PROCEDURE - 1

ORGANIC COMPOUNDS WATER SAMPLING

REF: Regulation 11-10

1. APPLICABILITY

1.1 This procedure is used to sample cooling tower water for the quantification of hydrocarbon concentration. 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.

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 vials/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 in a temperature environment of 0 - 6ºC 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 sampling. The sample vial or bottle should not be overfilled to avoid washing out the preservative.

4.6 A field blank or trip 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. Preprocessed vials/bottles that meet conditions in SW-846, Chapter 4 are also acceptable. Clear glass sample vials may be used in conjunction with an opaque travel container. Minimize light exposure to the sample to the extent possible.

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

5.4 Stainless steel ball valves.

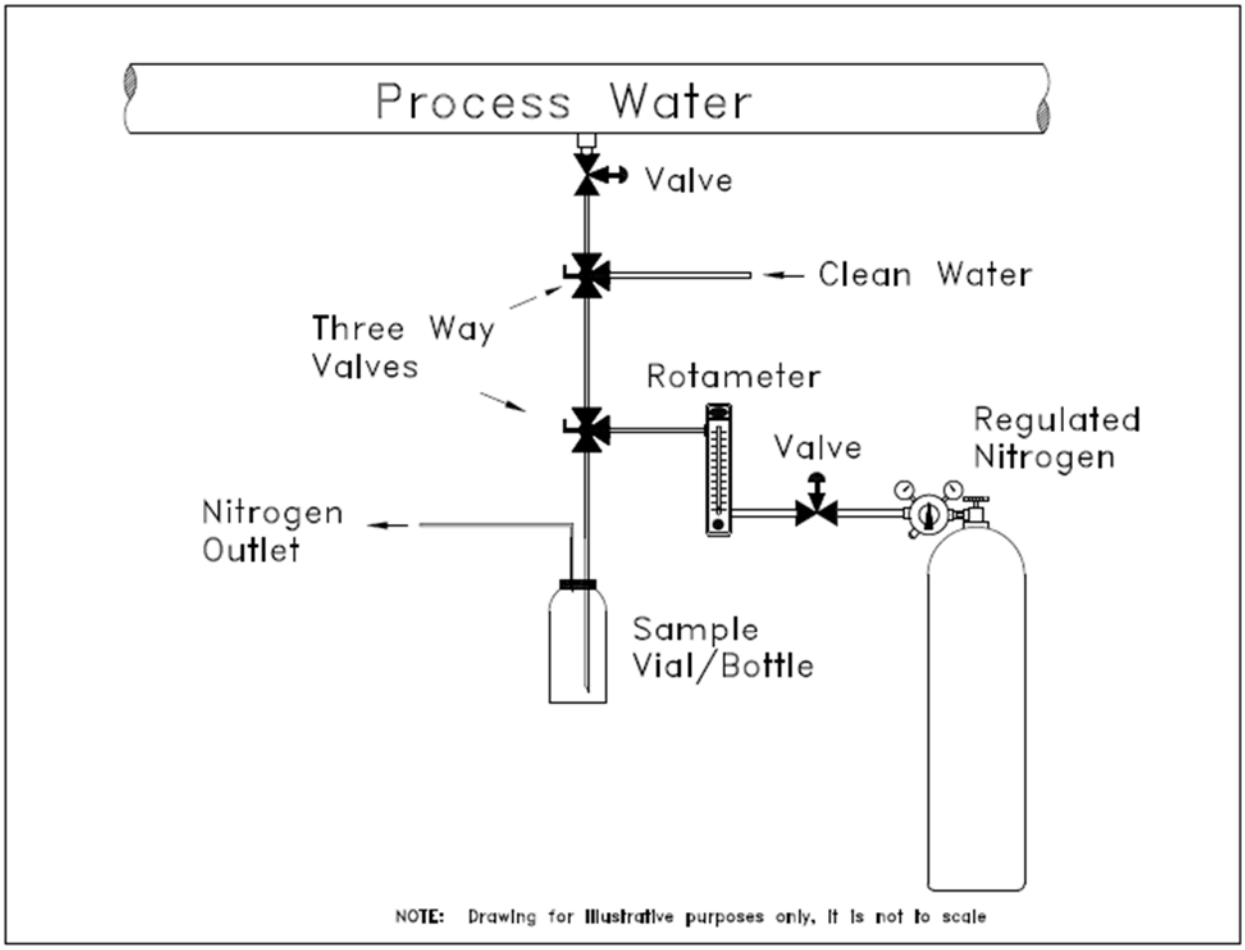
5.5 Stainless steel 3-way valves.

5.6 Rotameter with ± 2% accuracy.

5.7 Temperature data logger.

5.8 Organic-free reagent water. The water should be as defined in SW-846, Chapter 1.

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 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 Once every 30 days take a field blank sample. Flush organic-free reagent water through the system for a minimum of five sample line volumes before stopping the flow of water. Remove external surface residuals and use organic-free reagent 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 organic-free reagent water going through the system. Label the field blank with site ID, date, time, and sample type information. The organic-free reagent water flush is not necessary unless taking a field blank sample. The system may be exempt from the organics free reagent water flushes upon system design submittal and approval by the Source Test Manager. Field blanks will then be replaced with trip blanks.

6.4 Allow sample water to flush through the sample line for a minimum of five sample line volumes. Stop the flow of water and connect 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. If the trip blanks do not meet QC requirements in the lab analysis methods, the sample transportation containers and sample vial, cap, and septa type must be reassessed. All samples collected from the last passing field or trip blank shall be reviewed to ensure that contamination did not negatively affect results, the review documented, and the rationale for the determination noted. These records shall be made available upon request.

7. SAMPLING

7.1 Preservatives should be added prior to sampling. 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. If the sample requires both preservatives be used, follow the sampling directions for aqueous samples with residual chlorine in SW-846, Chapter 4 instead of this procedure.

7.2 Purge the sample vial or bottle with a minimum of 2 sample vial/bottle volumes of nitrogen.

7.3 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. Rinse the inside of the cap and septum with process water.

7.4 Close the vial/bottle with a Teflon lined screw cap or unpunctured septum and screw cap. Alternatively, VOA vials that come precleaned according to EPA

specifications and packaged with preservative may be used. Invert the vial to ensure that there is no head space. If bubbles are visible the sample should be discarded and a new sample should be taken.

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

7.6 Refrigerate immediately to keep the samples in a temperature environment of 0 - 6°C 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. The sample should not be opened until laboratory analysis. Analyze the sample within 5 business days.

8. AUXILIARY TESTS

Auxiliary tests provide supplementary or additional information that may be necessary to complete required calculations or the test procedure.

8.1 Organics speciation and concentration. Use the methodology referenced in BAAQMD Regulation 11-10-603 in conjunction with EPA Method 5030 or 5035. 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. REFERENCES

9.1 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.

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

9.3 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.

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

9.5 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.

9.6 United States Environmental Protection Agency SW-846 Compendium “Organic Analytes,” Test Methods for Evaluating Solid Waste: Physical/Chemical Methods, Chapter 4, Revision 5, July 2014.