

3.5.8.1 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 nozzles become nicked or corroded, they shall be replaced and calibrated before use. Each nozzle must be permanently and uniquely identified.

3.5.8.2 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 or corroded and if it meets design and intercomponent spacing specifications.

3.5.8.3 Metering System.

3.5.8.3.1 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 with the pump. For these cases, the following leak check procedure will apply: make a ten-minute calibration run at 0.00057 m^3/min (0.02 cfm). At the end of the run, take the difference of the measured wettest 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).

3.5.8.3.2 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 calibration has changed by more than 5%, recalibrate the meter over the full range of orifice settings, as outlined in APTD-0576.

3.5.8.3.3 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 min. A loss of pressure on the manometer indicates a leak in the meter box. Leaks 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 test series must be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

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

3.5.8.5 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 the 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%.

3.5.8.5.1 Impinger and dry-gas meter thermocouples: For the thermocouples used to measure the temperature of the gas leaving the impinger train, three-point calibration at ice water, room air, and boiling water temperatures is necessary. Accept the thermocouples only if the readings at all three temperatures agree to ± 2C (3.60 °F) with those of the absolute value of the reference thermometer.

3.5.8.5.2 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. Use of a point at room air temperature is recommended. The thermometer and thermocouple must agree to within 1.5% at each of the calibration points. A calibration curve (equation) may be constructed (calculated) and the data extrapolated to cover the entire temperature range suggested by the manufacturer.

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

3.5.8.7 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.

3.5.9 Calculations

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

3.5.9.1 Calculation of Total Formaldehyde: To determine the total formaldehyde in mg, use the following equation:

$$\text{Total mg formaldehyde} = C_d \times V \times DF \times \frac{\text{[g/mole aldehyde]}}{\text{[g/mole aldehyde]}} \times 10^3 \text{ mg/}\mu\text{g}$$

[g/mole DNPH derivative]

where:

C_d = measured concentration of DNPH-formaldehyde derivative, µg/ml.
V = organic extract volume ml.
DF = dilution factor.

3.5.9.2 Formaldehyde concentration in stack gas.

Determine the formaldehyde concentration in the stack gas using the following equation:

C_f = K [total formaldehyde, mg] $V_{m(std)}$

where:

K = 35.31 ft^3/m^3 if $V_{m(std)}$ is expressed in English units
= 1.00 m^3/m^3 if $V_{m(std)}$ is expressed in metric units.
$V_{m(std)}$ volume of gas sample a measured by dry gas meter, corrected to standard conditions, dscm (dscf).

3.5.9.3 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop are obtained from the data sheet.

3.5.9.4 Dry Gas Volume: Calculate Vm(std) and adjust for leakage, if necessary, using the equation in section 6.3 of EPA method 5.

3.5.9.5 Volume of Water Vapor and Moisture Content: Calculate the volume of water vapor and moisture content from equations 5-2 and 5-3 of EPA method 5.

3.5.10 Determination of Volume to be Sampled

To determine the minimum sample volume to be collected, use the following sequence of equations.

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

Max FORM Mass = [(WF) (FORM conc) (100-%DRE)]/100

where:

WF = mass flow rate of waste feed per h, g/h (lb/h).
FORM = concentration of FORM (wt %) introduced into the combustion process.
DRE = percent Destruction and Removal Efficiency required.
Max FORM= mass flow rate (g/h [lb/]) of FORM emitted from the combustion sources.

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

Max FORM conc= [Max FORM Mass] / $DV_{eff(std)}$

where:

$DV_{eff(std)}$ = volumetric flow rate of exhaust gas, dscm (dscf).
FORM conc = anticipated concentration of the FORM in the exhaust gas stream, g/dscm (lb/dscf).

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

$[LDL_{FORM}$ X 10 / FORM conc] V_{tbc}

where:

LDL_{FORM} = detectable amount of FORM in entire sampling train.
V_{tbc} = minimum dry standard volume to be collected at dry-gas meter.

3.5.10.4 The following analytical detection limits and DNPH Reagent Capacity (based on a total volume of 200 ml in two impingers) must also be considered in determining a volume to be sampled.

3.5.11 Quality Control

3.5.11.1 Sampling: See EPA Manual 600/4-77-02b for Method 5 quality control.

3.5.11.2 Analysis: The quality assurance program required for this method includes the analysis of the field and method blanks, procedure validations. and analysis of field spikes. The assessment of combustion data and positive identification and quantitation of formaldehyde are 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 required information to take corrective action if problems are observed in laboratory operations or in field sampling activities.

3.5.11.2.1 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, methylene chloride and water, and unused DNPH reagent. 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 sampling train). The probe of the blank train must 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 blank sampling train.

3.5.11.2.2 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.

3.5.11.2.3 Field Spike: A field spike is performed by introducing 200 µL of the Field Spike Standard into an impinger containing 200 ml of DNPH solution. Standard impinger recovery procedures are followed and the spike is used as a check on field handling and recovery procedures. An aliquot of the field spike standard is retained in the laboratory for derivatization and comparative analysis.

3.5.12 Method Performance

3.5.12.1 Method performance evaluation: The expected method performance parameters for precision, accuracy, and detection limits are provided in Table 3.5-3.

Addition of a Filter to the Formaldehyde Sampling Train

As a check on the survival of particulate material through the impinger system, a filter can be added to the impinger train either after the second impinger or after the third impinger. Since the impingers are in an ice bath, there is no reason to heat the filter at this point.

Any suitable medium (e.g., paper, organic membrane) may be used for the filter if the material conforms to the following specifications:

(1) the filter has at least 95% collection efficiency (<5% penetration) for 3 µm 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.

(2) the filter has a low aldehyde blank value (<0.015 mg formaldehyde/cm^2 of filter area). Before the test series, determine the average formaldehyde blank value of at least three filters (from the lot to be used for sampling) using the applicable analytical procedures.

Table 3.5-3.- Expected Method Performance for Formaldehyde

Parameter	Precision[1]	Accuracy[2]	Detection limits[3]
Matrix: Dual trains	± 15% RPD	± 20%	1.5 X 10^{-7} lb/ft^3 (1.8 ppbv).

[1]Relative percent difference limit for dual trains.
[2]Limit for field spike recoveries.
[3]The lower reporting limit having less than 1% probability of false positive detection.

Recover the exposed filter into a separate clean container and return the container over ice to the laboratory for analysis. If the filter is being analyzed for formaldehyde, the filter may be recovered into a container or DNPH reagent for shipment back to the laboratory. If the filter is being examined for the presence of particulate material, the filter may be recovered into a clean dry container and returned to the laboratory.

3.6 Analysis for Aldehydes and Ketones by High Performance Liquid Chromatography (HPLC) (Method 0011A)

3.6.1 Scope and Application

3.6.1.1 Method 0011A covers the determination of free formaldehyde in the aqueous samples and leachates and derived aldehydes/ketones collected by method 0011.

Compound name	CAS No.[1]

Formaldehyde	50-00-0
Acetaldehyde	75-07-0

[1]Chemical Abstract Services Registry Number

3.6.1.2 Method 0011A is a high performance liquid chromatographic (HPLC) method optimized for the determination of formaldehyde and acetaldehyde in aqueous environmental matrices and leachates of solid samples and stack samples collected by method 0011. When this method is used to analyze unfamiliar sample matrices, compound identification should be supported by at least one additional qualitative technique. A gas chromatograph/mass spectrometer (GC/MS) may be used for the qualitative confirmation of results from the target analytes, using the extract produced by this method.

3.6.1.3 The method detection limits (MDL) are listed in Tables 3.6-1 and 3.6-2. The MDL for a specific sample may differ from that listed, depending upon the nature of interferences in the sample matrix and the amount of sample used in the procedure.

3.6.1.4 The extraction procedure for solid samples is similar to that specified in method 1311 (1). Thus, a single sample may be extracted to measure the analytes included in the scope of other appropriate methods. The analyst is allowed the flexibility to select chromatographic conditions appropriate for the simultaneous measurement of contaminations of these analytes.

Table 3.6-1.-High Performance Liquid Chromatography Conditions and Method Detection Limits Using Solid Sorbent Extraction

Analyte	Retention time (minutes)	MDL (µg/L)[1]
Formaldehyde	7.1	7.2

HPLC conditions: Reverse phase C18 column, 4.6 X 250 mm; isocratic elution using methanol/water (75:25, v/v); flow rates 1.0 mL/min.; detector 360 nm.
[1]After correction for laboratory blank.

Table 3.6-2.-High Performance Liquid Chromatography Conditions and Method Detection Limits Using Methylene Chloride Extraction

Analyte	Retention time (minutes)	MDL (µg/L)[1]
Formaldehyde	7.1	7.2
Acetaldehyde	8.6	171[1]

HPLC conditions: Reverse phase C18 column, 4.6 X 250 mm; isocratic elution using methanol/water (75:25, v/v); flow rates 1.0 mL/min.; detector 360 nm.
[1]These values include reagent blank concentrations of approximately 13 µg/L formaldehyde and 130 µg/L acetaldehyde.

3.6.1.5 This method is restricted to use by, or under the supervision of analysts experienced in the use of chromatography and in the interpretation of chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

3.6.1.6 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 available. The laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available.

3.6.1.7 Formaldehyde has been tentatively classified as a known or suspected, human or mammalian carcinogen.

3.6.2 Summary of Method

3.6.2.1 Environmental Liquids and Solid Leachates.

3.6.2.1.1 For wastes comprised of solids or for aqueous wastes containing significant amounts of solid material, the aqueous phase, if any, is separated from the solid phase and stored for later analysis. If necessary, the particle size of the solids in the waste is reduced. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase of the waste. A special extractor vessel is used when testing for volatiles. Following extraction, the aqueous extract is separated from the solid phase by filtration employing 0.6 to 0.8 µm glass fiber filters.

3.6.2.1.2 If compatible (i.e., multiple phases will not form on combination), the initial aqueous phase of the waste is added to the aqueous extract, and these liquids are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume weighted average concentration.

3.6.2.1.3 A measured volume of aqueous sample or an appropriate amount of solids leachate is buffered to pH 5 and derivatized with 2,4-dinitrophenylhydrazine (DNPH), using either the solid sorbent or the methylene derivatization/extraction option. If the solid sorbent option is used, the derivative is extracted using solid sorbent cartridges, followed by elution with ethanol. If the methylene chloride option is used, the derivative is extracted with methylene chloride. The methylene chloride extracts are concentrated using the Kuderna-Danish (K-D) procedure and solvent exchanged into methanol prior to HPLC analysis. Liquid chromatographic conditions are described which permit the separation and measurement of formaldehyde in the extract by absorbance detection at 360 nm.

3.6.2.2 Stack Gas Samples Collected by Method 0011.

3.6.2.2.1 The entire sample returned to the laboratory is extracted with methylene chloride and the methylene chloride extract is brought up to a known volume. An aliquot of the methylene chloride extract is solvent exchanged and concentrated or diluted as necessary.

3.6.2.2.2 Liquid chromatographic conditions are described that permit the separation and measurement of formaldehyde in the extract by absorbance detection at 360 nm.

3.6.3 Interferences

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

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

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

3.6.3.2 Analysis for formaldehyde is especially complicated by its ubiquitous occurrence in the environment.

3.6.3.3 Matrix interferences may be caused by contaminants that are coextracted from the sample. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the matrix being sampled. No interferences have been observed in the matrices studied as a result of using solid sorbent extraction as opposed to liquid extraction. If interferences occur in subsequent samples, some additional cleanup may be necessary.

3.6.3.4 The extent of interferences that may be encountered using liquid chromatographic techniques has not been fully assessed. Although the HPLC conditions described allow for a resolution of the specific compounds covered by this method, other matrix components may interfere.

3.6.4 Apparatus and Materials

3.6.4.1 Reaction vessel-250 ml Florence flask.

3.6.4.2 Separatory funnel-205 ml, with Teflon stopcock.

3.6.4.3 Kuderna-Danish (K-D) apparatus.

3.6.4.3.1 Concentrator tube-10 ml graduated (Kontes K-570050-1025 or equivalent). A ground glass stopper is used to prevent evaporation of extracts.

3.6.4.3.2 Evaporation flask-500 ml (Kontes K-570001-500 or equivalent). Attach to concentrator tube with springs, clamps, or equivalent.

3.6.4.3.3 Snyder column-Three ball macro (Kontes K-503000-0121 or equivalent).

3.6.4.3.4 Snyder column-Two ball macro (Kontes K-569001-0219 or equivalent).

3.6.4.3.5 Springs- 1/2 inch (Kontes K-662750 or equivalent).

3.6.4.4 Vials-10, 25 ml, glass with Teflon lined screw caps or crimp tops.

3.6.4.5 Boiling chips-Solvent extracted with methylene chloride, approximately 10/40 mesh (silicon carbide or equivalent).

3.6.4.6 Balance-Analytical, capable of accurately weighing to the nearest 0.0001 g.

3.6.4.7 pH meter-Capable of measuring to the nearest 0.01 units.

3.6.4.8 High performance liquid chromatograph (modular).

3.6.4.8.1 Pumping system-Isocratic, with constant flow control capable of 1.00 ml/min.

3.6.4.8.2 High pressure injection valve with 20 µL loop.

3.6.4.8.3 Column-250 mm X 4.6 mm ID, 5 µm particle size, C18 (or equivalent).

3.6.4.8.4 Absorbance detector-360 nm.

3.6.4.8.5 Strip-chart recorder compatible with detector-Use of a data system for measuring peak areas and retention times is recommended.

3.6.4.9 Glass fiber filter paper.

3.6.4.10 Solid sorbent cartridges-Packed with 500 mg C18 (Baker or equivalent).

3.6.4.11 Vacuum manifold-Capable of simultaneous extraction of up to 12 samples (Supelco or equivalent).

3.6.4.12 Sample reservoirs-60 ml capacity (Supelco or equivalent).

3.6.4.13 Pipet-Capable of accurately delivering 0.10 ml solution (Pipetman or equivalent).

3.6.4.14 Water bath-Heated, with concentric ring cover, capable of temperature control ((±) 2 °C). The bath should be used under a hood.

3.6.4.15 Volumetric Flasks-250 or 500 ml.

3.6.5 Reagents

3.6.5.1 Reagent grade 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.

3.6.5.2 Organic-free water-All references to water in this method refer to organic-free reagent water, as defined in chapter I SW-846.

3.6.5.3 Methylene chloride, CH_2Cl_2-HPLC grade or equivalent.

3.6.5.4 Methanol, CH_3OH-HPLC grade or equivalent.

3.6.5.5 Ethanol (absolute), CH_3CH_2OH-HPLC grade or equivalent.

3.6.5.6 2,4-Dinitrophenylhydrazine (DNPH) (70% (W/W)), $[2,4\text{-}(O_2N)_2C_6H_3]NHNH_2$, in organic-free reagent water.

3.6.5.7 Formalin (37.6 percent (w/w)), formaldehyde in organic-free reagent water.

3.6.5.8 Acetic acid (glacial), CH_3CO_2H.

3.6.5.9 Sodium hydroxide solutions NaOH, 1.0 N and 5 N.

3.6.5.10 Sodium chloride, NaCl.

3.6.5.11 Sodium sulfite solution, Na_2SO_3, 0.1 M.

3.6.5.12 Hydrochloric Acid, HCl, 0.1 N.

3.6.5.13 Extraction fluid-Dilute 64.3 ml of 1.0 N NaOH and 5.7 ml glacial acetic acid to 900 ml with organic-free reagent water. Dilute to 1 liter with organic-free reagent water. The pH should be 4.93 ± 0.02.

3.6.5.14 Stock standard solutions.

3.6.5.14.1 Stock formaldehyde (approximately 1.00 mg/ml)-Prepare by diluting 265 µl formalin to 100 ml with organic-free reagent water.

3.6.5.14.1.1 Standardization of formaldehyde stock solution-Transfer a 25 ml aliquot of a 0.1 M Na_2SO_3 solution to a beaker and record the pH. Add a 25.0 ml aliquot of the formaldehyde stock solution (section 3.6.5.14.1) and record the pH. Titrate this mixture back to the original pH using 0.1 N HCl. The formaldehyde concentration is calculated using the following equation:

Concentration (mg/ml) = 30.03 X (N HCl) X (ml HCl) 25.0

where:

N HCl = Normality of HCl solution used.
ml HCl = ml of standardized HCl solution used.
30.03 = MW of formaldehyde.

3.6.5.14.2 Stock formaldehyde and acetaldehyde-Prepare by adding 265 µL formalin and 0.1 g acetaldehyde to 90 ml of water and dilute to 100 ml. The concentration of acetaldehyde in this solution is 1.00 mg/ml. Calculate the concentration of formaldehyde in this solution using the results of the assay performed in section 3.6.5.14.1.1.

3.6.5.14.3 Stock standard solutions must be replaced after six months, or sooner, if comparison with check standards indicates a problem.

3.6.5.15 Reaction Solutions.

3.6.5.15.1 DNPH (1.00 µg/L)-Dissolve 142.9 mg of 70% (w/w) reagent in 100 ml absolute ethanol. Slight heating or sonication may be necessary to effect dissolution.

3.6.5.15.2 Acetate buffer (5 N) Prepare by neutralizing glacial acetic acid to pH 5 with 5 N NaOH solution. Dilute to standard volume with water.

3.6.5.15.3 Sodium chloride solution (saturated) Prepare by mixing of the reagent grade solid with water.

3.6.6 Sample Collection, Preservation, and Handling

3.6.6.1 See the introductory material to this Chapter, Organic Analytes, section 4.1 of SW-846.

3.6.6.2 Environmental liquid and leachate samples must be refrigerated at 4 °C, and must be derivatized within 5 days of sample collection and analyzed within 3 days of derivatization.

3.6.6.3 Stack gas samples collected by Method 0011 must be refrigerated at 4 °C. It is recommended that samples be extracted within 30 days of collection and that extracts be analyzed within 30 days of extraction.

3.6.7 Procedure

3.6.7.1 Extraction of Solid Samples.

3.6.7.1.1 All solid samples should be homogeneous. When the sample is not dry, determine the dry weight of the sample, using a representative aliquot.

3.6.7.1.1.1 Determination of dry weight-In certain cases, sample results are desired based on a dry weight basis. When such data is desired, or required, a portion of sample for dry weight determination should be weighed out at the same time as the portion used for analytical determination.

Warning: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from drying a heavily contaminated hazardous waste sample.

3.6.7.1.1.2 Immediately after weighing the sample for extraction, weigh 5-10 g of the sample into a tared crucible. Determine the % dry weight of the sample by drying overnight at 105 °C. Allow to cool in a desiccator before weighing:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

3.6.7.1.2 Measure 25 g of solid into a 500 ml bottle with a Teflon lined screw cap or crimp top, and add 500 ml of extraction fluid (section 3.6.5.13). Extract the solid by rotating the bottle at approximately 30 rpm for 18 hours. Filter the extract through glass fiber paper and store in sealed bottles at 4 °C. Each ml of extract represents 0.050 g solid.

3.6.7.2 Cleanup and Separation.

3.6.7.2.1 Cleanup procedures may not be necessary for a relatively clean sample matrix. The cleanup procedures recommended in this method have been used for the analysis of various sample types. If particular circumstances demand the use of an alternative cleanup procedure, the analyst must determine the elution profile and demonstrate that the recovery of formaldehyde is no less then 85% of recoveries specified in Table 3.6-3. Recovery may be lower for samples which form emulsions.

3.6.7.2.2 If the sample is not clean, or the complexity is unknown, the entire sample should be centrifuged at 2500 rpm for 10 minutes. Decant the supernatant liquid from the centrifuge bottle, and filter through glass fiber filter paper into a container which can be tightly sealed.

3.6.7.3 Derivatization.

3.6.7.3.1 For aqueous samples, measure a 50 to 100 ml aliquot of the sample. Quantitatively transfer the sample aliquot to the reaction vessel (section 3.6.4.1).

3.6.7.3.2 For solid samples, 1 to 10 ml of leachate (section 3.6.7.1) will usually be required. The amount used for a particular sample must be determined through preliminary experiments.

Table 3.6-3.-Single Operator Accuracy and Precision Using Solid Sorbent Extraction

Analyte	Matrix type	Average percent recovery	Standard deviation percent	Spike range (µg/L)	No. of analyses
Formaldehyde	Reagent water	86	9.4	15-1430	39
	Final effluent	90	11.0	46.8-1430	16
	Phenol formaldehyde sludge	93	12.0	457-1430	15

Note: For all reactions, the total volume of the aqueous layer should be adjusted to 100 ml with water.

3.6.7.3.3 Derivatization and extraction of the derivative can be accomplished using the solid sorbent (section 3.6.7.3.4) or methylene chloride option (section 3.6.7.3.5).

3.6.7.3.4 Solid Sorbent Option.

3.6.7.3.4.1 Add 4 ml of acetate buffer and adjust the pH to 5.0 ± 0.1 with glacial acetic acid or 5 N NaOH. Add 6 ml of DNPH reagent, seal the container, and place on a wrist-action shaker for 30 minutes.

3.6.7.3.4.2 Assemble the vacuum manifold and connect to a water aspirator or vacuum pump. Assemble solid sorbent cartridges containing a minimum of 1.5 g of C18 sorbent, using connectors supplied by the manufacturer, and attach the sorbent train to the vacuum manifold. Condition each cartridge by passing 10 ml dilute acetate buffer (10 ml 5 N acetate buffer dissolved in 250 ml water) through the sorbent cartridge train.

3.6.7.3.4.3 Remove the reaction vessel from the shaker and add 10 ml saturated NaCl solution to the vessel.

3.6.7.3.4.4 Add the reaction solution to the sorbent train and apply a vacuum so that the solution is drawn through the cartridges at a rate of 3 to 5 ml/min. Release the vacuum after the solution has passed through the sorbent.

3.6.7.3.4.5 Elute each cartridge train with approximately 9 ml of absolute ethanol, directly into a 10 ml volumetric flask. Dilute the solution to volume with absolute ethanol, mixed thoroughly, and place in a tightly sealed vial until analyzed.

3.6.7.3.5 Methylene Chloride Option.

3.6.7.3.5.1 Add 5 m of acetate buffer and adjust the pH to 5.0 ± 0.5 with glacial acetic acid or 5 N NaOH. Add 10 ml of DNPH reagent, seal the container, and place on a wrist-action shaker for 1 hour.

3.6.7.3.5.2 Extract the solution with three 20 ml portions of methylene chloride, using a 250 ml separatory funnel, and combine the methylene chloride layers. If an emulsion forms upon extraction, remove the entire emulsion and centrifuge at 2000 rpm for 10 minutes. Separate the layers and proceed with the next extraction.

3.6.7.3.5.3 Assemble a Kuderna-Danish (K-D) concentrator by attaching a 10 ml concentrator tube to a 500 ml evaporator flask. Wash the K-D apparatus with 25 ml of extraction solvent to complete the quantitative transfer.

3.6.7.3.5.4 Add one to two clean boiling chips to the evaporative flask and attach a three ball Snyder column. Preset the Snyder column by adding about 1 ml methylene chloride to the top. Place the K-D apparatus on a hot water bath (80-90 °C) so that the concentrator tube is partially immersed in the hot water and the entire lower rounded surface of the flask is bathed with hot vapor. Adjust the vertical position of the apparatus and the water temperature, as required, to complete the concentration in 10-15 min. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood with condensed solvent. When the apparent volume of liquid reaches 10 ml, remove the K-D apparatus and allow it to drain and cool for a least 10 min.

3.6.7.3.5.5 Prior to liquid chromatographic analysis, the solvent must be exchanged to methanol. The analyst must ensure quantitative transfer of the extract concentrate. The exchange is performed as follows:

3.6.7.3.5.5.1 Following K-D concentration of the methylene chloride extract to <10 ml using the macro Snyder column, allow the apparatus to cool and drain for at least 10 minutes.

3.6.7.3.5.5.2 Momentarily remove the Snyder column, add 5 ml of the methanol, a new glass bed, or boiling chip, and attach the micro Snyder column. Concentrate the extract using 1 ml of methanol to prewet the Snyder column. Place the K-D apparatus on the water bath so that the concentrator tube is partially immersed in the hot water. Adjust the vertical position of the apparatus and the water temperature, as required, to complete concentration. At the proper rate of distillation the balls of the column will actively chatter, but the chambers will not flood. When the apparent volume of liquid reaches <5 ml, remove the K-D apparatus and allow it to drain and cool for at least 10 minutes.

3.6.7.3.5.5.3 Remove the Snyder column and rinse the flask and its lower joint with 1-2 ml of methanol and add to concentrator tube. A 5-ml syringe is recommended for this operation. Adjust the extract volume to 10 ml. Stopper the concentrator tube and store refrigerated at 4 °C if further processing will not be performed immediately. If the extract will be stored longer than two days, it should be transferred to a vial with a Teflon-lined screw cap or crimp top. Proceed with liquid chromatographic analysis if further cleanup is not required.

3.6.7.4 Extraction of Stack Gas Samples Collected by Method 0011.

3.6.7.4.1 Measure the aqueous volume of the sample prior to extraction (for moisture determination in case the volume was not measured in the field). Pour the sample into a separatory funnel and drain the methylene chloride into a volumetric flask.

3.6.7.4.2 Extract the aqueous solution with two or three aliquots of methylene chloride. Add the methylene chloride sxtracts to the volumetric flask.

3.6.7.4.3 Fill the volumetric flask to the line with methylene chloride. Mix well and remove an aliquot.

3.6.7.4.4 If high levels of formaldehyde are present, the extract can be diluted with mobile phase, otherwise the extract must be solvent exchanged as described in section 3.6.7.5.3.3. If low levels of formaldehyde are present, the sample should be concentrated during the solvent exchange procedure.

3.6.7.5 Chromatographic Conditions.

Column	C18, 250 mm X 4.6 mm ID, 5 µm particle size
Mobile Phase	methanol/water, 75:25 (v/v), isocratic
Flow Rate	1.0 ml/min
UV Detector	360 nm
Injection Volume	20 µ1

3.6.7.6 Calibration.

3.6.7.6.1 Establish liquid chromatographic operating parameters to produce a retention time equivalent to that indicated in Table 3.6-1 for the solid sorbent options, or in Table 3.6-2 for methylene chloride option. Suggested chromatographic conditions are provided in section 3.6.7.5. Prepare derivatized calibration standards according to the procedure in section 3.6.7.6.1.1. Calibrate the chromatographic system using the external standard technique (section 3.6.7.6.1.2).

3.6.7.6.1.1 Preparation of calibration standards.

3.6.7.6.1.1.1 Prepare calibration standard solutions of formaldehyde and acetaldehyde in water from the stock standard (section 3.6.5.14.2). Prepare these solutions at the following concentrations (in µg/ml) by serial dilution of the stock standard solution: 50, 20, 10. Prepare additional calibration standard solutions at the following concentrations, by dilution of the appropriate 50, 20, or 10 µg/ml standard: 5, 0.5, 2, 0.2, 1, 0.1.

3.6.7.6.1.1.2 Process each calibration standard solution through the derivatization option used for sample processing (section 3.6.7.3.4 or 3.6.7.3.5).

3.6.7.6.1.2 External standard calibration procedure.

3.6.7.6.1.2.1 Analyze each derivatized calibration standard using the chromatographic conditions listed in Tables 3.6-1 and 3.6-2, and tabulate peak area against concentration injected. The results may be used to prepare calibration curves for formaldehyde and acetaldehyde.

3.6.7.6.1.2.2 The working calibration curve must be verified on each working day by the measurement of one or more calibration standards. If the response for any analyte varies from the previously established responses by more the 10%, the test must be repeated using a fresh calibration standard

after it is verified that the analytical system is in control. Alternatively, a new calibration curve may be prepared for that compound. If an autosampler is available, it is convenient to prepare a calibration curve daily by analyzing standards along with test samples.

3.6.7.7 Analysis.

3.6.7.7.1 Analyze samples by HPLC, using conditions established in section 3.6.7.6.1. Tables 3.6-1 and 3.6-2 list the retention times and MDLs that were obtained under these conditions. Other HPLC columns, chromatographic conditions, or detectors may be used if the requirements for section 3.6.8.1 are met, or if the data are within the limits described in Tables 3.6-1 and 3.6-2.

3.6.7.7.2 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time for a compound can be used to calculate a suggested window size; however, the experience of the analyst should weigh heavily in the interpretation of the chromatograms.

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

3.6.7.7.4 If the peak area measurement is prevented by the presence of observed interferences, further cleanup is required. However, none of the 3600 method series have been evaluated for this procedure.

3.6.7.8 Calculations.

3.6.7.8.1 Calculate each response factor as follows (mean value based on 5 points):

$$RF = \frac{\text{concentration of standard}}{\text{area of the signal}}$$

>>>> See the accompanying hardcopy volume for non-machine-readable data that appears at this point. <<<<

3.6.7.8.2 Calculate the concentration of formaldehyde and acetaldehyde as follows:

µg/ml = (RF) (area of signal) (concentration factor)

where:

$$\text{concentration factor} = \frac{\text{Final volume of Extract}}{\text{Initial Extract volume}}$$

Note: For solid samples, a dilution factor must be included in the equation to account for the weight of the sample used.

3.6.7.8.3 Calculate the total weight of formaldehyde in the stack gas sample as follows:

total µg/ml = (RF) (area of signal) (concentration factor)

where:

$$\text{concentration factor} = \frac{\text{Final Volume of Extract}}{\text{Initial Extract Volume}}$$

3.6.8 Quality Control

3.6.8.1 Refer to Chapter One of SW-846 for guidance on quality control procedures.

3.6.9 Method Performance

3.6.9.1 The MDL concentrations listed in Table 3.6-1 were obtained using organic-free water and solid sorbent extraction. Similar results were achieved using a final effluent and sludge leachate. The MDL concentrations listed in Table 3.6-2 were obtained using organic-free water and methylene chloride extraction. Similar results were achieved using representative matrices.

3.6.9.2 This method has been tested for linearity of recovery from spiked organic-free water and has been demonstrated to be applicable over the range from 2 X MDL to 200 X MDL.

3.6.9.3 In a single laboratory evaluation using several spiked matrices, the average recoveries presented in Tables 3.6-3 and 3.6-4 were obtained using solid sorbent and methylene chloride extraction, respectively. The standard deviations of the percent recovery are also included in Tables 3.6-3 and 3.6-4.

3.6.9.4 A representative chromatogram is presented in Figure 3.6-1.

3.6.10 References

1. Federal Register, 1986, 51, 40643-40652; November 7.

2. EPA Methods 6010, 7000, 7041, 7060, 7131, 7421, 7470, 7740, and 7841, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846, Third Edition. September 1988. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, DC 20460.

Table 3.6-4.- Single Operator Accuracy and Precision Using Methylene Chloride Extraction

Analyte	Matrix type	Average percent recovery (x)	Standard deviation percent (p)	Spike range (µg/L)	No. of analyses
Formaldehyde	Reagent Water	91	2.5	50-1000	9
	Groundwater	92.5	8.2	50	6
	Liquids	69.6	16.3	250	12
Acetaldehyde	Reagent Water	60.3	3.2	50-1000	9
	Groundwater	63.6	10.9	50	12
	Liquids (2 types)	44.0	20.2	250	12
	Solids	58.4	2.7	0.10-1.0[a]	12

[a]Spike range in units of mg/g.
x = Average recovery expected for this method.
p = Average standard deviation expected for this method.

>>>> See the accompanying hardcopy volume for non-machine-readable data that appears at this point. <<<<

>>>> End of File FR94B. This article is continued in File FR94C. <<<<