PROCEDURE - 1

ORGANIC COMPOUNDS WATER SAMPLING

REF: Regulation 11-10

1. APPLICABILITY

1.1 This procedure is used to sample cooling tower water for quantification of the concentration of hydrocarbons. After sampling, the appropriate analytical water methods are selected based on process stream content.

2. PRINCIPLE

2.1 A continuous sample of cooling tower water is passed through a water collection system. The sample vial or bottle is purged with an inert gas before water is diverted into it. Water input and output points have a direct interface to prevent volatile compound loss from vaporization in ambient air. The sample is transported to a lab for hydrocarbon analysis.

2.2 Alternatively, the sample may be analyzed for total hydrocarbon (THC) by a FID analyzer if the process stream compound response factors are less than 2 relative to methane. An equivalent methodology may also be used if approved by the Source Test Manager.

3. RANGE AND SENSITIVITY

3.1 Range and sensitivity are determined by lab analysis methodology and instrumentation.

4. INTERFERENCES

4.1 The water collection system and sample vials/bottles should be kept clean to prevent contamination. Sample vials/bottles should only be opened immediately before usage and capped immediately after.

4.2 Headspace in the sample bottles and exposure to the environment should be minimized to prevent vaporization and loss of volatile organic compounds.

4.3 Rubber can absorb volatile organic compounds. Use of that material is prohibited.

4.4 Temperature changes affect compound vapor pressures and can alter results. Keep samples at 4ºC or less and monitor temperature until lab analysis to prevent loss of volatile organic compounds.

4.5 Proper preservatives should be used to prevent the oxidation or volatilization of compounds before laboratory analysis. If the preservative is added before sample collection, the sample vial or bottle should not be overfilled to avoid washing out the preservative.

4.6 A field blank is taken to demonstrate that no diffusion of hydrocarbons through the septum seal or threaded screw top seal occurs.

5. APPARATUS

5.1 High purity nitrogen gas for purging. It should be certified to contain less than or equal to 0.1 ppmv total hydrocarbon (THC).

5.2 Amber glass sample vials or bottles and Teflon lined screw caps or screw caps with Teflon faced silicon septum. Vials should be a minimum of 25 mL and bottles should be 1 L or 1 qt. Wash with phosphate-free detergent, rinse with tap and then distilled water, and dry at 105ºC or use preprocessed vials/bottles.

5.3 ¼ inch and ⅛ inch stainless steel or Teflon tubing. Tubing length should be minimized.

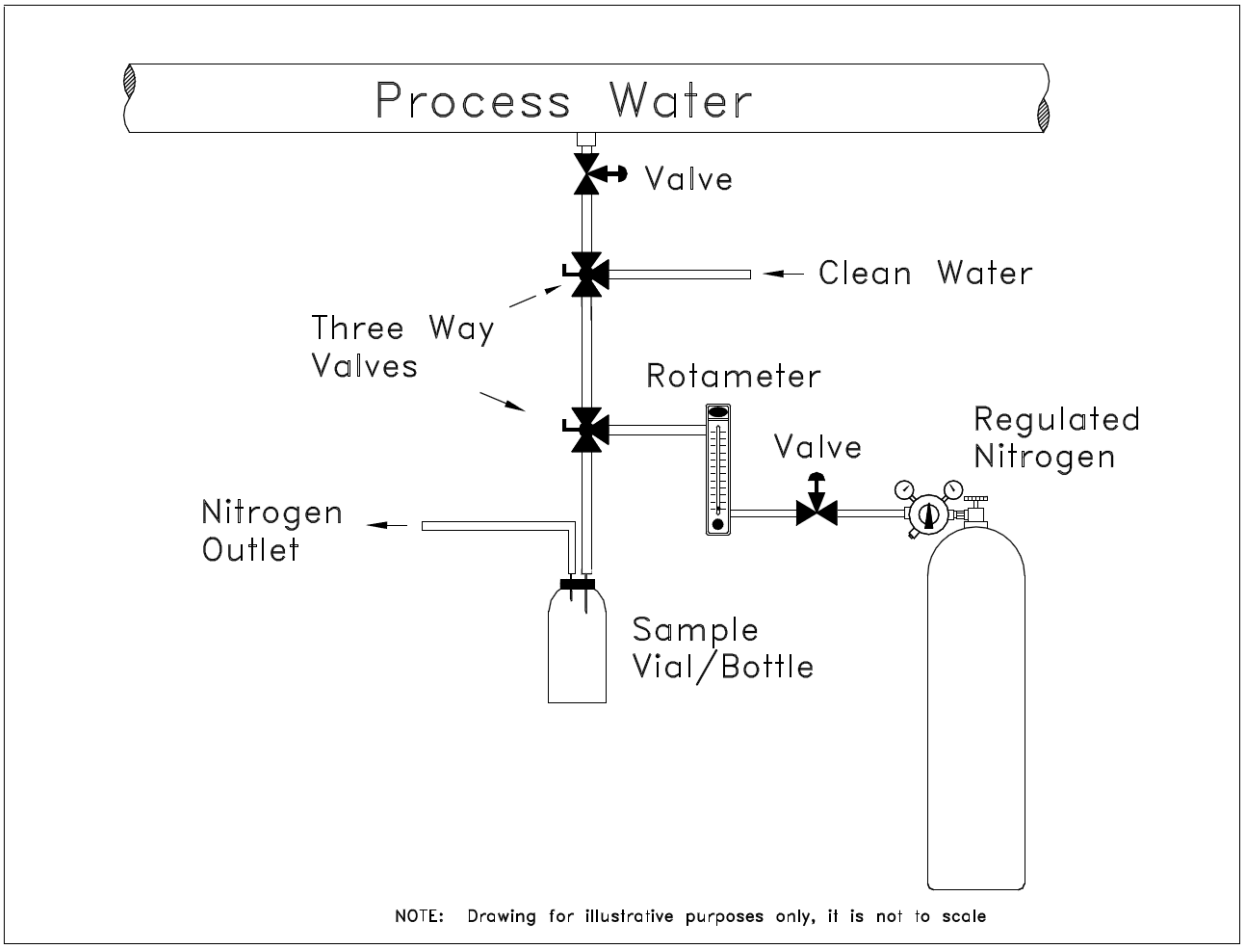
5.4 Stainless steel ball valves.

5.5 Stainless steel 3-way valves.

5.6 Rotameter with $\pm$ 2% accuracy.

5.7 Temperature data logger.

Figure 1



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 1. Use ⅛ inch tubing for the nitrogen purge outlet and ¼ inch tubing for all other sections. The tubing should extend into the bottle cap or septum. Inlet tubing should extend 80% down the length of the sample vial/bottle. An alternate sampling apparatus with threaded Teflon screw top or threaded glass top may also be acceptable upon approval by the Source Test Manager. Source Test should be supplied a detailed written description along with a diagram.

6.3 Flush clean water through the system for a minimum of five sample line volumes before stopping the flow of water. Use clean water to thoroughly rinse the external side of tubing at and below the cap level and the cap itself if using a reusable Teflon or glass one. Connect a sample vial or bottle and fill it with clean water going through the system to take a field blank sample. Label the field blank with site ID, date, time, and sample type information.

6.4 Allow sample water to flush through the sample line for a minimum of five sample line volumes before stopping the flow of water and connecting the sample vial or bottle. If the field blanks do not meet QC requirements in the lab analysis methods, the system should be disassembled and cleaned with a dilute phosphate-free detergent solution, rinsed with tap and then distilled water, and air dried.

7. SAMPLING

7.1 Purge the sample vial or bottle with a minimum of 5 sample vial/bottle volumes of nitrogen.

7.2 Switch the 3-way valves to direct process water into the sample vial/bottle. When the vial/bottle is full, remove the cap and tubing from the sample vial/bottle and continue to fill the volume previously displaced by tubing. Fill to the top of the vial/bottle to form a meniscus and minimize headspace as much as possible.

7.3 If the sample contains residual chlorine, neutralize with sodium thiosulfate. If the sample contains aromatic compounds with a tendency to degrade like benzene, toluene, and ethyl benzene, acidify to less than pH 2 with 1:1 HCl. Use the minimum time necessary to add preservative and close the vial/bottle with a Teflon lined screw cap or unpunctured septum and screw cap.

7.4 Label the sample with site ID, date, time, preservation method if applicable, and sample type information.

7.5 Refrigerate or put the samples on ice immediately to keep the samples at 4°C or less during transport to the laboratory. Set the temperature logger to take a minimum of one measurement per minute. Keep the temperature data logger with the samples and upload the log to ensure the temperature does not deviate. Analyze the sample within 7 days.

7.6 Flush clean water through the system for a minimum of five sampling line volumes. Use clean water to thoroughly rinse the external side of the tubing at and below the cap level and the cap if using a reusable Teflon or glass one.

8. AUXILIARY TESTS

8.1 Organics speciation and concentration. EPA method 8260B, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry and/or EPA method 8270D, Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry. Use the appropriate methods depending on process stream content. Alternate analytical methods may be approved by the Laboratory Services Manager.

8.2 Residual chlorine measurement. EPA method 330.4, Total Residual Chlorine by Titration or EPA method 330.5, Chlorine, Total Residual (Spectrophotometric, DPD).

9. LABORATORY WATER ANALYSIS PROCEDURE

Water sample analysis will be expressed as Total Hydrocarbon (THC) concentration in parts per billion by weight (ppb-w). Analysis will be performed according to EPA Methods 8260 and/or 8270, utilizing the appropriate and applicable EPA sample preparation method(s) (5000, 5030, 5031, 5032, and/or 5035). Analysis will identify and calculate ppb-w concentration for compounds from C1 up to C15 having the potential to be found in the associated process stream. Alternative analytical and sample preparation methodologies may be used with prior documented approval from the Air District's Laboratory Services Manager.

10. REFERENCES

11.1 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.

11.2 Washington State Department of Health Procedure "Volatile Organic Chemical (VOC) Sampling Procedure," DOH PUB #331-220.

11.3 U.S. Geological Survey Guide "Field Guide for Collecting Samples for Analysis of Volatile Organic Compounds in Stream Water for the National Water-Quality Assessment Program," Open-File Report 97-401, 1997.

11.4 United States Environmental Protection Agency Method 624 "Purgeables," Part 136 Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, Appendix A, 1984.

11.5 United States Environmental Protection Agency Method 625, "Base/Neutrals and Acids," Part 136 Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, Appendix A, 1984.