

SOURCE TEST PROCEDURE ST- 40**STRIPPABLE VOLATILE ORGANIC COMPOUNDS****REF: Regulation 11-10****1. APPLICABILITY**

- 1.1 This procedure is used to quantify the concentration of volatile organic compounds stripped from cooling tower water by air. It is an adapted version of the Texas Commission on Environmental Quality (TCEQ) Air Stripping Method (Modified El Paso Method) for Determination of Volatile Organic Compound Emissions from Water Sources.
- 1.2 The use of a flame ionization detector (FID) for measurement of organic compounds is not allowed if the compound response factors are greater than 2 relative to methane.

2. PRINCIPLE

- 2.1 A continuous sample of cooling tower water is passed through a packed column. Air is passed through the column with countercurrent flow, stripping the volatile organic compounds from the water. The stripping air is analyzed for volatile organic compound concentration. Air and water input and output points have a direct interface to prevent volatile compound loss from vaporization in ambient air.
- 2.2 FID Direct Measurement: Stripping air is connected to a FID analyzer with a direct interface. The sample is analyzed for total volatile organic compounds.
- 2.3 Integrated Sample: Stripping air is routed at a constant, measured flow into an evacuated stainless steel canister or Tedlar bag. The sample is analyzed for total volatile organic compounds by FID. Alternatively, the sample may be speciated by gas chromatography (GC) or an equivalent methodology approved by the Source Test Manager.

3. RANGE AND SENSITIVITY

- 3.1 The minimum measurable concentration of volatile organic compounds by FID is 1 ppmv when interferences are not present. The minimum detection limit of the FID analyzer should be 0.050 ppmv and the minimum sensitivity should be 2% of full scale.

- 3.2 The minimum measurable concentration of volatile organic compounds by GC is 0.5 ppmv.

4. INTERFERENCES

- 4.1 FID Analysis: Response factors vary amongst hydrocarbons. Propane used as a span gas minimizes this variability and is mandatory in this method. A FID should not be used on compounds with response factor multipliers greater than 2 relative to methane. Use of an alternative span gas or detection method must be approved by the Source Test Manager.
- 4.2 FID analyzers that use air from the sample or ambient sampling environment can have an elevated baseline. Analyzers using those air sources should be calibrated in the same location as sampling.
- 4.3 Rubber and drying agents can absorb volatile organic compounds. Use of those materials is prohibited.
- 4.4 The pressure drop across the rotameter control valve can cause gas bubble formation in the water rotameter and affect the flow measurement.
- 4.5 Temperature changes affect compound vapor pressures and can alter results.

5. APPARATUS

- 5.1 Clear, heavy walled glass column, 36 in long with an internal diameter of 3 in.
- 5.2 Packing material. Use 6 mm – 8 mm beryl saddles and pack the column to a depth of 26 in.
- 5.3 Neoprene stoppers.
- 5.4 Securing clamps.
- 5.5 Stainless steel or Teflon tubing, ¼ in diameter and no longer than 50 ft.
- 5.6 Air rotameter with $\pm 2\%$ accuracy. Rotameter should be calibrated according to TCEQ Modified El Paso Method specifications.
- 5.7 Water rotameter with $\pm 2\%$ accuracy. Rotameter should be calibrated according to TCEQ Modified El Paso Method specifications.
- 5.8 Type K temperature probe. Temperature probe should be calibrated according to TCEQ Modified El Paso Method specifications.

- 5.9 Clear glass flasks – 250 ml. Leave one flask empty for moisture knockout and fill one flask with water to act as a bubbler. The bubbler shows that there is sufficient flow out of the system and no external air being drawn in.
- 5.10 Flame ionization detector analyzer or gas chromatograph with appropriate detectors for sample compounds.
- 5.11 Tedlar bags. Use bags that are a minimum of 20 L.
- 5.12 Evacuated stainless steel canisters. Sample canisters should meet all requirements in the US EPA Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, Compendium Method TO-14A.
- 5.13 Zero-air. Air is used for calibration and stripping. It should be certified to contain less than or equal to 0.1 ppmv total hydrocarbon (THC).
- 5.14 High-level calibration gas. Sample concentration should be between 10-100% of the high-level gas concentration. Calibration gas should be certified and within 2% of the stated concentration. Propane should be used unless a surrogate is approved by the Source Test Manager.
- 5.15 Mid-level calibration gas. Concentration should be 20-50% of the high-level calibration gas concentration and certified within 2% of the stated concentration. Propane should be used unless a surrogate is approved by the District.
- 5.16 Orifice plate, mass flow controller, or needle valve.
- 5.17 For more detail and diagrams of the apparatus, refer to Figures 1 and 2 in the TCEQ Modified El Paso Method.

Figure 40-1

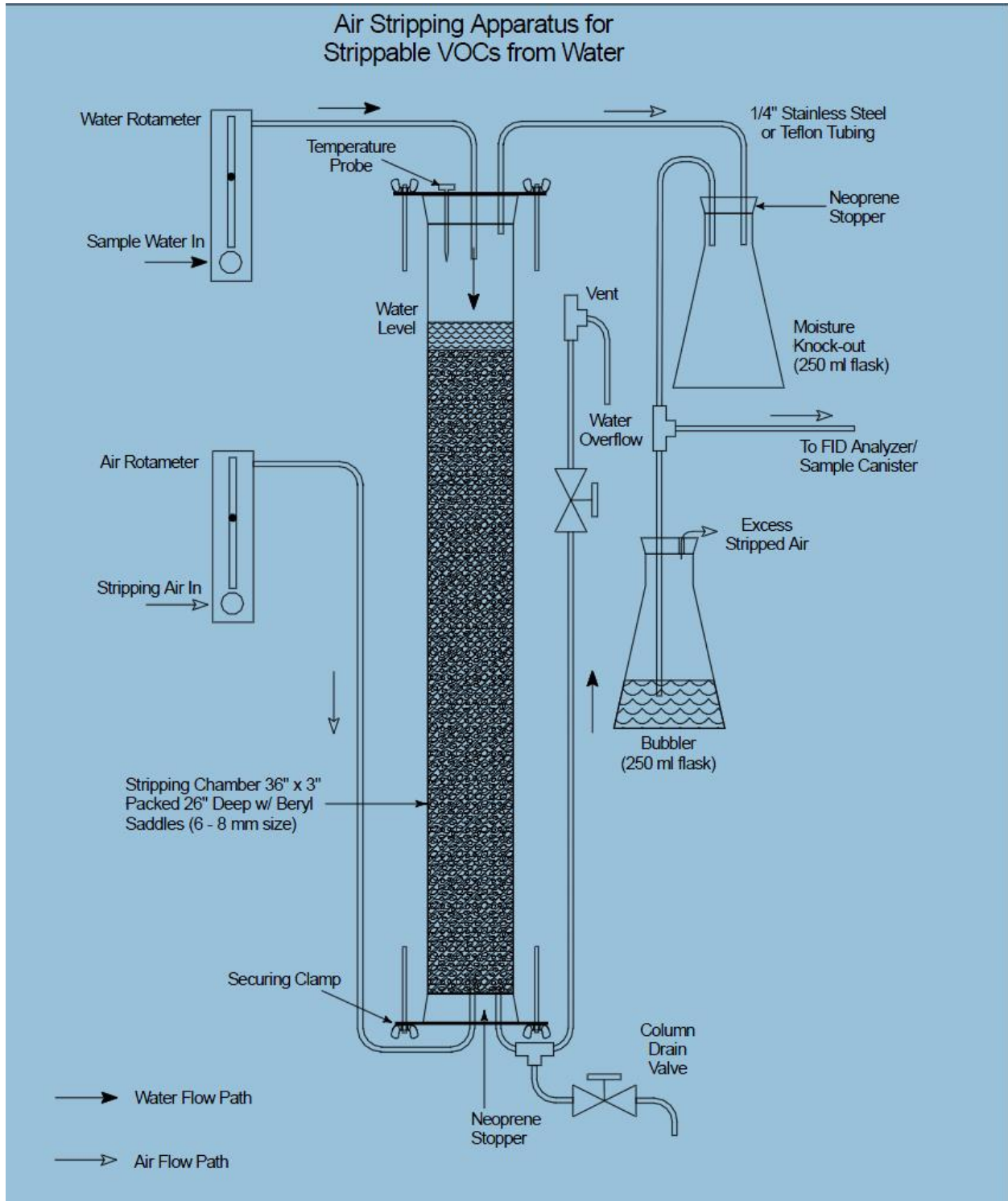


Figure 1 from the TCEQ Modified El Paso Method.

Figure 40-2
Air Stripping Apparatus
Stripping Chamber End Cap Design

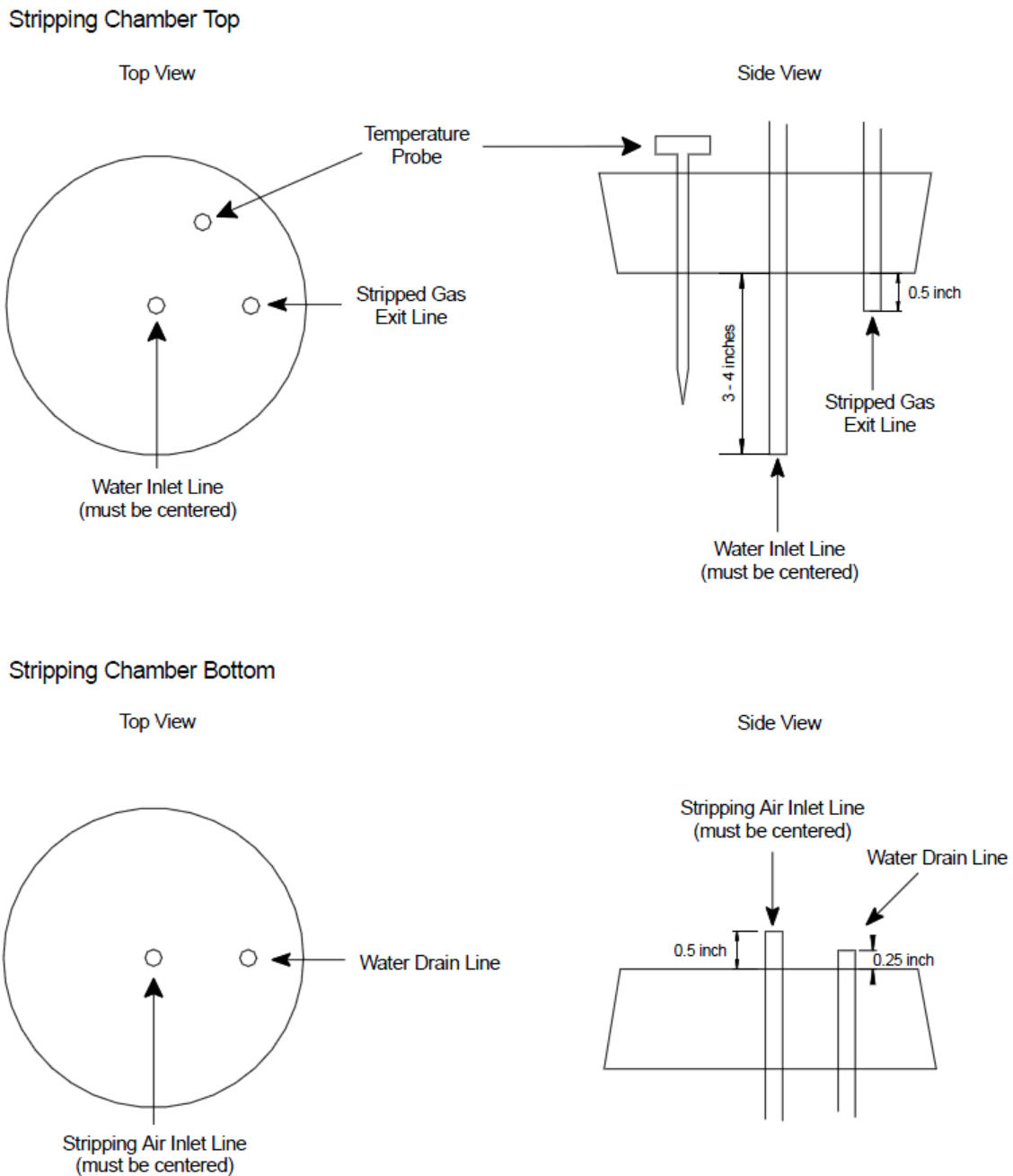


Figure 2 from the TCEQ Modified El Paso Method.

6. PRE-TEST PROCEDURES

- 6.1 Select a sampling point that meets the site criteria outlined in the TCEQ Modified El Paso Method. Choose a point in the return line header prior to distribution to different cells and release to atmosphere. Water should be under pressure and drawn from the vertical section near the base of the riser pipe or from the top of the horizontal section prior to the riser.
- 6.2 Assemble the sampling system as shown in Figure 40-1 and Figure 40-2.
- 6.3 Cleaning procedures should follow those outlined in the TCEQ Modified El Paso Method.
- 6.4 Leak test the sampling system by introducing zero-air into the system at a flow rate of 2500 ml/min and spraying Snoop solution or equivalent onto connections. No bubbling should be observed before proceeding.
- 6.5 Allow sample water to flush through the sample line for a minimum of five sample line volumes before connecting the water line to the apparatus. Make sure there are no air bubbles in the water rotameter.
- 6.6 Level the apparatus to prevent channeling.
- 6.7 Warm up the instruments according to manufacturers' instructions.
- 6.8 Introduce zero-air and span-gas into the analyzers and calibrate the instruments according to manufacturers' instructions. The analyzer should read 0.0 ± 0.2 ppmv with zero-air as the input and within $\pm 5.0\%$ of the high-level and mid-level calibration gas certified values. The mid-level calibration gas is optional if the VOC emissions are determined by GC or GC/MS speciation.

7. SAMPLING

- 7.1 Set the air flow rate to 2500 ml/min.
- 7.2 Fill the column with water to the top of the beryl saddle packing. Set the water flow rate to 125 ml/min.
- 7.3 Allow the apparatus to stabilize for at least ten minutes if possible without overflowing the column. Record the stabilization time, barometric pressure, ambient temperature, and cooling tower process water flow rate.

- 7.4 Attach the sample canister to the air outlet. A critical orifice, needle valve, or mass flow controller should be used to control the flow into the canister. Set flow to 1/10th of the canister volume per minute or less. Open the canister valve.
- 7.5 Sample for at least 10 minutes. Record the air flow rate, the water flow rate, the chamber temperature, and the canister vacuum every 2 minutes.
- 7.6 When finished, close the canister valve. Record the final sample canister vacuum, sample collection time, and sample ID. Analyze stainless steel canister samples within 7 days of sample collection.
- 7.7 Tedlar bags may be used if quality assurance and quality control guidelines are followed as described in Title 40, Code of Federal Regulations, Part 60, Appendix A, Method 18 for all target compounds. Results must be corrected for percent recoveries. Tedlar bags must be new, unused, and checked for leaks and contamination. Control the flow rate going into the bag by attaching a needle valve to the bubbler outlet and controlling the bypass. Set the bypass so that flow to the Tedlar bag is between 500 ml/min and 1000 ml/min. Analyze Tedlar bag samples within 72 hours of sample collection.
- 7.8 Before analysis, record the sample canister vacuum to determine if leaking has occurred. Pressurize the canister to 20 psig with nitrogen. Connect the canister to the FID analyzer and open the valve. The sample flow rate should be the same flow rate used for calibration and be held constant throughout the analysis.
- 7.9 Alternatively, the canister or Tedlar bag may be sent to a lab for analysis by the Bay Area Air Quality Management District (BAAQMD) Standard Operating Procedure for the Analysis of Hydrocarbons in Gaseous Samples (Hydrocarbons by GC).

8. AUXILIARY TESTS

- 8.1 Volatile organic compound speciation and concentration. Use BAAQMD Standard Operating Procedure for the Analysis of Hydrocarbons in Gaseous Samples (Hydrocarbons by GC) to determine VOC speciation and concentration if any compounds have a response factor greater than 2 relative to methane.

9. CALCULATIONS

- 9.1 Use Equation 1 to calculate the concentration of air strippable compounds in the sample water matrix.

$$C = \frac{M \times (P \times 0.03342) \times b \times c}{R \times (T + 273) \times a} \quad (1)$$

C = Concentration of air strippable volatile organic compounds in the water matrix, ppmw.

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

P = Pressure in the column, in Hg. Typically assumed the same as atmospheric pressure.

b = Stripping air flow rate, ml/min.

c = Concentration of volatile organic compounds in the stripped air, ppmv.

a = Sample water flow rate, ml/min.

R = Gas Constant, 82.054 ml-atm/mol-K.

T = Column temperature, °C.

0.03342 = Conversion from in. Hg to atm, atm/in Hg.

273 = Conversion from Celsius to Kelvin.

- 9.2 Use Equation 2 to calculate the mass emission rate of volatile organic compounds.

$$E = \frac{C \times F \times 60 \times 8.329}{1,000,000} \quad (2)$$

E = Mass emission rate of volatile organic compounds, lb/hr.

C = Concentration of air strippable volatile organic compounds in the water matrix, ppmw.

F = Water circulation rate of source, gal/min.

60 = Conversion from minutes to hours, min/hr.

8.329 = Specific weight of water at 70°F, lb/gal.

1,000,000 = Conversion from ppm, ppm.

10. REPORTING

Figure 10.1

Distribution: Firm Permit Services Requester	BAY AREA AIR QUALITY MANAGEMENT DISTRICT 375 Beale Street, Suite 600 San Francisco, California 94105 (415) 771-6000 SUMMARY OF SOURCE TEST RESULTS	Report No. _____ Test Date: _____ <u>Test Times:</u> Run A: _____ Run B: _____ Run C: _____
Source Information		BAAQMD Representatives
Firm Name and Address:	Firm Representative and Title: Phone No.	Source Test Team:
Permit Conditions:	Source(s): Site No Permit Con. No Facility ID Hr./Day Day/Yr. Operates	Permit Services / Enforcement Test Requested by:
Operating Parameters:		
Applicable Regulations:		VN Recommended:

Source Test Results and Comments:

METHOD PARAMETER

OUTLET
RESULTS

LIMITS
REGULATION PERMIT

ST – 40 Strippable Volatile Organic Compounds, ppmv

NO COMMERCIAL USE OF THESE RESULTS IS AUTHORIZED

Air Quality Engineer Date	Supervising Air Quality Engineer Date	Air Quality Engineering Manager Date
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11. REFERENCES

- 11.1 Bay Area Air Quality Management District Laboratory SOP Hydrocarbon “Standard Operating Procedure for the Analysis of Hydrocarbons in Gaseous Samples,” February 19, 2008.
- 11.2 Texas Commission on Environmental Quality Method “Air Stripping Method (Modified El Paso Method) for Determination of Volatile Organic Compound Emissions from Water Sources,” Sampling Procedures Manual, Appendix P, January 2003.
- 11.3 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 February 4, 2016.
- 11.4 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 the Determination of Toxic Organic Compounds in Ambient Air, EPA Document Number 625/R96/010b, January 1999.