APPENDIX P

COOLING TOWER MONITORING

General

Cooling tower monitoring describes the characterization of volatile organic air pollutants that are capable of being air-stripped from a water matrix. While generic or indicator monitoring may be required to identify the existence of volatile organic compound (VOC) emissions, speciated compound characterizations may also be required in some instances to characterize the specific compounds present.

Historically, a method for cooling tower water characterization was developed for use by El Paso Products Company in the early 70's. This method utilized a dynamic or flow-through system for air stripping a sample of the water and analyzing the resultant off-gases for VOCs using a common flame ionization detector (FID) analyzer, and has been the popular choice in Texas for many years. The El Paso Products method, however, has been overshadowed nationally by the use of purge and trap analysis of water samples utilizing gas chromatography and/or mass spectrometry techniques. While direct water analysis has been shown to be effective for cooling tower measurements of heavier molecular weight organic compounds with relatively high boiling points, Texas Commission on Environmental Quality (TCEQ) has determined that this approach may be ineffective for capture and measurement of volatile organic compounds with lower boiling points, such as ethylene, propylene, 1,3-butadiene, and butenes. VOCs with a low molecular weight and boiling point are generally lost in the sample collection step of purge/trap type analyses. Consequently, TCEQ requires that the air stripping method presented in this manual be used for cooling tower and other applicable water matrix emission measurements of VOCs with boiling points below 140 ^{o}F. Specific procedures for cooling tower sampling and analysis for VOCs with boiling points of 140 ^{o}F and greater must be submitted to TCEQ for approval on a case-by-case basis.

Air Stripping Method (Modified El Paso Method) for Determination of Volatile Organic Compound Emissions from Water Sources

1.0 Principle and Applicability

1.1 Principle. A continuous stream of cooling water, process water, or wastewater is supplied via a hard pipe or direct interface to an air stripping column apparatus for analysis. Air flowing countercurrent to the water strips volatile organic compounds from the water for analysis. Some gases may flash from the water immediately upon entering the apparatus and these gases are trapped and mixed with the air stripped compounds. The concentration of the air stripped compounds combined with the flashed gases is determined at the apparatus air outlet by a suitable detector and/or by sampling. Concentrations of air stripped compounds in the air exhaust, along with the air and water flow rates, are used to determine concentrations of strippable volatile compounds in the water. A FID analyzer is used to determine a value of "combined" or "total" strippable volatile organic compounds. Samples may also be collected in sample canisters for shipment to analytical laboratories for speciation of air contaminants. A gas chromatograph (GC) with an appropriate detector may be used to determine specific stripped species.

1.2 Applicability. This method is applicable to cooling tower water systems and may be applicable to qualitative and/or quantitative measurements on other sources such as API separators and wastewater systems.

2.0 Sensitivity

2.1 The sensitivity of this method for the onsite analysis by FID analyzer is typically 0.1 to 0.5 part-per-million, by volume (ppmv) methane in the stripped air, depending on the specific analyzer. The sensitivity of the GC speciation analysis will vary depending on the detector used. Detection limits as low as 2 - 50 part-per-billion, by volume (ppbv) in the stripped air may be possible with the use of a gas chromatograph equipped with a mass spectrometer (GC/MS).

2.2 FID Response. Response factors are not used to correct the total VOC measurement by FID analyzer. Speciation analysis of the VOCs present in the stripped gas would be required to correctly apply any proportioned response factor to the total VOC measurement, in which case, the results should be calculated from the speciated analysis rather than the total VOC results. Some chemicals, such as formaldehyde, will not respond well on a FID, having particularly high response factors and, therefore, high detection limits. The total VOC

procedure by FID should not be used on sources for which any potential targeted VOC has a response factor multiplier greater than 2 relative to methane. Such sources must either be sampled following the speciation procedure in Section 6.2, or an alternative detector, approved by the TCEQ, must be used in the total VOC procedure in Section 6.1. Alternative sampling and analysis procedures such as sorbent tube sample collection and analysis by high performance liquid chromatography (HPLC) are subject to TCEQ approval.

3.0 Equipment and Materials

3.1 Air stripping apparatus. An air stripping apparatus as presented in Figure 1 and meeting the following requirements:

3.1.1 The stripping chamber shall be a cylinder 36 inches in length with an internal diameter of 3 inches, and constructed of clear, heavy-walled glass.

3.1.2 The stripping chamber packing material shall be beryl saddles between 6 to 8 millimeter size. The depth of the packing material will be 26 inches.

3.1.3 The end caps of the stripping chamber must meet the dimensions specified in Figure 2. Neoprene stoppers are recommended; however, securing clamps will be required to prevent leakage. Black rubber stoppers are not allowed due to the potential absorption and release of organic compounds. Alternative designs for the end caps, such as customized threaded plastic caps with Neoprene gaskets, are acceptable provided the materials used are non-reactive with the sample matrix or target compounds, and the end caps meet the specifications in Figure 2. The tip of the water sample inlet line is intentionally left 5 to 6 inches above the water level in the stripping chamber to help accelerate the response of the system as some VOCs will be released immediately as the water falls into the chamber.

3.1.4 Tubing used in the air stripping apparatus for transporting gas and water shall be 1/4 inch stainless steel or Teflon material. Stainless steel or Teflon 1/4 inch tubing of minimal length shall be used to route water sample from the sample tap to the air stripping apparatus. The water sample tubing from the sample tap shall not be more than 50 feet in length.

3.1.5 Drying agents, such as Drierite™, for removing moisture from the stripped air stream before analysis by FID or collection in sample canisters are strictly prohibited to prevent loss of VOCs to the drying agents. An empty, clear-glass flask is used as a knock-out to remove some of the moisture in the stripped air stream, but gas exiting the stripping chamber will essentially be at saturated moisture for the ambient conditions. Different styles of knockout flasks are acceptable; however, the flask must be clear-glass and 500 ml or less in size. Some FID analyzers may not be able to monitor for prolonged periods under such conditions and intermittent monitoring may be required.

3.1.6 A T-union with one leg leading to a bubbler must be included as shown in Figure 1. Excess air not drawn into the analyzer probe or sample canister is vented

through the bubbler and serves to indicate that sufficient flow has been established. This is to assure that the sample is only from the stripped air and is not drawing in any external air. With the bubbler in place, care must be taken not to pull water into the FID analyzer or sample canister.

3.1.7 Gas bubble formation in the water rotameter can sometimes result from the pressure drop across the water rotameter control valve. Significant gas bubbles can interfere with accurate measurement of the sample water flow to the stripping chamber. A suggested possible solution to this problem is to place a control valve downstream of the water rotameter. By opening the rotameter to the fully open position or using a non-metering rotameter, and controlling the flow with the valve after the rotameter, the pressure drop occurs after the rotameter and bubble formation may be minimized. This approach may require a fine-adjusting control valve to achieve the flow rate control desired, and the tester must be certain that the water rotameter can withstand the pressure in the water source being sampled.

Note: The TCEQ air stripping apparatus design is based on the apparatus designed by El Paso Products Company of Odessa, Texas (see Reference 9.1)

3.2 Flame Ionization Detector (FID) Analyzer. Analyzers with analog type readouts and those normally used for leak detection are generally not appropriate for this method because such instruments are designed for much higher concentration measurement than would be expected in the air stripping apparatus effluent. FID analyzers used in conjunction with the method must:

3.2.1 be a digital readout type, readable to 0.1 ppmv.

3.2.2 be able to meet the calibration requirements specified in Section 4.1.

3.2.3 have a sampling rate less than 2000 ml/min since the stripping air flow rate is 2500 ml/min and an excess air flow is required.

3.3 Gases for Air Stripping Apparatus Operation and FID Analyzer Calibration.

3.3.1 Zero Calibration Gas and Stripping Air. Air, certified to contain less than or equal to 0.1 ppmv of total hydrocarbon (THC).

3.3.2 High-Level Calibration Gas. Cylinder gas standard of methane in air, certified by the manufacturer to be within ±2% of the specified concentration. If the sample concentration of VOCs in the stripped gas is less than 10 ppmv as methane, the span gas calibration standard shall be 10 ppmv methane. Higher concentration span calibration standards may be necessary for some sources. If a higher calibration standard is required, select a high-level concentration such that the measured sample concentrations are between 10% and 100% of the high-level calibration gas concentration.

3.3.3 Mid-Level Calibration Gas. Cylinder gas standard of methane in air, certified by the manufacturer to be within ±2% of the specified concentration. The mid-level calibration gas concentration shall be between 20% and 50% of the high-level

calibration gas concentration. (See note under 4.1.2.4.)

3.3.4 Certified gases must be used within the manufacturer's specified shelf life, or recertified upon expiration.

3.3.5 Subject to TCEQ approval, calibration gas standards other than methane may be used for sources that have only one or a predominate potential VOC present in the water matrix.

3.4 A gas chromatograph equipped with appropriate detector(s) for laboratory or field speciation of the specific organic components.

3.5 Sample canisters. Internally passivated stainless steel canisters for collection of air stripped samples for speciation analysis by GC. Sample canisters shall meet all requirements of Compendium Method TO-14A (US EPA Compendium for Determination of Toxic Organic Compounds in Ambient Air, EPA Document Number 625/R96/010B). Each sample canister shall be equipped with a) a vacuum gauge and b) either a needle valve for manually regulating flow rate or an automated flow regulator (i.e., a critical orifice or mass flow controller).

3.5.1 Tedlar™ bags may be used in place of stainless steel sample canisters, if the following provisions are met:

3.5.1.1 Bag samples must be analyzed according to Title 40 Code of Federal Regulations, Part 60, Appendix A, Method 18.

3.5.1.2 The recovery study for bag sampling in Section 8.4.2 of Method 18 must be performed for all the target compounds. The recovery study is performed by metering a known volume of zero air through a water blank stripping apparatus into the Tedlar™ bag and then spiking the bag with the target compounds. This step checks not only the potential loss of compounds due to the permeability of the Tedlar™, but also loss due to condensed moisture in the bag. Percent recovery for <u>each</u> target compound must be between 70 - 130%, or Tedlar™ bags are not acceptable for sample collection. When Tedlar™ bags are acceptable, as specified in Method 18, analysis results for target compounds must be corrected for the percent recoveries.

3.5.1.3 Tedlar™ bags must be new and unused.

3.5.1.4 Tedlar™ bags shall be checked for leaks and contamination as described in Method 18, Section 16.1.3.2.

3.5.1.5 Samples in Tedlar™ bags must be analyzed within 72 hours of collection. Recovery study bags must be stored for the same period of time as the sample bags.

4.0 Calibration.

4.1 FID Analyzer Calibration.

4.1.1 Initial/Periodic Instrument Performance Evaluation. Perform the calibration precision and response time tests as described in Sections 8.1.2 and 8.1.3 of Method 21 in 40 CFR 60, Appendix A.

4.1.2 Calibration Procedure.

4.1.2.1 Warmup period. Follow manufacturer's recommendations.

4.1.2.2 Zero calibration. Introduce the zero gas (or stripping air) to the FID analyzer. Calibrate the analyzer to read 0.0 ± 0.2 ppmv.

4.1.2.3 High-level calibration. Introduce the high-level calibration gas (10 ppmv methane) to the FID analyzer. Calibrate the analyzer to read within ± 5.0% of the calibration gas certified value.

4.1.2.4 Mid-level calibration check. Introduce the mid-level calibration to the FID analyzer. The FID analyzer response on the mid-level calibration gas must agree within ± 5.0% of the calibration gas certified value. Note: The mid-level calibration step is optional if the VOC emissions determination is based solely on the results of the GC speciation analysis of the sample canister or Tedlar™ bag samples.

4.2 GC Calibration.

4.2.1 GC analysis by Method 18.

4.2.1.1 Follow the calibrations procedures described in Sections 8.2.1.5.2.1 and 10.0 in Method 18.

4.2.1.2 Alternative procedure. If a facility or laboratory is performing the same analysis on samples collected by this method on a daily basis, then the calibration and standardization procedures in Section 10.0 of 40 CFR 60, Appendix B, Performance Specification (PS) 9, may be used. The initial and periodic calibrations must satisfy all the requirements of Method 18 Sections 8.2.1.5.2.1 and 10.0, as well as those in Section 10.0 of PS9.

4.2.2 GC analysis by Compendium Method TO-14A (US EPA Compendium for Determination of Toxic Organic Compounds in Ambient Air, EPA Document Number 625/R96/010B)

4.2.2.1 Follow the appropriate calibration procedures described in Section 10 of TO-14A for the selected detector(s) in the GC system.

4.3 Air rotameter calibration.

4.3.1 Calibrate the air supply rotameter system with a dry gas meter, soap film flowmeter, or similar direct volume measuring device with an accuracy of ± 2 percent.

4.3.2 Operate the rotameter at 2500 cc/min for at least three calibration runs for 10 minutes each. When three consecutive calibration flow rates agree within ± 5 percent, average the three flow rates.

4.3.3 If the average measured calibration flow rate agrees within ± 5% of the rotameter reading, the rotameter is acceptable. If the difference between the

rotameter reading and the measured calibration flow rate exceeds ± 5%, then remark the rotameter to the calibrated flow rate.

4.3.4 Perform the rotameter calibration before the first field test and semiannually, thereafter.

4.4 Water rotameter calibration.

4.4.1 Calibrate the water rotameter with a Class A volumetric flask, graduated cylinder, or similar container with a volume known to ± 2% accuracy and capable of holding a volume at least 4 times the calibration flow rate (i.e., a 500 ml volumetric flask to calibrate the rotameter at 125 ml/min.)

4.4.2 Operate the water rotameter at 125 ml/min while filling the container. Record the time required to fill the container and calculate the actual flow rate based on the container volume and time required to fill the container. Repeat until three consecutive flow rates agree within ± 5% of the mean.

4.4.3 If the average measured calibration flow rate agrees within ± 5% of the rotameter reading, the rotameter is acceptable. If the difference between the rotameter reading and the calibration flow rate exceeds ± 5%, then remark the rotameter to the calibrated flow rate.

4.4.4 Perform the rotameter calibration before the first field test and semiannually, thereafter.

4.4.5 Alternatively, a Class A volumetric flask or graduated cylinder may be used in the field test to collect water at the stripping chamber water exit and recording the time required to fill the container. If this approach is used, the water rotameter need not be calibrated.

4.5 Temperature probe calibration.

4.5.1 Calibrate the stripping chamber temperature probe against an ASTM mercury thermometer or equivalent. The calibration shall be performed at or near 0 °C, 20 °C, and 40 °C.

4.5.2 If the absolute temperature (in degrees Kelvin) measured by the temperature probe agree within ± 1.5% at each reference point, the temperature probe is acceptable.

4.5.3 Perform the temperature probe calibration before the first field test and semiannually, thereafter.

5.0 Pretest Preparations

5.1 Selection of the sampling site.

5.1.1 Sample sites for cooling towers must meet the following criteria:

5.1.1.1 The sample port in the cooling tower return line header must be in a location where the feed rates to the cooling tower water are still under

pressure and prior to the release of the pressure to atmospheric or any vents in the return line header. For example, if the cooling tower has an open trough along the top of the tower which distributes water to each of the cells, the water supply for the test should be taken prior to the cooling water entering the distributing trough.

5.1.1.2 The sample port/probe should not extend beyond the plane of the pipe wall into water matrix.

5.1.1.3 Samples should be drawn from either the vertical section near the base of the riser pipe (from the inside of the elbow to the riser) or the top of a horizontal section prior to the riser pipe at a location where the pipe will be completely full.

5.1.1.4 For cooling towers with multiple risers, samples must be drawn from a location prior to the risers unless sample ports are installed on each riser and the distribution of water flow to each riser can be determined.

5.1.2 Sample sites for sources other than cooling towers were not considered during the development of this method and selection criteria for such sources may be subject to TCEQ approval.

5.2 Sample canister preparation. These procedures are typically performed by the laboratory conducting the speciation analysis.

5.2.1 Before each use, sample canisters shall be cleaned, certified, and prepared according the procedures described in Section 11.1 of TO-14A.

5.2.2 Evacuate canisters to less than 0.05 mm Hg pressure at least 24 hours prior to sample collection. Record the canister ID, vacuum, date, and time on a label attached to the sample canister.

5.3 Setup of Apparatus.

5.3.1 Assure the unit is vertically level using a bubble indicator or some other level indicator. If the stripping chamber is not level, channeling of the water or air flow may occur in the chamber and result in inefficient stripping.

5.3.2 Connect the zero air supply to the air inlet of the air stripping apparatus.

5.4 Perform the calibration procedures for the FID analyzer as described in Section 4.1.

5.4.1 If VOC emissions are to be determined only by sampling with sample canisters and GC speciation, the mid-level calibration is optional since the FID analyzer is only used for monitoring for system stabilization.

5.4.2 Record calibration results on a data sheet similar to that in Figure 3.

5.4.3 Some analyzers draw fuel air for the FID separately from the sample stream. If the fuel air is drawn from ambient air without purification, variations in the ambient level of THC may cause the instrument to drift. This can be especially problematic if the analyzer is calibrated indoors and then taken out to process areas for the test. Dramatic changes in ambient temperature may also cause instrument

drift. Every effort should be made to calibrate the instrument under the same conditions it is to be used. When moving from source to source, a calibration check shall be performed on the analyzer to determine if changes in the ambient conditions (i.e., temperature or ambient THC) have caused instrument drift. Calibration drift checks shall be documented on the field data sheets. If the analyzer is not within the calibration specifications given in 4.1.2, the FID analyzer must be recalibrated.

5.5 Blank/Background Determination: The blank checks are especially important for stripping systems that are used on multiple sources and the possibility of cross contamination exists.

5.5.1 Zero Air Check

5.5.1.1 A zero air check is mandatory before each test, regardless if the system was previously used on a different source or not.

5.5.1.2 Open the zero air supply to the apparatus and adjust rotameter to read 2500 ml/min.

5.5.1.3 Monitor the air effluent from the apparatus with the FID analyzer to determine the baseline reading of the empty stripping chamber and apparatus. Record the analyzer reading on the data sheet.

5.5.1.4 If the zero air check indicates a background $ 1.0 ppmv as methane in the stripped gas, then the apparatus should be purged thoroughly to remove the contamination until an acceptable background is measured (< 1.0 ppmv as methane).

5.5.2 Water Blank Check.

5.5.2.1 Water blank checks shall be performed by the following schedule:

5.5.2.1.1 A water blank check shall be performed on all stripping apparatus systems, mobile and dedicated systems, before initial use in the field and at least once per month thereafter.

5.5.2.1.2 For mobile systems used on multiple sources, a water blank check between sources is optional (except as noted in 5.5.2.1.3), but is strongly recommended.

5.5.2.1.3 A water blank check is mandatory before beginning a test if the previous test or source for which the stripping apparatus was used indicated a total VOC reading (ppmv as methane in the stripped air) 10 times greater than the applicable allowable emission rate or action level on the current source. See Equation 7-3 in Section 7.4.

5.5.2.2 In order to ensure the entire sampling system is free of contamination, the water blank check is performed through the sampling line and water rotameter. Using either a pump or gravity, fill the stripping chamber with clean distilled water through the sample line and water rotameter until the packing is just submerged. Adjust the water flow rate to 125 ml/min.

5.5.2.3 Restart the air supply and adjust to 2500 ml/min. Monitor the air effluent from the apparatus with the FID analyzer to determine the baseline

reading of the apparatus while the system is flowing with clean water. Record the analyzer reading on the data sheet.

5.5.2.4 If the water blank check indicates a background $ 1.0 ppmv as methane in the stripped gas, then the apparatus should be cleaned and purged thoroughly to remove the contamination until an acceptable background is measured (< 1.0 ppmv as methane).

5.5.2.5 Drain the blank water from the stripping chamber before sampling.

5.5.3 Recommended cleaning procedure. If air and water blanks are not sufficient to remove contamination from the system, the system should be disassembled and the components cleaned thoroughly.

5.5.3.1 The stripping chamber should be cleaned with hot soapy water, followed by 5 rinses of tap water and 5 rinses of distilled water. The chamber may be baked off at 150 ºC for at least 1 hour, if an oven is available large enough to hold the chamber. Otherwise, the chamber will have to be air dried.

5.5.3.2 The beryl saddles, moisture knock-out flask, and Neoprene stoppers should be cleaned with hot soapy water, followed by 5 rinses of tap water, 5 rinses of distilled water, then baked off in an oven at 150 ºC for at least 1 hour.

5.5.3.3 Teflon™ and stainless steel tubing, unions, and valves that contact water or stripped air sample should be cleaned with hot soapy water, rinsed by flushing with 5 volumes of tap water and 5 volumes of distilled water, then purged with zero air or nitrogen while baked at 150 ºC in an oven for at least 1 hour. Stainless tubing too long to fit inside an available oven without bending should just be purged with zero air or nitrogen after cleaning.

5.5.3.4 The water rotameter should be cleaned according to the manufacturer's recommendations, followed by flushing with distilled water and purging with zero air or nitrogen.

5.5.3.5 Some components, such as plastic caps for the knock-out flasks and some valves, may be heat sensitive and may be damaged if baked at 150ºC. Such components should be baked at a lower temperature for longer periods, purged with zero air or nitrogen without heating, or simply air dried, as appropriate.

6.0 Sampling. This method presents two sampling approaches; an on-site determination of total VOC using a FID analyzer, and an off-site determination of speciated VOCs by sample collection in sample canisters followed by laboratory gas chromatography. Permit or applicable rule requirements may prohibit using the on-site FID analyzer approach without prior approval by the TCEQ. If the tester wishes to use both the on-site total VOC results and the laboratory speciated results for mass emission determinations, then all requirements of both approaches must be followed, including the mid-level calibration for the FID analyzer.

6.1 On-site determination of VOC emissions by FID analyzer.

6.1.1 Connect the water sample supply line to the sample port on the source (i.e., cooling tower return line header). Before connecting the water sample line to the air stripping apparatus water inlet, allow the sample water to flush through the sample line for at least 5 sample line volumes.

6.1.2 With the stripping air flowing at 2500 ml/min to the column, connect the sample line to the water inlet of the air stripping apparatus and start the sample water flow into the chamber. Sample water flow rates higher than 125 ml/min during the filling stages are permissible; however, reduce the flow to 125 ml/min once the beryl saddles are submerged. Adjust the water overflow as necessary to maintain the water level just above the beryl saddle packing. The column drain valve should not be used to control the water level, particularly if the overflow is used to obtain the sample water flow rate as described in Section 4.4.5. Periodically check the water rotameter during sampling for gas bubble formation and the bubbler to assure that sufficient air flow is maintained. Record a notation in the data sheet comments section if any gas bubbles are observed in the water rotameter.

6.1.3 After the water level in the stripping chamber has reached the appropriate level and the air and sample water flow rates are set to 2500 ml/min and 125 ml/min, respectively, allow the stripping apparatus system to stabilize for a minimum of 10 minutes before making sample measurements. Longer stabilization time may be required depending on the organic compounds present and the particular water matrix. Before starting the test run record the time required for stabilization, barometric pressure, ambient temperature, and the process water flow rate (i.e., cooling tower water flow rate in gallons per minute).

6.1.4 At two minute intervals, record the FID analyzer measurement, water rotameter flow rate, air rotameter flow rate, and stripping chamber temperature. Adjust the air and water rotameter flows as necessary to maintain the target flows of 2500 ml/min and 125 ml/min, respectively; however, actual measured flows must be recorded. Monitor and record the data for a minimum of ten minutes.

6.1.5 Average the data from Section 6.1.4 and follow the calculations described in Section 7.0 to determine the air strippable concentration and, if applicable, the mass emission rate of VOCs from the water matrix.

6.2 Off-site determination of VOC by GC analysis. Samples of the stripped compound(s) may be taken from the exhaust of the air stripping apparatus and analyzed off-site by gas chromatography for speciated VOC results. It is strongly recommended that multiple samples be collected since a sample container may leak or be lost during shipment to the laboratory.

6.2.1 Connect the water sample supply line to the sample port on the source (i.e., cooling tower return line header). Before connecting the water sample line to the air stripping apparatus water inlet, allow the sample water to flush through the sample

line for at least 5 sample line volumes.

6.2.2 With the stripping air flowing at 2500 ml/min to the column, connect the sample port of the water to be analyzed to the water inlet of the air stripping apparatus and start the sample water flow into the chamber. Sample water flow rates higher than 125 ml/min during the filling stages are permissible; however, reduce the flow to 125 ml/min once the beryl saddles are submerged. Adjust the water overflow as necessary to maintain the water level just above the beryl saddle packing. The column drain valve should not be used to control the water level, particularly if the overflow is used to obtain the sample water flow rate as described in Section 4.4.5. Periodically check the water rotameter during sampling for gas bubble formation and the bubbler to assure that sufficient air flow is maintained. Record a notation in the data sheet comments section if any gas bubbles are observed in the water rotameter.

6.2.3 After the water level in the stripping chamber has reached the appropriate level and the air and sample water flow rates are set to 2500 ml/min and 125 ml/min, respectively, allow the stripping apparatus system to stabilize for a minimum of 10 minutes before making sample measurements. Longer stabilization time may be required depending on the organic compounds present and the particular water matrix. Record the time required for stabilization, barometric pressure, ambient temperature, process water flow rate (i.e., cooling tower water flow rate in gallons per minute), and the total VOC concentration measured by the FID analyzer.

6.2.4 Before collection of a canister sample, check and record the initial canister vacuum. If the canister vacuum has changed by more than 50 mm Hg (2 in Hg) from the initial evacuation, then the canister shall be considered as leaking and cannot be used.

6.2.5 Connect the sample canister to the air outlet of the air stripping apparatus with the stripping air flowing and the sample canister valve shut. Excess air flow will be vented through the bubbler.

6.2.6 Open the sample canister valve to begin sampling. During collection, monitor and record the water rotameter flow rate, air rotameter flow rate, and stripping chamber temperature at 2 minute intervals. Adjust the air and water rotameter flows as necessary to maintain the target flows of 2500 ml/min and 125 ml/min, respectively; however, actual measured flows must be recorded. When using an automated flow controller to regulate the flow rate into the sample canister, such as a critical orifice or mass flow controller, select a flow rate equivalent to 1/10th the canister volume per minute or less. If the canister flow rate is controlled manually (i.e., without a critical orifice or other flow controller), great care must be taken to not sample at a rate over the stripping air flow rate. For manually controlled sampling, adjust the needle valve such that the change in canister vacuum is between 75 to 125 mm Hg (3 to 5 in Hg) per minute. The canister must be only partially filled to help prevent condensation in the canister. Fill the sample canister until the vacuum gauge reads between 125 and 250 mm Hg subambient pressure (-5 and -10

in Hg).

6.2.7 Once sample collection is complete, record the final sample canister vacuum, sample collection time, and sample ID on the data sheet. Connect the FID analyzer to the stripping chamber air exhaust and record the final total VOC concentration.

6.2.8 Where the possibility of condensibles exists in a sample, the sample container may be heated above the stripping chamber temperature to help assure a representative sample analysis. Copies of field data sheets should be included with the samples so the laboratory is aware of the conditions at which the samples were collected.

6.2.9 Upon receipt of the sample(s) and prior to analysis, the laboratory must check and record the vacuum of the canister(s) to determine if any leakage has occurred. Dilution air (meeting the specifications of Section 3.1.1) should only be added to the canister at the laboratory performing the analysis and after the canister vacuum has been recorded.

6.2.10 If Tedlar™ bags are acceptable (see Section 3.5.1) for the target compounds then follow the procedures in Steps 6.2.1 through 6.2.9 with the following exceptions:

6.2.10.1 References to canister vacuum/pressure are not applicable to Tedlar™ bags.

6.2.10.2 Flow rate into the sample bag may be controlled by placing a rotameter downstream of the bubbler and controlling the flow rate of the bypass. Maintain a bypass flow of approximately 1.5 to 2.0 liter/min to fill the bag at approximately 0.5 to 1.0 liter/min.

6.2.10.3 Tedlar™ bags must be at least 10 liter size.

6.2.10.4 Tedlar™ bags shall be filled to approximately 80% capacity during sampling.

6.2.10.5 If sample dilution is required, dilution gas should not be added to the bag. Instead, a known volume of gas may be extracted from the bag and diluted with a known volume of zero air.

6.2.11 The sample(s) obtained for speciation analysis shall be analyzed according to the procedures in either EPA Method 18 (Title 40 Code of Federal Regulations Part 60 Appendix A) or Compendium Method TO-14A (US EPA Compendium of Methods for Determination of Toxic Organic Compounds in Ambient Air, EPA Document Number 625/R96/010B).

6.2.11.1 The target list of compounds for the analyses shall be determined by permit or regulatory requirements. In the absence of such requirements, a target list shall be generated based on a presurvey sample and analysis by GC/MS. Subject to TCEQ approval, process knowledge may also be used to generate a target list for the analysis.

6.2.11.2 All unidentified compounds detected beyond the target compounds shall be quantified based an appropriate surrogate, such as propane.

6.2.11.3 Calibration of the GC system for speciation analyses shall be

performed according to Section 4.2.

6.2.12 Appropriate chain of custody documents should be completed and accompany all canister and Tedlar™ bag samples, even in cases where a single company performs sampling and analysis.

6.2.13 Average the stripping chamber air and water flow rates and the stripping chamber temperature. Follow the calculations described in Section 7.0 to determine the air strippable concentration and, if applicable, the mass emission rate for each compound in the water matrix.

7.0 Calculations.

7.1 Calculation of the concentration of air strippable compound(s) in the water matrix is by the following equation:

Equation 7-1

$$C = \frac{M \times (P \times 0.03342 \frac{atm}{inHg}) \times b \times c}{R \times (T + 273) \times a}$$

Where:

a = Sample water flow rate, ml/min.

b = Stripping air flow rate, ml/min.

c = Concentration of compound in the stripped air, ppmv, from the FID analyzer or GC results. The total VOC result from the FID analyzer may be corrected based on the background check from either the zero air or water blank check, but only from the pretest background check. Post-test background checks may include residual contamination from the current test run. In no case shall the total VOC concentration by the FID analyzer be corrected by more than 1.0 ppmv as methane.

C = Concentration of air strippable compound in the water matrix, part-per-million by weight (ppmw).

M = Molecular weight of the compound, g/mol.

P = Pressure in the stripping chamber, in Hg (typically assumed to be same as atmospheric pressure).

R = 82.054 ml-atm/mol-K.

T = Stripping chamber temperature, ^{o}C.

The equation is a material balance and the value "C" represents the concentration in ppmw of the compound in the water matrix that was stripped and does not represent the total concentration of the compound in the water matrix prior to air stripping. The concentration of stripped VOC in the air is on a volume basis, but the concentration of strippable VOC in the water is on a weight basis in a liquid phase; so the concentration value will appear much

higher for the air phase.

7.2 Molecular weight. For total VOC based on the portable FID analyzer procedure in Section 6.1, calculate total VOC concentration in the water and emission rate based on the molecular weight of methane, unless an alternative reference calibration standard is approved by the TCEQ. For speciated VOC results based on procedures in Section 6.2, calculate individual compound concentrations and emission rates based on the respective compound molecular weights.

7.3 Calculation of VOC mass emission rate(s) from the concentration of strippable VOCs in the water and the water circulation rate:

Equation 7-2

$$E = C \times F \times \frac{60\,\text{min}}{hr} \times \frac{8.337 lb}{gallon} \times \frac{1}{1{,}000{,}000\,ppm}$$

Where:
C = Concentration of air strippable compound in the water matrix, part-per-million by weight (ppmw).
E = Mass emission rate of VOCs, lb/hr.
F = Water circulation rate of source, gallons/min.

7.4 Calculation of methane concentration in stripped air equivalent to a mass emission rate or action level (see Section 5.5.2.1.3). Equations 7-1 and 7-2 above are combined as follows:

Equation 7-3

$$c' = \frac{R \times (T + 273) \times a}{16.04 \frac{lb}{mol} \times (P \times 0.03342 \frac{atm}{inHg}) \times b} \times \frac{E' \times 1{,}000{,}000\,ppm}{F \times 8.337 \frac{lb}{gallon} \times 60 \frac{\text{min}}{hr}}$$

Where:
E’ = Allowable mass emission rate of VOCs or action level, lb/hr.
c’ = Methane concentration in the stripped air equivalent to emission limit or action level, ppmv.

16.04 = Molecular weight of methane, lb/mol. If a different calibration gas is used for the portable FID analyzer, such as ethylene, use the appropriate molecular weight.

8.0 Use of Portable GC for Field Speciation Analysis. A portable GC, calibrated for a specific suite of compounds, may be used in place of a FID analyzer, in which case the calculations remain the same and the final result is the concentrations of speciated air strippable compounds in the water matrix.

8.1 Setup. Same as Section 5.1, except calibration procedures for field GC analysis will follow Section 4.2.

8.2 Blank/Background Check. Same as Section 5.5.

8.2.1 Note: In some situations where very low detection for specific compounds is required, it may be preferable to check for background using the field GC.

8.3 Sample Measurement. Same as Section 6.1 with the following exceptions:

8.3.1 The FID analyzer can be used during the stabilization period to monitor the air stripping apparatus effluent. Alternatively, the GC can be used to monitor during the stabilization period; however, such an approach may drastically increase the time needed.

8.3.2 A test shall consist of three separate injection/analyses of the stripped gases.

9.0 References.

9.1 Vernon, W. D. et. al., "A Device for Measuring Volatile Organic Carbon Emissions from Cooling Towers Water," Journal of Air Pollution Control Association, December, 1981, pages 1280-1282.

9.2 United States Environmental Protection Agency Method 18 "Measurement of Gaseous Organic Compound Emissions by Gas Chromatography," Code of Federal Regulations, Title 40, Part 60, Appendix A, as amended through October 17, 2000 (65 FR 61744).

9.3 United States Environmental Protection Agency Method 21 "Determination of Volatile Organic Compound Leaks," Code of Federal Regulations, Title 40, Part 60, Appendix A, as amended through October 17, 2000 (65 FR 61744).

9.4 United States Environmental Protection Agency Compendium Method TO-14A "Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography," Compendium of

Methods for Determination of Toxic Organic Compounds in Ambient Air, EPA Document Number 625/R96/010B, January 1999.

Figure 1

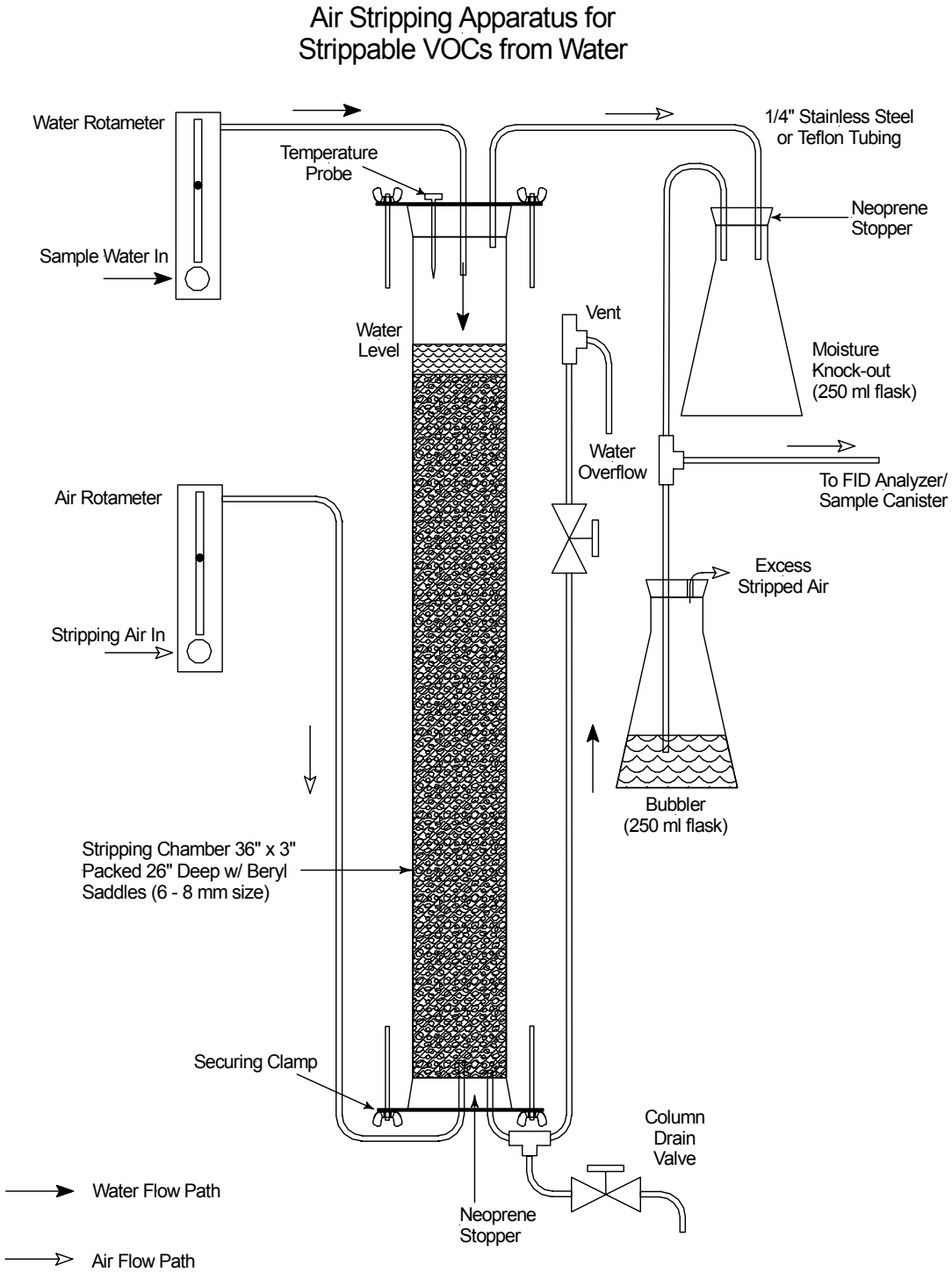
Air Stripping Apparatus for
Strippable VOCs from Water
Water Rotameter
Temperature Probe
1/4" Stainless Steel or Teflon Tubing
Neoprene Stopper
Sample Water In
Water Level
Vent
Moisture Knock-out (250 ml flask)
Water Overflow
To FID Analyzer/ Sample Canister
Air Rotameter
Excess Stripped Air
Stripping Air In
Bubbler (250 ml flask)
Stripping Chamber 36" x 3" Packed 26" Deep w/ Beryl Saddles (6 - 8 mm size)
Securing Clamp
Column Drain Valve
Neoprene Stopper
Water Flow Path
Air Flow Path

Figure 2

Air Stripping Apparatus
Stripping Chamber End Cap Design

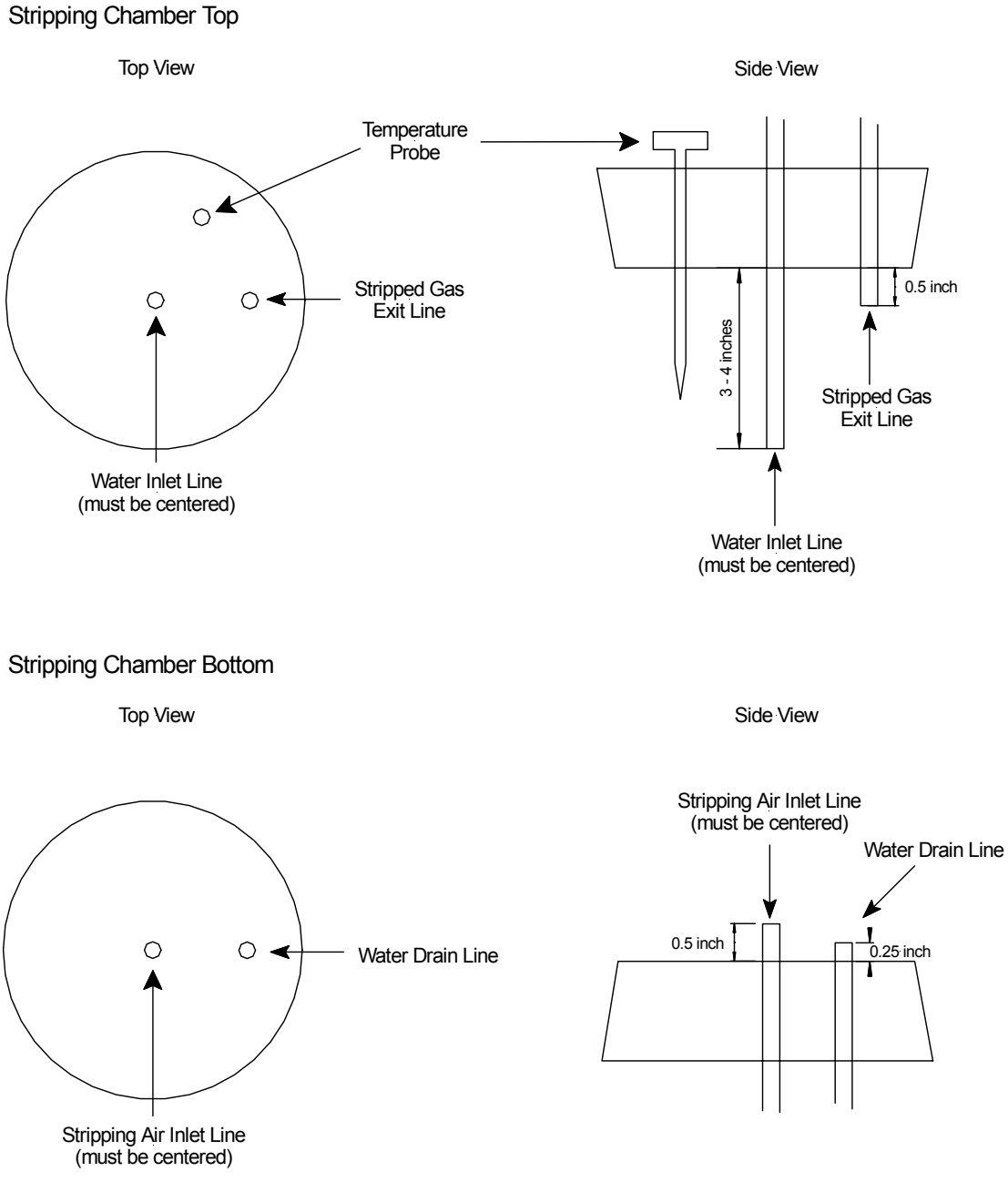

Figure 3
Air Strippable VOCs in Water
FID Analyzer Measurement Data Sheet

Regulated Entity: _____
Air Account No: _____
Unit Name: _____
EPN/FIN ID No: _____
Process Description: _____
Date/Time: _____
Barometric Pressure: _____
Process Water Flow: _____
Zero Air Background VOC: _____
Zero Water Background VOC: _____
Stabilization Time: _____

Regulated Entity No: _____
Instrument Model: _____
Instrument Serial No: _____
Operator(s): _____
Certified Gas Value: Zero: _____
Mid-level: _____
High-level: _____
FID Response Zero: _____
Mid-level: _____
High-level: _____
Expected VOC(s): _____

Time*	Air Stripping Apparatus Data			FID Reading (ppmv, wet)	Comments
	Water Flow (ml/min)	Air Flow (ml/min)	Temp. (°C)		
Average					

* Data recording time (after stabilization period), recorded as actual time of day.

Figure 4

Air Strippable VOCs in Water
Canister Sampling Data Sheet

Regulated Entity: _____
Air Account No: _____
Unit Name: _____
EPN/FIN ID No: _____
Process Description: _____
Date/Time: _____
Canister ID: _____
Sample ID: _____
Barometric Pressure: _____
Ambient Temperature: _____
Stabilization Time: _____
Process Water Flow: _____

Regulated Entity No: _____
Instrument Model: _____
Instrument Serial No: _____
Operator(s): _____
Certified Gas Value: Zero: _____
High-level: _____
FID Response Zero: _____
High-level: _____
Zero Air Background VOC: _____
Zero Water Background VOC: _____
Expected VOC(s): _____

Time*	Air Stripping Apparatus Data			Canister Flow Rate, if applicable (cc/min)	Canister Vacuum (mm Hg)	FID Reading, (ppmv, wet)	Comments
	Water (ml/min)	Air (ml/min)	Temp. (°C)				
Average							

* Data recording time (after stabilization period), recorded as actual time of day.