

Final Project Report

Assessment of Selected Leak Detection, Sampling, Testing, Measurement and Monitoring Methods for Estimating Emissions of Highly Reactive Volatile Organic Compounds from Industrial Cooling Waters

Prepared for

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Disclaimer

Information presented in Sections 3.0 and 4.0 of this report and Appendix G pertaining to the performance characteristics of the equipment identified in these Sections has been obtained directly from those manufactures of the equipment referenced in these Sections. The inclusion of such information does not constitute an endorsement of the performance characteristics stated in this Report. Neither The University of Texas at Austin nor the Texas Commission on Environmental Quality can provide a warranty or guarantee, expressed or implied, as to the accuracy, reliability or completeness of the data furnished by other organizations.

1.0 Introduction

This report summarizes the results of work performed in fulfillment of Texas Commission on Environmental Quality (TCEQ) Work Order No. 55078-03-07.

1.1 Background

1.2 Purpose and Objectives

As stated in the work order, the project objectives of the work order were:

“... to develop and produce detailed, quality assured sampling, testing, measurement, and monitoring systems for cooling water. These methods will be used to identify process fluid leaks into the cooling water as soon as possible and provide quality controlled data for water concentration and flow rate to calculate speciate volatile organic compound (VOC) cooling tower mass emission estimates. These methods may be used in future site testing and in the development of emission inventory estimates.”

In addition to these project objectives, measurement data quality objectives were also specified in the work order to support the intent of the work order. The measurement data quality objectives addressed two types of data. The first related to data obtained through laboratory testing and evaluations conducted under this work order. In this regard, all data collection and methodology evaluations conducted were required to be performed consistent with the guidelines in Attachment A of the work order entitled “Data Quality Control”. In addition measurement data, developed during the performance of the work order, should be accompanied by the Data Package and Data Usability Summary found in Attachment B of the work order.

The second type of data addressed in the Measurement Data Quality Objectives, as refined by the TCEQ during the course of the project, was the desired accuracy, precision, and sensitivity for systems for leak detection and sampling, measuring, monitoring, and testing of cooling water concentration and flow rate. These specifications are:

Detection Limit: ≤ 10 ppbw

Accuracy: Below 50 ppbw, ± 10 ppbw, absolute difference

Equal to or above 50 ppbw, $\pm 20\%$, as relative error or % difference

The methods, individually or in combination, must be capable of providing 90% speciation of the individual compounds in the total VOC. Speciated compounds of interest to the TCEQ considered in this study were benzene, ethylene, propylene, 1,3 butadiene, and all the butene isomers.

2.0 Scope of Work

The scope of work for this project as stated in the original work order was modified to reflect schedule constraints and priorities of the TCEQ once the project notice to proceed was issued. This scope of work was further refined during subsequent meetings with the TCEQ as interim progress reports were submitted. The final scope of work consisted four major tasks:

- A. Evaluation of Selected VOC Leak Detection Methods
- B. Evaluation of Selected Sampling, Measuring, Monitoring, and Testing Methods
- C. Evaluation of Instruments for Continuous Measurement of Cooling Water Flow
- D. Development of a Mass Transfer Model of VOC Emissions from Cooling Towers

The purpose of each task and the scope of work associated with it are described in the sections that follow.

2.1 Evaluation of Selected VOC Leak Detection Methods

Cooling tower heat exchange systems have been identified by the TCEQ as sources of emissions of VOCs of interest specified in the Work Order No. 55078-03-07 (TCEQ, 2003). These VOCs find their way into the cooling water through process fluid leaks in heat exchangers if the pressure of the process fluid being cooled is greater than the pressure on the cooling water side of the heat exchanger. They are stripped from the water in the cooling tower. The purpose of this task was to evaluate the sensitivity and accuracy of selected potential methods of detecting process fluid leaks of the high interest VOCs (benzene, ethylene, propylene, 1,3-butadiene, and all the butene isomers) into the cooling water.

Five leak detection methods were selected for evaluation in this task: the hydrocarbon trap, chlorine usage, oxidation-reduction potential, total organic carbon, and pH. For each method, a description of the method and principle of operation is provided including a discussion of the critical parameters of operation that could impact its acceptable use for this application. Each method is then evaluated for its suitability for this application and its ability to meet the TCEQ requirements for HRVOC leak detection.

The approach employed to evaluate the methods considered in this task consisted of a literature review and assessments of the sensitivity and accuracy of each method to detect the high interest VOCs. The purpose of the literature review was to obtain information on the principles of operation of each method, how it is currently being used in industry, its operating limitations, and its ability to satisfy the TCEQ measurement requirements as a leak detection method.

2.2 Evaluation of Selected VOC Sampling, Measuring, Monitoring, and Testing Methods

The TCEQ has defined in TCEQ Sampling Procedures Manual, Appendix P (included in Appendix A of this report), an acceptable method for monitoring of VOCs in cooling water and the requirements that alternative methods must satisfy to be acceptable. The purpose of this task was to evaluate selected sampling, measuring, monitoring and testing methods or systems that are being or could be used to comply with the TCEQ Sampling Procedures Manual, Appendix P to obtain data on an Appendix P. Both semi-continuous and continuous (at least one measurement every 15 minutes) were considered for this evaluation. Where possible this evaluation focused on systems rather than on instruments as the overall accuracy of the method

is required by Appendix P, not the accuracy of an instrument used to analyze the sample. For the compounds of interest, i.e., benzene, ethylene, propylene, 1,3-butadiene, and all the butene isomers, sample collection, transfer and processing can introduce greater errors in the overall measurement than that of the analytical instrument.

This evaluation attempted to address the following issues for each system

- A) A comprehensive list of recommendations for improvement for each methodology, ranked in order of importance to achieve the data quality objectives this work order and associated cost for implementation by users. Associated cost for implementation shall include cost data for the instrumentation;
- B) A list of recommendations to adapt any appropriate methods for continuous or semi-continuous measurement;
- C) A description of any special considerations for VOC speciation;
- D) A comprehensive list of recommendations for the most appropriate sampling and analytical methodologies for each of the five compounds or groups of compounds of special interest, i.e., benzene, ethylene, propylene, 1,3-butadiene, and all the butene isomers;
- E) A technical assessment of each method to identify any compounds or classes of compounds for which the method would not be appropriate;
- F) An assessment of each method's ability to simulate the mass transfer that occurs at cooling towers and any recommendations to allow the method to better simulate the cooling tower;
- G) An assessment of each method's ability to be adapted to measure continuously or semi-continuously and any recommendations to accomplish that adaptation;
- H) A description of the assessment of matrix effects related to water quality (dissolved solids, salinity, residual chlorine, interaction of contaminant with water, etc.);
- I) A detailed description of the laboratory testing protocols including a demonstration of compliance with standards outlined in TCEQ WO No. 55078-03-07, Attachments A and B; and
- J) The results (raw and refined data) of any laboratory testing and analysis of that testing and any conclusions to be drawn from that testing;

This evaluation was performed as a series of subtasks with a compilation of the results of the subtask prepared as its own subtask. The subtasks were organized into two categories: laboratory testing, and literature reviews and surveys. The scope of work performed in each of these two categories are described in Sections 2.2.1 and 2.2.2.

2.2.1 TCEQ Sampling Procedures Manual, Appendix P Tests

The purpose of this task was to conduct tests in a laboratory setting using a Modified El Paso column system that complies with the TCEQ Sampling Procedures Manual, Appendix P to obtain data on an Appendix P compliant system using Summa canisters, Tedlar bags and EPA volatile organic analyses (VOA) vials to collect air and water samples. Additionally, this task was also to obtain data using a flame ionization detector (FID) analyzer to measure total VOC concentrations in the exhaust air for the system. A series of four tests were designed to provide for comparison of laboratory measurements using this system and to answer assess the methods ability to achieve measurement data quality objectives identified this work order for continuous monitoring of VOCs.

The VOC sampling, measuring, monitoring, and testing methods selected for evaluation in this task were: Modified El Paso Method with FID, Modified El Paso Method with Summa canister, Modified El Paso Method with Tedlar™ bag, and the method specified in 40 CFR 61, Subpart FF, Section 61.3559(c)(3) commonly known as the VOA method. The evaluation of these methods consisted of a series of four laboratory tests conducted with a special test system constructed for this evaluation. The test system and test procedure is described in detail in Appendix D of this report. The four tests performed are summarized in Table 1.

Table 1. Appendix P Tests Conducted

Background Water Quality	VOC Concentration in Background Water Entering El Paso System Air Stripping Column			
	Detection Limit (D) 10 ppbw Test ID: A-DI-D	Low Level (L) 50 ppbw Test ID: A-DI-L	Medium Level (M) 100 ppbw Test ID: A-DI-M	High Level (H) 1000 ppbw Test ID: A-DI-H
Dionized Water (Chlorine = 0 ppmw, TDS = CT TDS*)	3 Runs	3 Runs	3 Runs	3 Runs

* TDS = total dissolved solids, CT TDS = cooling tower total dissolved solids (nominal value)

2.2.2 Continuous VOC Monitoring/Sampling Methods

The purpose of this task was to perform a literature evaluation of other selected continuous VOC monitoring/sampling methods to determine:

- A. How the method achieves, determines, and assures equilibrium (steady-state) during measurements,
- B. Critical parameters for application and range of operation,
- C. Quality assurance/quality control, and calibration requirements,
- D. Recommended preventive maintenance schedule for the sampling portion of the device,
- E. The sensitivity of the method to environmental changes, and
- F. Whether the method are intrinsically safe.

This evaluation focused on identifying alternative monitoring/sampling systems that could detect the high interest highly reactive (HR) VOCs, i.e., ethylene, propylene, 1,3-butadiene, isomers of butene, and benzene, and also meet the minimum requirements set forth by the TCEQ in

Appendix P.

Approach

This scope of this evaluation consisted of a literature search and survey of selected VOC monitoring/sampling instrument manufacturers that may have products which can or may be used for continuous VOC monitoring of the following high interest HR VOCs: ethylene, propylene, 1,3-butadiene, isomers of butene, and benzene. The TCEQ has defined continuous as a minimum of one sample every 15 minutes. Technical information for this evaluation was to be obtained from equipment manufacturers, industrial representatives, and internet searches. Additionally, a questionnaire, included in Appendix F, was provided to each of the instrument manufacturers invited to participate in this evaluation.

The evaluation of each method/instrument was based entirely upon responses to the questionnaire as well as any additional product literature that was provided with their response. Responses received were reviewed and follow-up phone calls were placed clarify responses and to develop as consistent a level and type information as possible from each manufacturer. If no response to the survey was received after follow-up phone contact to ensure that the survey was received by the manufacturer, that company was then omitted from further inclusion in this evaluation. Due to budget and time constraints, this literature evaluation was limited to no more than ten systems and no lab or field-testing was conducted.

Sampling and Monitoring Criteria

One of the primary challenges in sampling for the HR VOCs is assuring that the compounds are not lost during the sample collection or analysis process. The selected continuous VOC monitoring/sampling methods were evaluated based on their ability to meet this criterion as well as answers to the following questions.

- A. How does the method achieve, determine, and assure equilibrium (steady state) during measurements?
- B. What are the critical parameters for application of the instrument and its appropriate range of operation?
- C. What are the QA/QC or calibration requirements?
- D. What is the recommended preventative maintenance schedule for the sampling portion of the device?
- E. What is the sensitivity of the method to environmental changes (e.g., ambient temperature, humidity, wind), and is it intrinsically safe?

The questionnaire submitted to the instrument manufacturers requested additional information that was also used in this evaluation. This information included characteristics about the system/instrument such as ease of use, maintainability, and cost. When possible, the instrumentation was evaluated as a complete sampling and analysis system. However, this was often not possible since several manufacturers provided information about their sampling instrumentation separately from their analysis instrumentation.

2.3 Evaluation of Instruments for Continuous Measurement of Cooling Water Flow Rate

Industrial cooling towers remove thermal energy from the cooling water that is transferred to it

from the process flows being cooled. The flow rate of the cooling water is adjusted to achieve the desired thermal performance, i.e., temperature control of the process flow.

The purpose of this task was to gather information on typical measurement devices that are currently being used or that may be used to measure cooling water flow rates, manufacturer information and contacts, technical specifications, flow measurement accuracy, and any limitations in their application to industrial cooling water. A recent study (URS, 2003) conducted by URS Corporation for the Texas Environmental Research Consortium found that the flow rate of cooling water in industrial cooling towers in the Houston, Texas area was measured directly in less than 17% (15) of the towers for which data was provided (90). For the others, the cooling water flow rate provided in the survey was an estimate based on pump capacity.

This task was limited to information that could be obtained through a literature review. No laboratory or field testing/measurements were performed as part of this task.

The approach used to evaluate the cooling water flow measurement devices was to identify the most common flow meters used and those that may be used through a literature review of applicable industrial cooling tower systems, from conversations with chemical process industry representatives, and from cooling tower design company manufacturers. These flow meters were grouped (types) by the measurement principle(s) employed. For these flow meter types, technical information was compiled on sizes, models and costs, the principle(s) on which the measurement is based, and the expected measurement accuracy based on the manufacturers' literature and other critical application parameters, i.e., location in the pipeline, upstream and downstream pipeline characteristics, ease of calibration, and frequency, level and ease of maintenance required to remain in calibration between calibration intervals. One flow meter typically representative of each of the major types (method of flow measurement) of flow meters most commonly used or that may be used in cooling water applications was then included in this evaluation. The selection of the representative for each type was based primarily on accuracy and characteristics of the product that are found in most other models of that type meter. Based on this information, an evaluation of the quantitative and qualitative aspects of the measurements that these devices may provide in use and their relative costs both initially and for maintenance.

This study was not an exhaustive review of all types of flow meters. Due to budget and time constraints, the study was limited to the information that could be obtained from literature reviews and from process industry representatives, flow meter manufacturers and cooling tower design companies. It should be emphasized that the information developed in this manner without laboratory or field measurements will be extremely limited in use and should not be the basis for measurement decisions or selection of equipment for all cooling water systems

2.4 Development of a Mass Transfer Model of VOC Emissions from Cooling Towers

The purpose of this task was to provide information that could be used to address Item F in Section 2.2 of this report. Specifically, how does the mass transfer that occurs in a methods procedure for measuring the concentration of the VOCs in the cooling water compare to the mass transfer that occurs in the cooling tower when these VOCs are dissipated to the air during the evaporative cooling that occurs in the cooling tower. To assist in making this comparison, a

computer model of the mass transfer that occurs in a cooling tower was developed to simulate the mass transfer of VOCs that are released from the cooling water in the cooling tower.

3.0 Results and Analysis of Results

3.1 Evaluation of Selected Leak Detection Methods

3.1.1 Summary of Method Descriptions and Characteristics

3.1.1.1 Hydrocarbon Trap

Method Description

Results of the literature search using the University of Texas at Austin (UT) library database and the Internet to obtain journal articles, reports, and conference papers related to hydrocarbon traps produced only one product of a hydrocarbon trap method suitable for detection of VOCs in cooling tower water. This hydrocarbon trap is the *Leak-Appear Hydrocarbon Trap*, which is manufactured by BetzDearborn Inc. The *Leak-Appear Hydrocarbon Trap* for water is a continuous monitoring device that collects hydrocarbon vapors from the cooling water passing through it. The Trap can be used in any refinery, hydrocarbon processing plant, or similar facility where hydrocarbons are suspected of being present in the cooling water system. Figure 1 shows the Leak-Appear Hydrocarbon Trap by BetzDearborn Inc. Figure 2 shows a detailed installation drawing. The *Leak-Appear Hydrocarbon Trap* is installed by tapping into the cooling water return riser of the cooling tower and discharging directly into the cooling tower basin.



Figure 1. Leak-Appear Hydrocarbon Trap (GEBetz, 2003)

The trap must be connected to the cooling tower return riser such that a flow of 5 gallons per minute will flow through the trap. The maximum operating pressure of the trap is 20psig. The *Leak-Appear Hydrocarbon Trap* includes a flow-restricting device that controls the water flow rate to a maximum flow rate of 5 gallons per minute (1.1m³/h). As water flows through the trap, hydrocarbon vapors are separated from the water flow and rise into the calibration cylinder, which is a graduated cylinder mounted vertically and perpendicular to the water flow. Over time, the water in the calibration cylinder is displaced by the hydrocarbon vapors. These vapors can be extracted with a syringe and injected into a gas chromatograph (GC) to determine the composition of the vapor in the cylinder. From the hydrocarbon components identified in the GC analysis, and the rate of accumulation of hydrocarbon vapors in the calibration cylinder, the cooling water recirculation rate, and the flow through the hydrocarbon trap, and an estimate of the severity of any leaks from one or more heat exchangers can be made. Process samples can then be collected from the suspect exchangers and analyzed for comparison to the sample collected from the calibration cylinder.

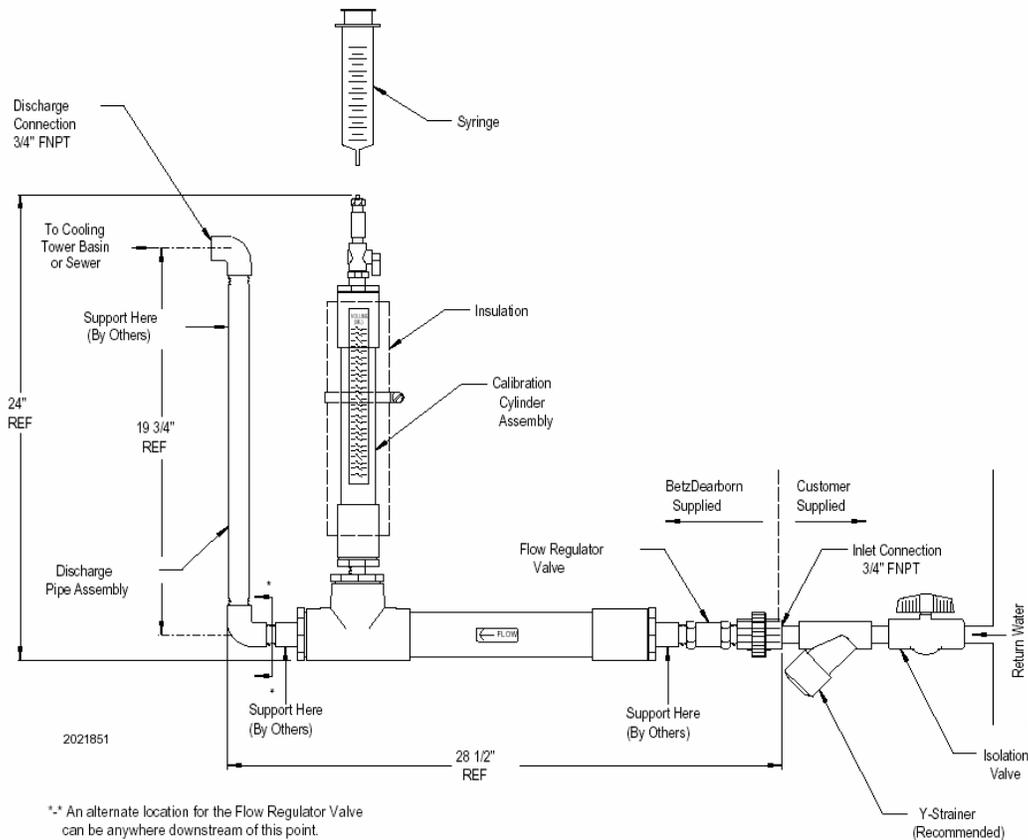


Figure 2. Typical Installation Drawing (GEBetz, 2003)

Principle of Operation

The *Installation, Operation & Maintenance Instruction Manual* of the *Leak-Appear Hydrocarbon Trap* states that the *Leak-Appear Hydrocarbon Trap* can be operated in either of two configurations: Sensitive Mode or Monitor Mode.

The *Sensitive Mode* utilizes a pressure drop, created by the flow-regulating valve located at the trap inlet, from the static pressure in the line at the cooling water return riser to about 1psig to cause separation of gases from the water. Because the trap must be installed to empty directly into the cooling tower basin, i.e., 0psig static head at the basin, this 1psig is the static pressure drop through the device after the flow-regulating valve. Air and hydrocarbons are forced out of the water when the pressure in the water decreases due to the pressure drop caused by the flow-regulating valve. This is due to the fact that the solubility of air (and gases) in water is a function of temperature and pressure. Their solubility generally decreases with increasing temperature and decreases as the partial pressure (or concentration in the air above the liquid) decreases.

Therefore if the static head in the line at the return riser is 30psig, then the pressure drop used primarily to cause separation of gases from the liquid will be 29psi. Therefore, even without a process leak, some air will be collected in the trap due to the action of the pressure drop. This would also be due to the fact that air is less soluble in the warm water returning to the cooling

tower that at the cooler temperature when it leaves the cooling tower. Therefore, a gas phase is always formed in the calibration cylinder in this mode. There is no indication in the product literature how efficient the design of the unit is at capturing the gases in the calibration cylinder once they are extracted from the water. The less efficient the unit is the less accurate and sensitive the unit would be. The fact that the unit will remove air and hydrocarbons will not affect the performance of the trap as long as there are not significant amounts of air in the line. Any air collected in the calibrated cylinder can be compensated for in the GC analysis.

The manufacturer of this equipment does not report an overall sensitivity or detection limit but indicates in their product literature that the trap “is sensitive enough to extract contaminants from cooling water in the parts per billion (mg/L) range.” The specification for the detection limit for the high interest VOCs (benzene, ethylene, propylene, 1,3-butadiene, and all butene isomers) in this assessment is 10ppbw (10µg/L). The following relationship describes the relationship for the solubility of a gas in water.

$$C_l = C_g / (H_c \cdot ^\circ K)$$

where

C_l = Concentration of the gas in the liquid (mol/L)

C_g = Partial pressure of the gas (atm)

H_c = Henry’s Law constant (atm-L/mol-°K)

°K = Temperature (°Kelvin)

The following table provides the values of H_c for the high interest VOCs.

VOC	H_c (atm-L/mol-°K)
Benzene	1.862E-05
Ethylene	7.651E-04
Propylene	6.577E-04
1,3-butadiene	2.470E-04
1 butene	7.819E-04
c-2 butene	7.718E-04
t-2 butene	7.517E-04

It can be calculated from the above equation that if a leak of 1 butene occurred, its equilibrium solubility at 1 psig, the pressure in the trap after the pressure drop, and a water temperature of 85°F (29.4°C), which is in the range of typical cooling tower water return temperatures, would be 4.512mol/L (253g/L). For 1,3-butadiene, its solubility would be 14.3mol/L (801g/L). These two compounds provide the minimum and maximum solubilities, respectively, of the VOCS of interest with very high vapor pressures, i.e., ethylene, propylene, 1,3-butadiene, and all butene isomers. Since a detection limit of 10ppbw of 1 butene is equivalent to 10µg /L, it does not appear that the pressure drop would be adequate to extract and therefore detect concentrations as low as 10ppbw. For compounds such as benzene, which would have a solubility of 190mol/L (14,795g/L) at 85°F (29.4°C) and 1psig, the pressure drop in the trap would fail to detect these higher solubilities (concentrations) of benzene in the water. These calculations have assumed that the partial pressure of the gas is equal to the total pressure, i.e., that air is not present in the line. Since air can be present in the line, the actual solubilities would be lower depending on the

amount of air in the line. Even if these partial pressures were two orders of magnitude lower, the solubilities would still be far in excess of 10µg /L.

For the VOCs, which have very high vapor pressures, these typical cooling water conditions (20psig and 85°F and 1 psig and 85°F) would ensure that there would be no VOC in the liquid phase. Therefore the solubility of the VOC as predicted by Henry's Law would be a good approach to theoretically estimate the amount of the compound that would remain in solution at 1psig and 85°F. For benzene, the trap would perform even poorer in that most of the benzene will not volatilize at 85°F, since its boiling point is 216°F (102°C). Hence more of the compound will remain in solution and will not be affected by the pressure drop of the trap.

The *Monitor Mode* does not utilize a pressure drop; the water passing through the trap is at header pressure. In this configuration, the flow regulator valve is located at the trap outlet. The hydrocarbon trap will collect vapors only when the capacity of the water to hold the dissolved gas is exceeded. In this mode, the trap can operate for months without any measured displacement in the sample cylinder. Vapors will collect in the trap only when a leak of sufficient severity exists such that the gas's solubility in water is exceeded. For the compounds of interest, the solubility would be the solubility at 20psig and 85°F (29.4°C). These solubilities will be 2.2 times more (2.4atm/1.07atm) than at 1psig with the pressure drop across the regulating valve.

3.1.1.2 Chlorine Usage

Method Description

Molecular chlorine in the form of sodium hypochlorite is added to the recirculating water used in cooling towers to control biofouling. Sometimes gaseous chlorine is used. Chlorine is a strong oxidizing agent capable of reacting with many impurities in water including ammonia, proteins, amino acids, iron, manganese, and residual organic material. The amount of chlorine required to react with these substances is referred to as the chlorine demand.

Chlorine also reacts readily with organic compounds such as organic nitrogen, phenols, and most acetyl groups. As such, chlorine will also react with most VOCs including the ones of interest in this study. The following examples explain the reaction between chlorine and ethylene. Ethylene (C₂H₄) has a double bond as shown in Figure 3.

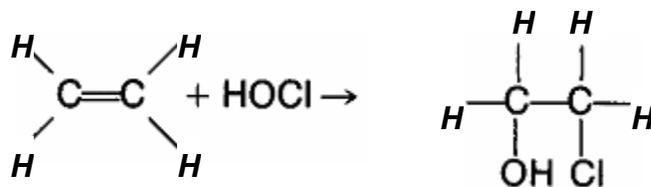


Figure 3. Ethylene structure (cited from Snoeyink and Jenkins, 1980)

For most compounds with double bonds, this reaction is too slow to be of importance in water treatment .

Trihalomethanes have the general form CHX₃ where X can be Cl, Br, or I. Chloroform, CHCl₃,

is of particular interest because of the chlorine reaction with organic substances. A series of reactions demonstrating the basic steps by which chloroform may be produced during water treatment is shown in Figure 4.

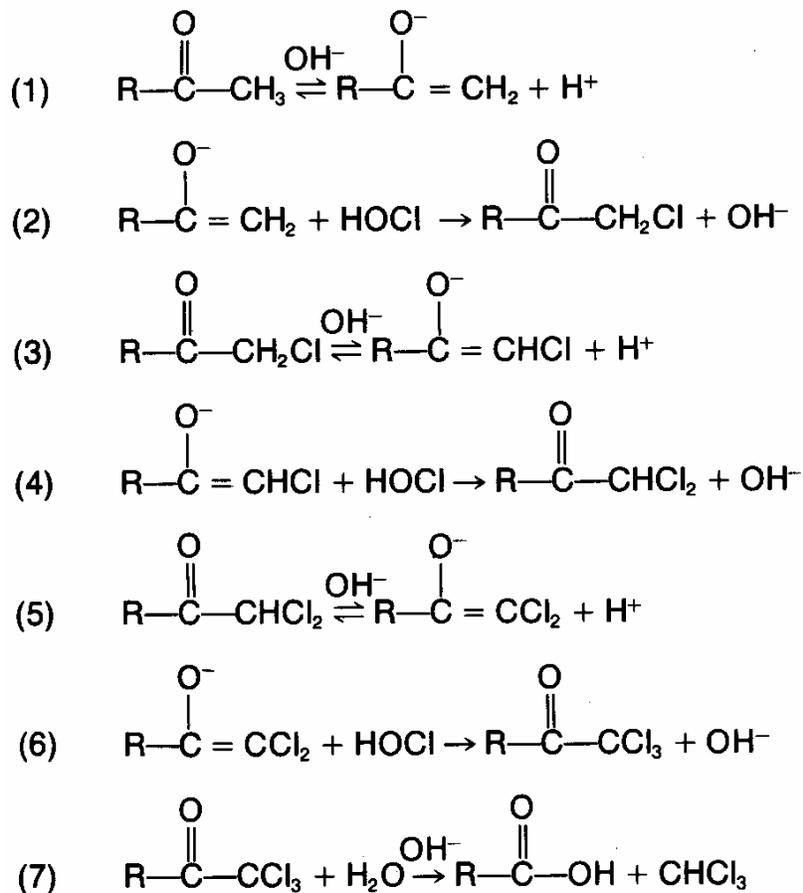


Figure 4. Trihalomethane formation reactions (Cited from Snoeyink and Jenkins, 1980)

The slow steps in the reactions are (1), (3), and (5). Because these are favored in the presence of OH⁻, the reaction proceeds much more rapidly at high pH than at low pH. Not all compounds that have the acetyl group, react rapidly. For example, the reaction with acetone, is too slow for it to be of concern for trihalomethane formation.

Once chlorine has been added to the cooling water (the chlorine dose) and after sufficient time has elapsed to allow for chemical reactions to occur, the chlorine demand (usage) can be determined by subtracting the total residual chlorine concentration in the cooling water from the chlorine dose that was added. The total residual chlorine consists of two components: free and combined. Free chlorine concentration includes the aqueous molecular chlorine, hypochlorous acid, an hypochlorite ion. The relative proportion of each of these forms is pH- and temperature dependent. At the pH of most waters, hypochlorous acid and hypochlorite ion will predominate. Combined chlorine consists of the chloramines species monochloramine, dichloramine and

nitrogen trichloride. Therefore, to assess chlorine usage, one must measure the chlorine concentration in the water. Methods to measure the residual free, combined and total chlorine concentrations are discussed in Appendix B of this report.

Residual (free) chlorine in cooling water should typically be the range of 0.2-0.5ppm (Cooling Technology Institute (CTI), 2003; Exxon Mobil Chemical, 2003). In order to maintain this concentration in cooling water, chlorine is added as needed. If there is a VOC leak into the cooling water, a higher chlorine demand will result because the VOC will react with the chlorine and consume chlorine in the cooling water. One approach to determine the effect of a leak of 10ppbw of VOCs, would be to compare the magnitude of the addition of the VOC material to the magnitude of other organic components in the water that are also being consumed by the chlorine. Since the typical TOC range in cooling water is 75ppm to 100ppm or 75mg/L to 100mg/L, the organic carbon introduced by a 10ppbw VOC leak would be approximately 8.6µg/L. This represents an increase in TOC of 0.011%. Since chlorine demand is an independent characteristic of the water quality that will depend on many factors, it may vary from 2 to 15ppm or more. If we assume a chlorine demand of 5.0ppm for illustrative purposes and that this chlorine demand is due exclusively to the presence of the organic materials in the cooling water, then a 0.011% increase in chlorine demand would be a 0.55ppb or a 0.55µg/L increase in chlorine demand and comparable decrease in residual chlorine concentration. The change in residual chlorine concentration would actually be less than this as the chlorine demand is driven by more than just the TOC content in the water, therefore the addition of the 10ppbw VOC leak would actually represent a smaller percentage of the chemical reactions creating the chlorine demand. Therefore the change in chlorine concentration due to a VOC leak of 10ppbw would be less than 0.55ppb or 0.55µg/L. If one could assume that this change in chlorine concentration were due solely to the VOC leak, then a measurement method with a detection limit at least this low would be required. However, as discussed in Appendix B, standard methods for measurement of chlorine in water typically have detection limits of 10 to 100µg/L. Hence detection of the changes in chlorine concentration at 10ppbw would not be possible. Furthermore, as discussed earlier in this section, both the chlorine concentration and the organic composition in the water will change due to other factors which cannot be distinguished from the change due to a VOC leak.

3.1.1.3 Oxidation-Reduction Potential (ORP) Method

Oxidation-Reduction Potential (ORP), measured in millivolts (mV) is a primary approach to standardizing water disinfection parameters. ORP is related to the concentration of oxidizers or reducers in a solution, and their activity or strength. It provides an indication of the solution's ability to oxidize or reduce another material. ORP monitoring is normally accomplished by using a platinum electrode. The process exposed to the platinum electrode produces a chemical reaction with the platinum and oxidizes or reduces the platinum band. This process generates a millivolt (mV) signal, which is normally of the magnitude of ±2000mV. Platinum electrodes have been utilized to monitor chlorine residuals in cooling tower systems and swimming pools. Normally, in these systems, the only variable changing is the chlorine level and, therefore, the ORP reading may be equated to chlorine residual.

For most purposes, water is generally considered “neutral” with regards to its ORP value. Water solutions are actually very weak oxidizing solutions, a result of dissolved oxygen that is nearly

always present. Consider the reaction between water and low carbon steel, where corrosion (oxidation of the steel) will occur. Well water or city-supplied water will generally have an ORP value of between 200 and 250mV, a range that is considered the “zero” point (or standard potential). This value is actually achieved from a standard offset created in the design of standard industrial ORP electrodes (platinum measuring surface with a silver/silver chloride reference) of approximately 190mV, plus an additional oxidizing capability from the dissolved oxygen and trace chlorine residual that is in the range of 10 to 60mV. The addition of oxidizing chemicals will increase this value to greater than 250mV, while the addition of reducing chemicals will suppress it to less than 200mV.

The ORP value does not represent the actual concentration (mg/L) of free residual or total chlorine. This is because the equilibrium between the two forms of chlorine in the water shifts with changing pH. The molecular form of free chlorine in water is HOCl, or hypochlorous acid, a strong, fast-acting oxidizer. As the pH increases, the HOCl converts to its ionic form, OCl⁻ (the hypochlorite ion), which is a weaker, slower acting oxidizer. As a result, the pH has a significant affect on the oxidizing strength of any chlorine solution. Monitoring the concentration of chlorine alone would not indicate oxidization strength. Further, if the chlorine is combined with an amine or a stabilizer, the total chlorine concentration is also affected. These mixtures also do not provide significant oxidizing capability. To maintain free chlorine in its most active form, solution pH should be maintained between 7.4 and 7.6. An increase to a pH of 8.0 will convert 80 percent of the free chlorine to the hypochlorite ion form. This is 80 to 300 times less effective as an oxidizer, depending on the specific bacteria involved.

As stated earlier, ORP is a measure of the oxidizing or reducing strength of the solution. VOCs in water are not oxidizers or reducers. Thus, the ORP would not be affected by the mere presence of VOCs in the water. The change in chlorine concentration in the water that would result from a VOC leak into the water would effect a change in the ORP value because chlorine is an oxidizer and some chlorine would be consumed in oxidizing the VOC. However, the ORP will be an accurate prediction of only free residual chlorine concentration if and only if the pH of the solution is constant because the free residual chlorine concentration value measured by the ORP also changes considerably as the pH of the sample. As an example, if the free chlorine concentration were 2.0ppm at a pH of 7.6 and the pH were changed to 8.0, the free chlorine concentration would decrease to 0.4ppm. Whereas the introduction of VOCs at a level of 10ppbw would cause a decrease in residual chlorine on the order of 0.55ppb or a 0.55µg/L (see Section 3.1.1.2). As explained in Section 3.1.1.5 in this report, pH change is strongly affected by many factors such as the addition of chlorine and other chemicals, including those used for water treatment. Hence, any change in ORP could not be exclusively attributed to the introduction of VOCs into the cooling water.

3.1.1.4 VOC Leak Detection by Measurement of Total Organic Carbon

In order to consider detection of the volatile organic compounds of interest in this study using the measurement of total organic carbon concentration (TOC) as the indicator requires use of a measurement method that can satisfy two criteria. The first criterion is to be able to accurately measure changes in the TOC concentration produced when any one or more of the volatile organic compounds of interest is leaked into the cooling water to produce a concentration of at least 10µg/L. Since TOC concentration measurements are measures of only the organic carbon

concentration, then a concentration 10µg/L of say ethylene (molecular weight, MW = 28), containing 2 carbon atoms per mole, would require a detection level concentration for the organic carbon concentration only of 8.6µg/L (10µg/L times 24µg C per mole divided by 28µg ethylene/mole). The TOC detection level concentration for each of the volatile organic compounds of interest are shown below.

VOC	MW	No. Carbon Atoms	TOC Detection Level (µg/L)
Benzene	78	6	9.2
Ethylene	28	2	8.6
Propylene	42	3	8.6
1,3-butadiene	54	4	8.9
1 butene	56	4	8.6
c-2 butene	56	4	8.6
t-2 butene	56	4	8.6

The second criterion that must be satisfied to accurately depend on TOC concentration measurements is to be able to determine that any change in TOC concentration can be attributed to the introduction of one or more of the volatile organic compounds of interest and not to some other organic source. Of these two criteria, the detection level criterion will be examined first.

To measure TOC at the concentrations found in cooling tower water, typically in the range of 75 to 100 mg/L, the standard measurement methods used depend on determining the fractions of total carbon (TC). The fractions of total carbon are defined as inorganic carbon and total organic carbon (TOC). Inorganic carbon consists of the carbonate, bicarbonate, and dissolved carbon dioxide (CO₂) compounds. TOC consists of all carbon atoms covalently bonded in organic molecules, dissolved organic carbon (DOC)—the fraction that passes through a 0.45-µm-pore-diam filter, suspended organic carbon (particulate organic carbon)—the fraction of TOC retained by a 0.45-µm-pore-diam filter, purgeable organic carbon (volatile organic carbon)—the fraction of TOC removed from an aqueous solution by gas stripping under specified conditions, and nonpurgeable organic carbon—the fraction of TOC not removed by gas stripping. In most water samples, the inorganic carbon fraction is many times greater than the TOC fraction.

To determine the quantity of organically bound carbon, the organic molecules must first be broken down and converted to a single molecular form that can be measured quantitatively. TOC methods utilize high temperature (above 950°C), catalysts, and oxygen or, alternatively, lower temperatures (<100°C) with ultraviolet irradiation, chemical oxidants, or combinations of these oxidants to convert organic carbon to CO₂. The CO₂ may be purged from the sample, dried, and transferred with a carrier gas to a nondispersive infrared analyzer or coulometric titrator. Alternatively, it may be separated from the sample liquid phase by a membrane selective to CO₂ into high purity water in which a corresponding increase in conductivity is related to the CO₂ passing through the membrane.

The determination of which method to use depends on the expected concentration of TOC in the sample. The High-Temperature Combustion Method, SM 5310B, is suitable for samples with higher levels of TOC that would require dilution for the various persulfate methods (SM 5310C or D). SM 5310B is also preferable to use on samples containing high levels of suspended

organic carbon, which may not be efficiently oxidized by persulfate and/or UV methods. The minimum detectable concentration of SM 5310B is 1 mg C/L. This method has some interferences that can introduce significant errors in the measurement of the inorganic carbon fraction due to the high vapor pressures of the organic compounds of interest in this study. Some or all of these volatilized compounds maybe lost in the purging of the CO₂ produced when the inorganic carbon is converted to CO₂ by acidification. However, one instrument manufacturer (LAR Analytical, Inc.) has developed an instrument that operates at a combustion temperature of more than 1200°C, which allows determination of total carbon and inorganic carbon without the loss of the volatile organic compounds either in the conversion of inorganic carbon to CO₂ or in the measurement of total carbon. Even with this proprietary design, the detection limit of this online system is only 0.1 mg C/L, well above the 8.6 µg/L required for this study.

The second criterion also cannot be met with TOC measurements in that this measurement method produces total measures of organic carbon with no attribution to the organic source. Therefore, this method is not a viable leak detection method.

3.1.1.5 pH Measurement

When a cooling tower is in operation, the pH of the cooling tower water will be affected by the addition of water treatment chemicals to control corrosion, organics in the water, the addition of CO₂ from air scrubbing, and the increased alkalinity due to operating at higher cycles (the ratio of solids in the circulating water to the solids in the make-up water). In general, the net effect is that the pH of the cooling tower water will increase. The presence of calcium bicarbonate and magnesium bicarbonate are the main reasons the alkalinity must be increased. The water treatment chemicals typically used include biocides (e.g., sodium hypochlorite, molecular chlorine gas, sodium bromide, ozone, chlorine dioxide, etc), surfactants, biodispersants and antifoams. Therefore, in most cases, an acid is added to the tower basin to reduce the pH of the blow down water to between pH 6 and 9, an acceptable level to discharge into a municipal sanitary sewer system. Furthermore, as discussed in Appendix C, the effect on pH by the addition of the water treatment chemicals depends on the chemical and its form.

The measurement of pH is typically made using Standard Method 4500-H+ B. Electrometric Method. This measurement method is described in the Appendix C. The detection limit for this method is 0.1 pH units. Therefore, this measurement method's sensitivity is very limited over the typical cooling water pH range (pH 6 to 9). Since the leak of a VOC into the cooling water would primarily affect the consumption of chlorine, probably by less than 0.011%, there would be no direct change in pH strictly due to any change in chlorine concentration. Additionally, since none of the VOCs of interest, i.e, benzene, ethylene, propylene, 1,3-butadiene, and all butene isomers, form aqueous solutions, they would not directly change the pH of the water.

3.1.2 VOC Leak Detection Methods Evaluation Summary

Hydrocarbon Trap

This device depends on a decrease in pressure across a flow regulating valve to extract hydrocarbons from the cooling water. This change in pressure is also related to change in the solubility. However, the solubilities for all of the VOCs of interest in this project at the high and low pressures of the device exceed the solubility equivalent to 10ppbw. Hence, the device would

extract no VOCs from the cooling water and would produce false negative measurements if used to detect leaks of these compounds.

Chlorine Usage

The change in chlorine concentration due to a VOC leak of 10ppbw would be less than 0.55ppb or 0.55µg/L. If one could assume that this change in chlorine concentration were due solely to a VOC leak, then a measurement method with a detection limit at least this value would be required. However, as discussed in Appendix B, standard methods for measurement of chlorine in water typically have detection limits of 10 to 100µg/L. Hence detection of the changes in chlorine concentration at 10ppbw would not be possible. Furthermore, both the chlorine concentration and the organic composition in the cooling water will change due to other factors. These changes cannot be distinguished from a change due to a VOC leak using chlorine concentration measurements only.

Oxidation-Reduction Potential

Oxidation-reduction potential is affected by the oxidizing potential of the chlorine not merely its concentration. The molecular form of free chlorine in water is HOCl, or hypochlorous acid, a strong, fast-acting oxidizer. As the pH increases, the HOCl converts to its ionic form, OCl⁻ (the hypochlorite ion), which is a weaker, slower acting oxidizer. As a result, the pH has a significant affect on the oxidizing strength of any chlorine solution. Monitoring the concentration of chlorine alone would not indicate oxidization strength. Hence, any change in ORP could not be exclusively attributed to the introduction of VOCs into the cooling water.

TOC

A detection limit of 8.6 µg/L C would be required to identify a 10ppbw leak of ethylene or 1 butene. The detection limit of currently available this online systems are only 0.1 mg C/L, well above the 8.6 µg/L required for this study. Additionally, the changes in concentration of organic carbon would not be able to be attributed to a change in a specific organic source, of which there are many in cooling water.

pH

The change in pH of the cooling water due only to a VOC leak would be only one of many factors contributing to the change in pH level. Additionally, the detection limit of the methods and instruments used to make this measurement are quite high (0.1 pH unit) coupled with the pH range (pH 6 to 9) found in cooling water make this approach relatively insensitive to small (less than 0.1 pH unit) changes in pH.

Leak Detection Methods Summary

None of the five methods evaluated meet the criteria required by the TCEQ for detecting VOC leaks in cooling water. In general the detection limits for these methods/instruments are too high and they are unable to exclusively attribute changes in the parameter measured to the introduction of a VOC due to a leak.

3.2 Evaluation of Selected VOC Sampling, Measuring, Monitoring, and Testing Methods

3.2.1 Modified El Paso Method Tests per TCEQ Sampling Procedures Manual, Appendix P
Four tests were conducted using the test system specially designed and built to test the modified El Paso Method system provided by the TCEQ. A detailed description of the test system is included in Appendix D along with the test procedure that was followed to perform each of the four tests shown in Table 1. Each test consisted of three runs at the same test conditions. For each test, water containing a known concentration of VOCs was introduced into the modified El Paso system following the TCEQ Sampling Procedures Manual, Appendix P.

The four VOC concentrations used were nominally 10 ppbw (detection limit), 50 ppbw (low level), 100 ppbw (medium level), and 1000 ppbw (high level). The detection limit concentration test (Test ID: A-DI-D) was designed to assess the performance of the FID analyzer and modified El Paso Test system at the detection limit as specified in the Measurement Data Quality Objectives, i.e., 10 ppbw. The results of the three runs for this test are summarized in Tables 2a, 2b, and 2c. The actual (versus nominal) speciated VOC concentration in the water is reported in the column “Reference VOC Concentration in Water”. Water samples of the inlet water flow to the El Paso air stripping column were collected in a VOA vial and a 0.5 L Tedlar bag. Results of the speciated analyses of the water samples using the special purge and trap system described in Appendix D and analyzed per EPA Method TO 14A are reported in Section 1 of the tables.

Gas samples were collected in Summa canisters at the El Paso air stripping column exhaust gas exit. The concentration of the total VOC concentration in the same exhaust stream was also measured using the Thermo Environmental Instruments Model TVA-1000B Toxic Vapor (FID) Analyzer (methane calibration). Results of the speciated analyses of the Summa canister samples per EPA Method TO 14A and the average FID reading are reported in Section 2 of the tables.

The three remaining tests were conducted using VOC concentrations in the water representative of a low level VOC concentration (Test ID: A-DI-L), a medium level VOC concentration (Test ID: A-DI-L), and a high level VOC concentration (Test ID: A-DI-H) in a cooling water stream. The three nominal VOC concentrations selected for these tests were: low level = 50 ppbw, medium level = 100 ppbw, and high level = 1000 ppbw. The results of the three runs for these tests are summarized in Tables 3a, 3b, 3c, 4a, 4b, 4c, 5a, 5b, and 5c. The actual (versus nominal) speciated VOC concentration in the water is reported in the column “Reference VOC Concentration in Water”. As in the detection limit test, water samples of the inlet water flow to the El Paso air stripping column were collected in a VOA vial and a 0.5 L Tedlar bag. Results of the speciated analyses of the water samples are reported in Section 1 of the tables. Additionally for these three tests, water samples at the outlet of the El Paso air stripping column were also obtained in 0.5 L Tedlar bags and analyzed. Results of the speciated VOC concentrations are reported in Section 1 as well. Using this result and the “Reference VOC Concentration in Water”, a stripping efficiency of the El Paso column was calculated and is also presented in Section 1.

Table 2a
Test ID: A-DI-D
Results Summary - Run # 1

Section 1: El Paso Column Inlet - Water Sampling Analyses: VOA Vial and Tedlar Bag

		Reference VOC Concentration in Water	Speciated VOC Concentration in VOA Vial (Inlet Sample)	VOA Vial Accuracy (% Difference)	Speciated VOC Concentration in Tedlar Bag (Inlet Sample)	Tedlar Bag Accuracy (% Difference)
Compound	MW	ppbw	ppbw	%	ppbw	%
Ethylene	28	0.5	0.2	-60	0.2	-60
Propylene	42	1.0	0.3	-70	0.3	-70
t-2-butene	56	1.5	0.4	-73	0.4	-73
1-butene	56	1.3	0.4	-69	0.4	-69
isobutene	56	3.5	0.4	-89	1.7	-51
c-2-butene	56	1.6	0.4	-75	0.4	-75
1,3 butadiene	54	1.6	0.3	-81	0.3	-81
Total		11.0	2.4	-78	3.7	-66

Section 2: El Paso Column Exit - Gas Sampling Analyses: Summa Canister and FID Analyzer

		Reference VOC Concentration in Water	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7-1, Using Summa Canister Sample Analysis (TO-14A)	Summa Canister Accuracy (Absolute Difference)	FID Analyzer Average Reading	Calculated Inlet TVOC Conc in Water per App. P, Eq. 7-1, Using FID Aver Reading
Compound	MW	ppbw	ppbw	ppbw	ppmv	ppbw as methane
Ethylene	28	0.5	0.7	0.2		
Propylene	42	1.0	1.2	0.2		
t-2-butene	56	1.5	1.8	0.3		
1-butene	56	1.3	1.6	0.3		
isobutene	56	3.5	4.3	0.8		
c-2-butene	56	1.6	1.9	0.3		
1,3 butadiene	54	1.6	1.8	0.2		
Total		11.0	13.3	2.3	0.64	8.45

Table 2b
Test ID: A-DI-D
Results Summary - Run # 2

Section 1: El Paso Column Inlet - Water Sampling Analyses: VOA Vial and Tedlar Bag

		Reference VOC Concentration in Water	Speciated VOC Concentration in VOA Vial (Inlet Sample)	VOA Vial Accuracy (% Difference)	Speciated VOC Concentration in Tedlar Bag (Inlet Sample)	Tedlar Bag Accuracy (% Difference)
Compound	MW	ppbw	ppbw	%	ppbw	%
Ethylene	28	0.5	0.2	-60	0.7	40
Propylene	42	1.0	0.3	-70	1.4	40
t-2-butene	56	1.5	0.4	-73	0.8	-47
1-butene	56	1.3	0.4	-69	1.3	0
isobutene	56	3.5	0.4	-89	3.0	-14
c-2-butene	56	1.6	0.4	-75	1.7	6
1,3 butadiene	54	1.6	0.3	-81	1.7	6
Total		11.0	2.4	-78	10.6	-4

Section 2: El Paso Column Exit - Gas Sampling Analyses: Summa Canister and FID Analyzer

		Reference VOC Concentration in Water	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7-1, Using Summa Canister Sample Analysis (TO-14A)	Summa Canister Accuracy (Absolute Difference)	FID Analyzer Average Reading	Calculated Inlet TVOC Conc in Water per App. P, Eq. 7-1, Using FID Aver Reading
Compound	MW	ppbw	ppbw	ppbw	ppmv	ppbw as methane
Ethylene	28	0.5	0.6	0.1		
Propylene	42	1.0	1.0	0.0		
t-2-butene	56	1.5	1.3	0.2		
1-butene	56	1.3	1.3	0.0		
isobutene	56	3.5	3.9	0.4		
c-2-butene	56	1.6	1.6	0.0		
1,3 butadiene	54	1.6	1.6	0.0		
Total		11.0	11.3	0.3	0.73	9.64

Table 2c
Test ID: A-DI-D
Results Summary - Run # 3

Section 1: El Paso Column Inlet - Water Sampling Analyses: VOA Vial and Tedlar Bag

		Reference VOC Concentration in Water	Speciated VOC Concentration in VOA Vial (Inlet Sample)	VOA Vial Accuracy (% Difference)	Speciated VOC Concentration in Tedlar Bag (Inlet Sample)	Tedlar Bag Accuracy (% Difference)
Compound	MW	ppbw	ppbw	%	ppbw	%
Ethylene	28	0.5	0.2	-60	1.3	160
Propylene	42	1.0	0.3	-70	2.7	170
t-2-butene	56	1.5	0.4	-73	2.4	60
1-butene	56	1.3	0.4	-69	3.2	146
isobutene	56	3.5	0.4	-89	4.9	40
c-2-butene	56	1.6	0.4	-75	3.7	131
1,3 butadiene	54	1.6	0.3	-81	4.0	150
Total		11.0	2.4	-78	22.2	102

Section 2: El Paso Column Exit - Gas Sampling Analyses: Summa Canister and FID Analyzer

		Reference VOC Concentration in Water	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7-1, Using Summa Canister Sample Analysis (TO-14A)	Summa Canister Accuracy (Absolute Difference)	FID Analyzer Average Reading	Calculated Inlet TVOC Conc in Water per App. P, Eq. 7-1, Using FID Aver Reading
Compound	MW	ppbw	ppbw	ppbw	ppmv	ppbw as methane
Ethylene	28	0.5	0.6	0.1		
Propylene	42	1.0	1.1	0.1		
t-2-butene	56	1.5	1.3	0.2		
1-butene	56	1.3	1.3	0.0		
isobutene	56	3.5	4.1	0.6		
c-2-butene	56	1.6	1.7	0.1		
1,3 butadiene	54	1.6	1.6	0.0		
Total		11.0	11.7	0.7		

Table 3a
Test ID: A-DI-L
Results Summary - Run # 1

Section 1: El Paso Column Water Sampling Analyses - VOA Vial and Tedlar Bag

		Reference VOC Concentration in Water	Speciated VOC Concentration in VOA Vial (Inlet) Sample	VOA Vial Accuracy (% Difference)	Speciated VOC Concentration in Tedlar Bag (Inlet) Sample	Tedlar Bag Accuracy (% Difference)	Speciated VOC Concentration in Tedlar Bag (Outlet) Sample	El Paso Column VOC Stripping Efficiency
Compound	MW	ppbw	ppbw	%	ppbw	%	ppbw	%
Ethylene	28	2.7	0.6	-79	1.8	-34	0.17	94
Propylene	42	4.5	1.1	-76	2.9	-35	0.26	94
t-2-butene	56	5.9	1.2	-79	3.4	-42	0.32	95
1-butene	56	5.7	1.2	-78	3.5	-38	0.35	94
isobutene	56	17.7	6.4	-64	14.3	-19	0.34	98
c-2-butene	56	7.0	1.9	-72	4.6	-34	0.36	95
1,3 butadiene	54	7.5	2.4	-67	5.1	-31	0.30	96
Total		51.1	14.9	-71	35.7	-30	2.10	96

Section 2: El Paso Column Gas Sampling Analyses - Summa Canister and FID Analyzer

		Reference VOC Concentration in Water	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7-1, Using Summa Canister Sample Analysis (RM 18)	Summa Canister (RM 18) Accuracy (% Difference)	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7-1, Using Summa Canister Sample Analysis (TO-14A)	Summa Canister (TO-14A) Accuracy (% Difference)	FID Analyzer Average Reading	Calculated Inlet TVOC Concentration In Water per App. P, Eq. 7-1, Using FID Average Reading
Compound	MW	ppbw	ppbw	%	ppbw	%	ppmv	ppbw as methane
Ethylene	28	2.7	2.4	-13	2.4	-12		
Propylene	42	4.5	3.8	-16	3.8	-16		
t-2-butene	56	5.9	4.5	-25	4.5	-25		
1-butene	56	5.7	4.6	-18	4.6	-18		
isobutene	56	17.7	14.0	-21	14.0	-21		
c-2-butene	56	7.0	5.6	-21	5.6	-21		
1,3 butadiene	54	7.5	5.9	-22	5.9	-21		
Total		51.1	40.7	-20	40.8	-20		

Table 3a (Continued)
Test ID: A-DI-L
Results Summary - Run # 1

Section 3: El Paso Column Gas Sampling Analysis - Tedlar Bag

		Reference VOC Concentration in Water	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7- 1, Using Analysis (RM 18) of Gas Sample	Tedlar Bag (RM 18) Accuracy (% Difference)
Compound	MW			
Ethylene	28	2.7	2.6	-6
Propylene	42	4.5	4.3	-5
t-2-butene	56	5.9	5.5	-7
1-butene	56	5.7	5.3	-6
isobutene	56	17.7	17.1	-3
c-2-butene	56	7.0	6.7	-5
1,3 butadiene	54	7.5	7.1	-5
Total		51.1	48.6	-5

Table 3b
Test ID: A-DI-L
Results Summary - Run # 2

Section 1: El Paso Column Water Sampling Analyses - VOA Vial and Tedlar Bag

		Reference VOC Concentration in Water	Speciated VOC Concentration in VOA Vial (Inlet) Sample	VOA Vial Accuracy (% Difference)	Speciated VOC Concentration in Tedlar Bag (Inlet) Sample	Tedlar Bag Accuracy (% Difference)	Speciated VOC Concentration in Tedlar Bag (Outlet) Sample	El Paso Column VOC Stripping Efficiency
Compound	MW	ppbw	ppbw	%	ppbw	%	ppbw	%
Ethylene	28	2.7	0.9	-66	1.9	-66	0.15	95
Propylene	42	4.5	1.6	-64	3.2	-64	0.23	95
t-2-butene	56	5.9	1.8	-69	3.6	-69	0.29	95
1-butene	56	5.7	1.9	-66	3.8	-66	0.31	94
isobutene	56	17.7	8.3	-53	14.0	-53	0.33	98
c-2-butene	56	7.0	2.6	-62	4.8	-62	0.32	95
1,3 butadiene	54	7.5	2.9	-61	5.2	-61	0.26	96
Total		51.1	20.2	-60	36.4	-60	1.90	96

Section 2: El Paso Column Gas Sampling Analyses - Summa Canister and FID Analyzer

		Reference VOC Concentration in Water	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7-1, Using Summa Canister Sample Analysis (RM 18)	Summa Canister (RM 18) Accuracy (% Difference)	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7-1, Using Summa Canister Sample Analysis (TO-14A)	Summa Canister (TO-14A) Accuracy (% Difference)	FID Analyzer Average Reading	Calculated Inlet TVOC Concentration In Water per App. P, Eq. 7-1, Using FID Aver Reading
Compound	MW	ppbw	ppbw	%	ppbw	%	ppmv	ppbw as methane
Ethylene	28	2.7	2.4	-11	2.4	-11		
Propylene	42	4.5	3.8	-15	3.8	-15		
t-2-butene	56	5.9	4.5	-25	4.5	-24		
1-butene	56	5.7	4.7	-18	4.7	-17		
isobutene	56	17.7	14.8	-16	14.9	-16		
c-2-butene	56	7.0	5.7	-20	5.7	-19		
1,3 butadiene	54	7.5	6.1	-18	6.1	-18		
Total		51	42	-18	42.2	-17	2.80	37.2

Table 3b (Continued)
Test ID: A-DI-L
Results Summary - Run # 2

Section 3: El Paso Column Gas Sampling Analysis - Tedlar Bag

		Reference VOC Concentration in Water	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7- 1, Using Analysis (RM 18) of Gas Sample	Tedlar Bag (RM 18) Accuracy (% Difference)
Compound	MW	ppbw	ppbw	%
Ethylene	28	2.7	2.7	-3
Propylene	42	4.5	4.4	-3
t-2-butene	56	5.9	5.6	-5
1-butene	56	5.7	5.4	-4
isobutene	56	17.7	17.5	-1
c-2-butene	56	7.0	6.8	-3
1,3 butadiene	54	7.5	7.3	-3
Total		51.1	49.7	-3

Table 3c
Test ID: A-DI-L
Results Summary - Run # 3

Section 1: El Paso Column Water Sampling Analyses - VOA Vial and Tedlar Bag

		Reference VOC Concentration in Water	Speciated VOC Concentration in VOA Vial (Inlet) Sample	VOA Vial Accuracy (% Difference)	Speciated VOC Concentration in Tedlar Bag (Inlet) Sample	Tedlar Bag Accuracy (% Difference)	Speciated VOC Concentration in Tedlar Bag (Outlet) Sample	El Paso Column VOC Stripping Efficiency
Compound	MW	ppbw	ppbw	%	ppbw	%	ppbw	%
Ethylene	28	2.7	0.9	-68	2.2	-20	0.16	94
Propylene	42	4.5	1.5	-67	3.8	-15	0.25	94
t-2-butene	56	5.9	1.6	-73	3.8	-36	0.31	95
1-butene	56	5.7	1.7	-69	5.0	-11	0.34	94
isobutene	56	17.7	7.7	-57	14.7	-17	0.33	98
c-2-butene	56	7.0	2.4	-65	5.1	-27	0.34	95
1,3 butadiene	54	7.5	2.7	-64	5.6	-25	0.28	96
Total		51.1	18.6	-64	40.3	-21	2.00	96

Section 2: El Paso Column Gas Sampling Analyses - Summa Canister and FID Analyzer

		Reference VOC Concentration in Water	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7-1, Using Summa Canister Sample Analysis (RM 18)	Summa Canister (RM 18) Accuracy (% Difference)	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7-1, Using Summa Canister Sample Analysis (TO-14A)	Summa Canister (TO-14A) Accuracy (% Difference)	FID Analyzer Average Reading	Calculated Inlet TVOC Concentration In Water per App. P, Eq. 7-1, Using FID Aver Reading
Compound	MW	ppbw	ppbw	%	ppbw	%	ppmv	ppbw as methane
Ethylene	28	2.7	2.5	-10	2.5	-9		
Propylene	42	4.5	3.9	-13	4.0	-12		
t-2-butene	56	5.9	4.6	-22	4.7	-21		
1-butene	56	5.7	4.8	-16	4.8	-15		
isobutene	56	17.7	15.1	-14	15.3	-14		
c-2-butene	56	7.0	5.8	-18	5.8	-17		
1,3 butadiene	54	7.5	6.3	-17	6.3	-16		
Total		51.1	43.0	-16	43.4	-15	2.48	33.0

Table 3c (Continued)
Test ID: A-DI-L
Results Summary - Run # 3

Section 3: El Paso Column Gas Sampling Analysis - Tedlar Bag

		Reference VOC Concentration in Water	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7- 1, Using Analysis (RM 18) of Gas Sample	Tedlar Bag (RM 18) Accuracy (% Difference)
Compound	MW	ppbw	ppbw	%
Ethylene	28	2.7	2.8	2
Propylene	42	4.5	4.6	1
t-2-butene	56	5.9	6.0	1
1-butene	56	5.7	5.7	1
isobutene	56	17.7	18.4	4
c-2-butene	56	7.0	7.1	2
1,3 butadiene	54	7.5	7.6	1
Total		51.1	52.2	2

Table 4a
Test ID: A-DI-M
Results Summary - Run #1

Section 1: El Paso Column Water Sampling Analyses - VOA Vial and Tedlar Bag

		Reference VOC Concentration in Water	Speciated VOC Concentration in VOA Vial (Inlet) Sample	VOA Vial Accuracy (%) Difference)	Speciated VOC Concentration in Tedlar Bag (Inlet) Sample	Tedlar Bag Accuracy (%) Difference)	Speciated VOC Concentration in Tedlar Bag (Outlet) Sample	El Paso Column VOC Stripping Efficiency
Compound	MW	ppbw	ppbw	%	ppbw	%	ppbw	%
Ethylene	28	4.5	4.0	-12	3.2	-30	0.17	96
Propylene	42	10.4	9.5	-9	7.4	-28	0.27	97
t-2-butene	56	13.3	14.4	8	10.7	-20	0.33	98
1-butene	56	13.9	14.5	5	11.9	-14	0.36	97
isobutene	56	14.5	14.8	3	12.5	-14	0.35	98
c-2-butene	56	19.1	19.9	4	16.7	-12	0.37	98
1,3 butadiene	54	18.2	17.0	-7	14.1	-23	0.30	98
Total		93.8	94.1	0	76.4	-19	2.16	98

Section 2: El Paso Column Gas Sampling Analyses - Summa Canister and FID Analyzer

		Reference VOC Concentration in Water	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7-1, Using Summa Canister Sample Analysis (RM 18)	Summa Canister (RM 18) Accuracy (%) Difference)	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7-1, Using Summa Canister Sample Analysis (TO-14A)	Summa Canister (TO-14A) Accuracy (%) Difference)	FID Analyzer Average Reading	Calculated Inlet TVOC Concentration In Water per App. P, Eq. 7-1, Using FID Aver Reading
Compound	MW	ppbw	ppbw	%	ppbw	%	ppmv	ppbw as methane
Ethylene	28	4.5	4.2	-7.5	4.2	-7.5		
Propylene	42	10.4	9.4	-8.9	9.5	-8.5		
t-2-butene	56	13.3	11.6	-12.9	11.6	-12.8		
1-butene	56	13.9	13.4	-3.0	13.5	-2.8		
isobutene	56	14.5	13.9	-4.0	13.9	-3.8		
c-2-butene	56	19.1	17.7	-7.1	17.8	-6.9		
1,3 butadiene	54	18.2	15.4	-15.3	15.5	-15.1		
Total		93.8	85.7	-8.6	85.9	-8.4	3.48	45.9

Table 4b
Test ID: A-DI-M
Results Summary - Run #2

Section 1: El Paso Column Water Sampling Analyses - VOA Vial and Tedlar Bag

		Reference VOC Concentration in Water	Speciated VOC Concentration in VOA Vial (Inlet) Sample	VOA Vial Accuracy (% Difference)	Speciated VOC Concentration in Tedlar Bag (Inlet) Sample	Tedlar Bag Accuracy (% Difference)	Speciated VOC Concentration in Tedlar Bag (Outlet) Sample	El Paso Column VOC Stripping Efficiency
Compound	MW	ppbw	ppbw	%	ppbw	%	ppbw	%
Ethylene	28	4.5	3.7	-19	3.4	-24	0.16	96
Propylene	42	10.4	8.5	-18	7.8	-25	0.26	98
t-2-butene	56	13.3	12.1	-9	10.4	-22	0.32	98
1-butene	56	13.9	12.6	-9	11.7	-15	0.35	97
isobutene	56	14.5	13.3	-8	12.5	-14	0.37	97
c-2-butene	56	19.1	17.8	-7	16.7	-13	0.35	98
1,3 butadiene	54	18.2	16.0	-12	14.4	-21	0.29	98
Total		93.8	84.0	-11	76.8	-18	2.10	98

Section 2: El Paso Column Gas Sampling Analyses - Summa Canister and FID Analyzer

		Reference VOC Concentration in Water	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7-1, Using Summa Canister Sample Analysis (RM 18)	Summa Canister (RM 18) Accuracy (% Difference)	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7-1, Using Summa Canister Sample Analysis (TO-14A)	Summa Canister (TO-14A) Accuracy (% Difference)	FID Analyzer Average Reading	Calculated Inlet TVOC Concentration In Water per App. P, Eq. 7-1, Using FID Aver Reading
Compound	MW	ppbw	ppbw	%	ppbw	%	ppmv	ppbw as methane
Ethylene	28	4.5	4.8	5	4.8	6		
Propylene	42	10.4	10.5	1	10.5	2		
t-2-butene	56	13.3	12.4	-7	12.4	-7		
1-butene	56	13.9	14.2	2	14.2	2		
isobutene	56	14.5	14.8	2	14.8	2		
c-2-butene	56	19.1	18.8	-1	18.9	-1		
1,3 butadiene	54	18.2	17.0	-7	17.0	-7		
Total		93.8	92.4	-2	92.6	-1	2.85	37.7

Table 4c
Test ID: A-DI-M
Results Summary - Run #3

Section 1: El Paso Column Water Sampling Analyses - VOA Vial and Tedlar Bag

		Reference VOC Concentration in Water	Speciated VOC Concentration in VOA Vial (Inlet) Sample	VOA Vial Accuracy (% Difference)	Speciated VOC Concentration in Tedlar Bag (Inlet) Sample	Tedlar Bag Accuracy (% Difference)	Speciated VOC Concentration in Tedlar Bag (Outlet) Sample	El Paso Column VOC Stripping Efficiency
Compound	MW	ppbw	ppbw	%	ppbw	%	ppbw	%
Ethylene	28	4.5	4.4	-3	1.7	-61	0.17	96
Propylene	42	10.4	9.7	-6	4.6	-56	0.26	97
t-2-butene	56	13.3	12.3	-8	6.0	-55	0.33	98
1-butene	56	13.9	13.8	0	7.0	-49	0.36	97
isobutene	56	14.5	14.7	1	8.1	-44	0.38	97
c-2-butene	56	19.1	19.3	1	11.6	-39	0.36	98
1,3 butadiene	54	18.2	17.3	-5	11.4	-38	0.30	98
Total		93.8	91.5	-2	50.4	-46	2.16	98

Section 2: El Paso Column Gas Sampling Analyses - Summa Canister and FID Analyzer

		Reference VOC Concentration in Water	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7-1, Using Summa Canister Sample Analysis (RM 18)	Summa Canister (RM 18) Accuracy (% Difference)	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7-1, Using Summa Canister Sample Analysis (TO-14A)	Summa Canister (TO-14A) Accuracy (% Difference)	FID Analyzer Average Reading	Calculated Inlet TVOC Concentration In Water per App. P, Eq. 7-1, Using FID Aver Reading
Compound	MW	ppbw	ppbw	%	ppbw	%	ppmv	ppbw as methane
Ethylene	28	4.5	5.0	11	5.0	11		
Propylene	42	10.4	11.1	7	11.1	7		
t-2-butene	56	13.3	13.0	-2	13.1	-2		
1-butene	56	13.9	14.9	8	14.9	8		
isobutene	56	14.5	15.6	8	15.6	8		
c-2-butene	56	19.1	19.9	4	19.9	4		
1,3 butadiene	54	18.2	18.0	-1	18.0	-1		
Total		93.8	97.4	4	97.6	4	2.88	38.1

Table 5a
Test ID: A-DI-H
Results Summary - Run # 1

Section 1: El Paso Column Water Sampling Analyses - VOA Vial and Tedlar Bag

		Reference VOC Concentration in Water	Speciated VOC Concentration in VOA Vial (Inlet) Sample	VOA Vial Accuracy (% Difference)	Speciated VOC Concentration in Tedlar Bag (Inlet) Sample	Tedlar Bag Accuracy (% Difference)	Speciated VOC Concentration in Tedlar Bag (Outlet) Sample	El Paso Column VOC Stripping Efficiency
Compound	MW	ppbw	ppbw	%	ppbw	%	ppbw	%
Ethylene	28	51	18	-64	39	-24	0.17	100
Propylene	42	114	45	-61	86	-25	0.27	100
t-2-butene	56	133	54	-59	94	-29	0.33	100
1-butene	56	148	62	-59	113	-24	0.36	100
isobutene	56	155	67	-57	131	-16	0.38	100
c-2-butene	56	198	87	-56	152	-23	0.36	100
1,3 butadiene	54	185	81	-56	138	-25	0.30	100
Total		984	413	-58	752	-24	2.17	100

Section 2: El Paso Column Gas Sampling Analyses - Summa Canister and FID Analyzer

		Reference VOC Concentration in Water	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7-1, Using Summa Canister Sample Analysis (RM 18)	Summa Canister (RM 18) Accuracy (% Difference)	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7-1, Using Summa Canister Sample Analysis (TO-14A)	Summa Canister (TO-14A) Accuracy (% Difference)	FID Analyzer Average Reading	Calculated Inlet TVOC Concentration In Water per App. P, Eq. 7-1, Using FID Average Reading
Compound	MW	ppbw	ppbw	%	ppbw	%	ppmv	ppbw as methane
Ethylene	28	51	50	-1	50	-1		
Propylene	42	114	110	-4	111	-3		
t-2-butene	56	133	123	-8	124	-7		
1-butene	56	148	142	-4	143	-4		
isobutene	56	155	148	-4	150	-3		
c-2-butene	56	198	188	-5	190	-4		
1,3 butadiene	54	185	176	-5	178	-4		
Total		984	938	-5	946	-4	20.7	275

Table 5b
Test ID: A-DI-H
Results Summary - Run # 2

Section 1: El Paso Column Water Sampling Analyses - VOA Vial and Tedlar Bag

		Reference VOC Concentration in Water	Speciated VOC Concentration in VOA Vial (Inlet) Sample	VOA Vial Accuracy (% Difference)	Speciated VOC Concentration in Tedlar Bag (Inlet) Sample	Tedlar Bag Accuracy (% Difference)	Speciated VOC Concentration in Tedlar Bag (Outlet) Sample	El Paso Column VOC Stripping Efficiency
Compound	MW	ppbw	ppbw	%	ppbw	%	ppbw	%
Ethylene	28	51	21	-59	40	-21	0.18	100
Propylene	42	114	50	-57	91	-21	8.20	91
t-2-butene	56	133	60	-55	101	-24	0.35	100
1-butene	56	148	69	-54	119	-20	0.38	100
isobutene	56	155	75	-52	126	-19	0.37	100
c-2-butene	56	198	96	-52	160	-19	0.38	100
1,3 butadiene	54	185	88	-52	145	-22	0.32	100
Total		984	459	-53	781	-21	10.17	99

Section 2: El Paso Column Gas Sampling Analyses - Summa Canister and FID Analyzer

		Reference VOC Concentration in Water	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7-1, Using Summa Canister Sample Analysis (RM 18)	Summa Canister (RM 18) Accuracy (% Difference)	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7-1, Using Summa Canister Sample Analysis (TO-14A)	Summa Canister (TO-14A) Accuracy (% Difference)	FID Analyzer Average Reading	Calculated Inlet TVOC Concentration In Water per App. P, Eq. 7-1, Using FID Aver Reading
Compound	MW	ppbw	ppbw	%	ppbw	%	ppmv	ppbw as methane
Ethylene	28	51	60	17	60	17		
Propylene	42	114	133	16	133	16		
t-2-butene	56	133	150	12	149	12		
1-butene	56	148	172	16	171	16		
isobutene	56	155	182	18	183	18		
c-2-butene	56	198	229	16	229	16		
1,3 butadiene	54	185	215	16	214	16		
Total		984	1142	16	1138	16	22.5	299

Table 5c
Test ID: A-DI-H
Results Summary - Run # 3

Section 1: El Paso Column Water Sampling Analyses - VOA Vial and Tedlar Bag

		Reference VOC Concentration in Water	Speciated VOC Concentration in VOA Vial (Inlet) Sample	VOA Vial Accuracy (% Difference)	Speciated VOC Concentration in Tedlar Bag (Inlet) Sample	Tedlar Bag Accuracy (% Difference)	Speciated VOC Concentration in Tedlar Bag (Outlet) Sample	El Paso Column VOC Stripping Efficiency
Compound	MW	ppbw	ppbw	%	ppbw	%	ppbw	%
Ethylene	28	51	30	-41	32	-38	0.17	99
Propylene	42	114	70	-39	72	-37	0.27	100
t-2-butene	56	133	81	-39	82	-38	0.75	99
1-butene	56	148	94	-37	94	-36	1.07	99
isobutene	56	155	100	-36	101	-35	1.76	98
c-2-butene	56	198	128	-35	131	-34	3.10	98
1,3 butadiene	54	185	121	-35	121	-35	2.16	98
Total		984	624	-37	632	-36	9.28	99

Section 2: El Paso Column Gas Sampling Analyses - Summa Canister and FID Analyzer

		Reference VOC Concentration in Water	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7-1, Using Summa Canister Sample Analysis (RM 18)	Summa Canister (RM 18) Accuracy (% Difference)	Calculated Inlet VOC Concentration in Water per App. P, Eq. 7-1, Using Summa Canister Sample Analysis (TO-14A)	Summa Canister (TO-14A) Accuracy (% Difference)	FID Analyzer Average Reading	Calculated Inlet TVOC Concentration In Water per App. P, Eq. 7- 1, Using FID Aver Reading
Compound	MW	ppbw	ppbw	%	ppbw	%	ppmv	ppbw as methane
Ethylene	28	51	50	-1	50	-2		
Propylene	42	114	111	-3	111	-3		
t-2-butene	56	133	126	-6	125	-6		
1-butene	56	148	144	-3	143	-3		
isobutene	56	155	150	-3	150	-3		
c-2-butene	56	198	192	-3	190	-4		
1,3 butadiene	54	185	178	-4	177	-4		
Total		984	951	-3	946	-4	23.1	306

Gas samples were collected in Summa canisters at the El Paso air stripping column exhaust gas exit and the concentration of the total VOC concentration in the same exhaust stream was measured using the Thermo Environmental Instruments Model TVA-1000B Toxic Vapor (FID) Analyzer (methane calibration). Results of the speciated analyses of the Summa canister samples, per EPA Methods TO 14 A and RM 18, and the average FID reading are reported in Section 2 of the tables.

In addition to the samples collected for each of the four tests, during the low level VOC concentration test (Test ID: A-DI-L), as samples were collected in 10 L Tedlar bags at the El Paso air stripping column exhaust gas exit. Results of the speciated analysis for the Tedlar bags per EPA Method RM 18 are reported in Section 3 of Tables 3a, 3b and 3c. Gas samples of the exhaust gas at the exit of the El Paso air stripping column were collected in Tedlar bags only for this test.

The detection limits for the GC/FID system used to analyze all samples are shown in Table 6. For reference, the equivalent detection limits for gas (canister or 10 L Tedlar bag) samples and water (VOA vial or 0.5 L Tedlar bag) samples converted to weight basis concentrations, i.e., ppbw, at 24 °C are also provided in Columns B and C, respectively of Table 6. If the GC/FID analysis results of any individual species in a sample was equal to or less than the species minimum detection limit (Column A) when analyzed by the GC/FID system, the minimum detection limits in Columns B or C (as appropriate), corrected for sample temperature and dilution factor, was reported and used for all subsequent data analysis for that sample.

Table 6
Analysis System Minimum Detection Limits and
Equivalent Concentration (Weight Basis) for Samples

Compound	A) GC/FID ppbv (@ 24 °C)	B) Canister (Gas) Samples ppbw (@ 24 °C)	C) Water Samples ppbw (@ 24 °C)
ethylene	0.081	0.015	0.112
propylene	0.085	0.024	0.176
t-2 butene	0.079	0.030	0.218
1-butene	0.086	0.033	0.237
isobutene	0.084	0.032	0.232
c-2 butene	0.087	0.033	0.240
1,3 butadiene	0.075	0.028	0.199
Total	0.577	0.196	1.414

A statistical analysis of all of the test data will follow the overview of the results from the four tests.

Detection Limit VOC Concentration Test (Tables 2a, 2b and 2c)

It can be seen from the data in Section 1 of the detection limit level VOC concentration test, that the analysis of all of the VOA samples indicated that the VOC concentration in the water sample was at or below the detection limit of the analysis system. This was a -78% difference from the

reference value. The speciated VOC concentrations of the Tedlar bag water sample varied from -66% to 102%.

In Section 2 of the detection limit level VOC concentration test, the Summa canister, which was used in this test as a check on the VOC concentration in the water measured only 0.3% to 2.3% difference from the reference value. The average FID analyzer reading varied from 8.45 ppbw to 9.64 ppbw, when converted to TVOC concentration using TCEQ Sampling Procedures Manual, Appendix P, Equation 7.1. This represented a -23% to -12% difference, respectively, from the reference value.

Low Level VOC Concentration Test (Tables 3a, 3b and 3c)

It can be seen from the data in Section 1 of the low level VOC concentration test, that the analysis of all of the VOA samples indicated that the VOC concentration in the water sample had a -71% to -60% difference than the reference value. The speciated concentrations in the Tedlar bag varied from -60% to -21%.

In Section 2 of the low level VOC concentration test, the Summa canister samples measured a -20% to -16% difference from the reference value. The average FID analyzer reading varied from 33.9 ppbw to 37.2 ppbw, when converted to TVOC concentration using TCEQ Sampling Procedures Manual, Appendix P, Equation 7.1. This represented a -34% to -27% difference, respectively, from the reference value.

In Section 3 of the low level VOC concentration test, the Tedlar bag exhaust gas samples measured a -5% to 2% difference from the reference value.

Medium Level VOC Concentration Test (Tables 4a, 4b and 4c)

It can be seen from the data in Section 1 of the medium level VOC concentration test, that the analysis of all of the VOA samples indicated that the VOC concentration in the water sample had a -11% to 0% difference than the reference value. The speciated concentrations in the Tedlar bag varied from -46% to -18%.

In Section 2 of the medium level VOC concentration test, the Summa canister samples measured a -9% to 4% difference from the reference value. The average FID analyzer reading varied from 37.7 ppbw to 45.9 ppbw, when converted to TVOC concentration using TCEQ Sampling Procedures Manual, Appendix P, Equation 7.1. This represented a -60% to -51% difference, respectively, from the reference value.

High Level VOC Concentration Test (Tables 5a, 5b and 5c)

It can be seen from the data in Section 1 of the high level VOC concentration test, that the analysis of all of the VOA samples indicated that the VOC concentration in the water sample had a -58% to -37% difference than the reference value. The speciated concentrations in the Tedlar bag varied from -36% to -21%.

In Section 2 of the high level VOC concentration test, the Summa canister samples measured a -5% to 16% difference from the reference value. The average FID analyzer reading varied from 275 ppbw to 306 ppbw, when converted to TVOC concentration using TCEQ Sampling

Procedures Manual, Appendix P, Equation 7.1. This represented a -72% to -69% difference from the reference value.

Statistical Analysis

A fractional factorial analysis of covariance (ANACOVA) was completed to statistically evaluate data stemming from this study. A total of 169 VOC observations were made, all of which were compared, statistically, as total VOC (TVOC). Of these, 25 were measurements of “blank” water samples and 144 were samples spiked with target VOCs. The latter included both water and air samples. Air samples included those collected with Summa canisters, 10 L Tedlar[®] bags, and by direct in-line analysis using a flame ionization detector (FID) analyzer. A total of 24 spiked samples were measurements of stripped water residue, i.e., collected as effluent from the modified El Paso Method (EPM) system provided by the TCEQ.

The relative VOC ratio (Ω) was observed to be the most robust metric for statistical assessment and comparison of data. Here, Ω represents the ratio of the TVOC concentration in the water at the inlet of the EPM system to a reference level. The reference level (“ground truth”) is calculated as the theoretical inlet concentration in water based on the measured concentration in a stock solution, background water, and the mixing ratio of the two upstream of the EPM system inlet.

Air samples based on collection in Summa canisters, 10 L Tedlar[®] bags, or in-line analysis using an FID analyzer were used to determine mass flow rate of TVOC in the EPM system exhaust. These mass flow rates were used to back-calculate the TVOC concentration in the liquid influent assuming 100% removal (stripping) from water.

Replicate samples were analyzed for both accuracy and precision. Accuracy was defined as how close the measurements were to ground truth, on average. Precision was defined based on the degree of spread about the mean measurement and was summarized as a standard deviation.

Several comparisons were made to evaluate methods of measurement. These included differences in Summa canisters and 10 L Tedlar[®] bags (air samples), VOA vials and 0.5 L Tedlar[®] bags (water samples), VOA vials and Summa canisters (air vs. water blanks), and summa canister EPA Test Methods TO-14A and 18.

A summary of major findings is presented below. The reader is referred to Appendix H for a more detailed discussion of the statistical analysis.

1. In general, for spiked samples, analyses of the El Paso column outlet air stream only, i.e., exclusive of analyses of water effluent (residue), Ω was less than unity; TVOC measurements were less than ground truth. Exclusive of the FID analyzer (see major finding Number 7) this would be due to VOC losses in collection, storage/container losses, or losses/errors in the GC/FID analysis system used to make the speciated VOC measurement.
2. The use of VOA vials for spiked liquid inlet measurements led to consistent under-estimation of ground truth, with $\Omega = 0.22$ at target TVOC = 10 ppbw, 0.35 at 50 ppbw,

0.96 at 100 ppbw, and 0.51 at 1,000 ppbw.

3. With the exception of the 100 ppbw replicates, the mean Ω for collection of spiked inlet water samples in 0.5 L Tedlar[®] bags was closer to ground truth ($\Omega = 1.0$) than was collection using VOA vials. The Ω for 0.5 L Tedlar[®] bags was 1.1 at a target VOC = 10 ppbw, 0.73 at 50 ppbw, 0.72 at 100 ppbw, and 0.74 at 1,000 ppbw.
4. Direct measurements using the on-line FID led to relatively poor values of Ω , particularly at high concentrations of target TVOC. The Ω for FID was 0.82 at a target VOC = 10 ppbw, 0.69 at 50 ppbw, 0.43 at 100 ppbw, and 0.30 at 1,000 ppbw. The differences in total VOC results from the FID analyzer vs total VOC obtained through speciated analysis is due to differences in response factors and molecular weights in relation to methane, which was the basis for calibration of the FID analyzer.
5. Collection in Summa canisters led to the most consistent values of Ω across all TVOC concentrations in water. The Ω for Summa canisters was 1.1 at a target VOC = 10 ppbw, 0.82 at 50 ppbw, 0.98 at 100 ppbw, and 1.03 at 1,000 ppbw.
6. Based on 24 spiked water effluent samples collected in both VOA vials (6 samples) and 0.5 L Tedlar[®] bags (18 samples), the TVOC stripping efficiency across the EPM system ranged from 96% at a target TVOC concentration of 10 ppbw to 99% at a target TVOC concentration of 1,000 ppbw. The stripping efficiency increased with sequential increases in TVOC concentration in water, but was close to 100% in all cases. These results are consistent with the relatively high values of Ω determined by collection using Summa canisters.
7. Between VOA vials, 0.5 L Tedlar[®] bags (water samples), 10 L Tedlar[®] bags (air samples), and Summa canister methods, the Summa canisters led to the best precision in terms of replicate determination of Ω , varying by 8.81% around the mean.
8. For liquid samples, 0.5 L Tedlar[®] bags are both more accurate and precise than the use of VOA vials.
9. The difference in Ω between the use of Test Methods TO-14A and 18 was found to be statistically insignificant ($p = 0.6967$).
10. For air samples collected in 10 L Tedlar[®] bags vs Summa canisters at the target VOC concentration of 50 ppbw, the Ω for the 10 L Tedlar[®] bags was 0.98 and 0.82 for the Summa canisters. Both underestimated ground truth ($\Omega < 1$) and the 10 L Tedlar[®] bags were more accurate, $\Omega = 0.98$ vs $\Omega = 0.82$ for the Summa canisters.

3.2.2 Continuous VOC Monitoring/Sampling Methods

The results of this evaluation provide a description of each of the systems/instruments evaluated as well as details about equipment operation and, if available, performance data obtained for the selected method. The description, specifications, and results were summarized directly from the

product information provided by the manufacturers in response to the questionnaire in Appendix F. All of the manufacturers' responses to the questionnaire are included in Appendix G.

3.2.2.1 Results of Evaluation

Heated Total Hydrocarbon Analyzer

Product Description

The instrument is an on-line total hydrocarbon analyzer that utilizes an electronically flow controlled microprocessor based flame ionization detector (FID). A small portion of the gas sample is introduced directly to the detector flame. During the combustion process organic or hydrocarbon-based gases in the sample are ionized. The number of ions produced (voltage detected) is directly related to the concentration of the compound. VOCs can be stripped from the water matrix into an air matrix for monitoring by this instrument using the TCEQ Appendix P Sampling Method, a permeation device, or a proprietary (patent pending) Gas Stripper Assembly. The manufacturer's responses to the questionnaire are included in Appendix G, Questionnaire Response A.

Selected Product Specifications and Information

Heated Total Hydrocarbon Analyzer

Compounds	Total VOC (formaldehyde indirectly with a catalyst)
Detection Limit	< 5 ppb (for benzene given in Appendix G, Questionnaire Response C)
Equilibrium	Back pressure regulation system to assure sample is stable
Critical Parameters	Proper maintenance of sampling system key to measurement accuracy
Flow Rate (ml/min)	< 2000 ml/min
Temperature (°C)	< 200 °C
Humidity (%)	Up to 95% or dew points to 195 °C
Sample Pressure	206 kPa (30 psi), internal heated sample pump optional for lower pressures
Sampling Interval	Continuous
Response Time	< 5 seconds to 90% full scale, disregarding transport time
QA/QC, Calibration	Drift ±1% of Full Scale over 24 hours; can be calibrated either manually or automatically according to requirements in TCEQ Appendix P §4.1; zero and span parameters are stored internally and used for reference during continuous monitoring process
Preventative Maintenance	Maintaining air and fuel sources for FID as well as zero and span calibration gases; some primary sample conditioning required by end user to remove scales, algae, and particulate matter; sparger includes secondary filter (stainless steel screen) which is typically a quarterly preventative maintenance item. Sparger components and/or housing can be replaced as needed.
Environmental Changes	Typical environmental changes will not affect the analyzer. However, the analyzer should be protected from harsh outdoor weather. It can be enclosed in a cabinet to control environmental limits and area classification concerns. The operating conditions are: Temperature 32-104 °F; Humidity

	0-95%, non-condensing.
Intrinsic Safety	Can be manufactured using purge controls to be located in classified areas; Programmable relays can be selected for calibration, fault, and threshold alarms; FID will automatically relight if flame-out takes place, and if unsuccessful will shut off fuel, air, and sample to instrument
Size	17.625" W x 16.25" D x 9.25" H (44.7 cm W x 41.24 cm D x 23.48 H) Nominal weight: 45 lb (20.5 kg); Bench-top or rack-mount (19" panel); Power 90-260 VAC, @ 50-60 Hz (as specified)
Cost	Wall mount or panel mount enclosure: - with proprietary gas stripping system would list for < \$15,000. - with an Appendix P Sampling Method would be < \$20,000 Sample lines and support gas costs not included

On-line Field Gas Chromatograph

Product Description

The manufacturer also recommended as an option an on-line field gas chromatograph that uses a microprocessor controlled based (FID) or (PID). A small portion of the gas sample is automatically introduced into the appropriate column configuration via a sample loop and switching valves. No pre-concentration should be necessary for the levels requested in TCEQ Appendix P. Separation of the compounds takes place in the column(s). The speciated VOCs are then passed to the detector, where they are converted to concentrations. The VOCs can be stripped from the water matrix into an air matrix for monitoring by this instrument using an Appendix P Sampling Method, permeation device, or a proprietary (patent pending) Gas Stripper Assembly. The manufacturer's responses to the questionnaire are included in Appendix G, Questionnaire Response B.

Features that differ from those shown for the Heated Total Hydrocarbon Analyzer are included in the table below.

On-line Field Gas Chromatograph

Equilibrium	Traditional sample loop with baseline established at the beginning and end of each sample run
Temperature (°C)	< 150 °C
Humidity (%)	Up to 95% or dew points to 145 °C
Sampling Interval	Continuous
Response Time	< 15 minutes, disregarding transport time; Analyzer completes a C1-C5 analysis (7 compounds) in 45 seconds, start time to start time
Preventative Maintenance	Maintaining air and fuel sources for FID as well as zero and span calibration gases; The PID would need to be cleaned, although the detector in the GC mode is less susceptible to contamination.
Cost	Wall mount or panel mount enclosure: - with proprietary gas stripping system would list for < \$23,000. - with the El Paso style sparging system would be < \$28,000 Sample lines and support gas costs not included

The manufacturer provided the following additional information about their proprietary sparging system.

“The apparatus uses a nozzle instead of a trickling tower to strip the dissolved and entrained gases and volatiles from the water. The small nozzle creates a continuous stream of fine droplets, which releases gas from water in an enclosed headspace. The general technique can also be used for stripping volatiles and gases from drinking water and wastewater. The apparatus is compact, reliable, fast response and low in cost. The apparatus is the subject of a patent applied for and so a more detailed disclosure cannot be made at this time.”

Product Results

Results from lab testing comparing calibration curves and response times for two system configurations are included in Appendix G, Questionnaire Response C. From these results Appendix G, Questionnaire Response C, Table 1, the manufacturer concluded that the proprietary air stripping method exhibits a faster response time (29 seconds) compared to the traditional El Paso Method (300 seconds) due to the minimization of the amount of water in the air-stripping chamber. The manufacturer also concluded that the proprietary air stripping method is more sensitive (MDQ = 4.71 ppb vs 10.16 ppb for the El Paso Method) although less efficient (Gain = 64 pA/ppm vs 89 pA/ppm) than the El Paso Method. Finally the smaller size of the air stripper is cited as an advantage over the El Paso Method with regard to both maintenance and cost.

Process Mass Spectrometer

Product Description

The instrument is a quadrupole-based mass spectrometer that uses a membrane introduction interface for direct liquid sampling. It is a general-purpose instrument intended for installation in an environmentally controlled area. The manufacturer also offers an industrially hardened version of the instrument that carries its own environmentally controlled enclosure and can be used in hazardous area classifications up to and including Class I, Division 1. In summary, membrane interface mass spectrometry (MIMS) relies on the ability of various membrane materials to selectively block polar compounds (e.g. water) while allowing the non-polar species to migrate through the membrane. Typically, the membrane is a thin sheet, or tube, of dimethylsilicone. Other membranes are available and vary typically in their ability to enhance, or retard, the migration of specific compounds through the membrane. Because MIMS instruments separate the analytes of interest from the matrix, it is possible to achieve lower detection limits in the range of 1 ppb. The manufacturer notes the following benefits for this instrument: speed of analysis, specificity of analysis, and direct analysis of the sample stream. The manufacturer's responses to the questionnaire are included in Appendix G, Questionnaire Response D. Attachment A to Appendix G, Questionnaire Response D, was provided by the manufacturer as a more detailed description of how the instrument operates.

Selected Product Specifications

Process Mass Spectrometer

Compounds	Speciated on-line determination of VOCs in water; however, depends on the combination of VOCs in a given stream (see Appendix G, Questionnaire Response D, Table 1); no isomers
Detection Limit	1 ppb, generally
Equilibrium	During the calibration cycle (which is set up to duplicate the actual stream sampling conditions) all of the targeted component data is preserved in raw form. The raw form data is used to determine when equilibrium has occurred and time the actual stream sampling sequences accordingly. If the instrument will be used as a single-stream device, there is, essentially, no time required for equilibration.
Critical Parameters	Maintaining the consistency of the sample from the extraction point to the analyzer is key. Also, the condition of the membrane itself can lead to analytical inconsistencies.
Flow Rate (ml/min)	50-100 ml/min, with sampling bypass flow
Temperature (°C)	< 150 °C, controlled at interface
Humidity (%)	Not specified
Sample Pressure	2-50 psig, controlled at interface
Sampling Interval	Continuous, averages 2 minutes per analysis (majority of time spent assuring a sample has equilibrated); Sample concentration will have reached 100% of its calibrated value during the sampling interval.
Response Time	Mass Spec measurements in a few seconds
QA/QC, Calibration	Calibration is done with certified liquid phase standards at

	equivalent flows, pressures, and temperatures to the actual sample; Frequency and acceptance criteria are operator controlled
Preventative Maintenance	Yearly routine vacuum system servicing; requires no specialized training and approximately 8 hours of on-site time
Environmental Changes	The analysis method can be affected by changes in sample and/or membrane interface temperatures. The use of short, heated sample lines minimizes the risk of changing sample temperatures. The membrane interface is temperature controlled to a high degree as part of the instrument itself. The standard unit is general-purpose and must be housed in an environmentally controlled enclosure. The industrial version comes complete in an environmentally controlled enclosure.
Intrinsic Safety	Standard unit is not intrinsically safe, must be housed in appropriate non-classified area. Industrial version equipped with an X-purged, environmentally controlled housing to allow operation in hazardous areas up to and including Class 1, Division 1.
Size	14.375" x 24" x 15.5" (36.5 cm x 61 cm x 39.37 cm) Nominal weight: 80 lb (36 kg); General purpose bench-top; Power 115/230 VAC, 50/60 Hz; PC Required
Cost	Installed Costs: Standard Unit, equipped for single line sampling = \$65,000 Industrial Unit, equipped for single line sampling and configured for hazardous area location service = \$75,000

Product Results

The data included in Appendix G, Questionnaire Response D, was obtained in a laboratory environment and shows the response of the instrument to varying concentrations of methylene chloride in water.

Solid State Sensor Method

Product Description

Valuing, pressure regulation, and flow meters are used to send a filtered water sample into a Membrane Stripper Transfer Unit. The water passes along one side of a polymer membrane and VOCs in the water permeate through the membrane. Clean dry carrier gas flowing past the other side of the membrane evaporates the permeated VOCs and sweeps the gaseous VOCs through a GC injection valve and then into a tin oxide solid state sensor. The solid-state sensor that responds to total VOCs is very sensitive at low ppbw because of its exponential response. The GC is used to speciate the VOCs. Optionally, an automatic permeation tube can validate instrument response. The manufacturer's responses to the questionnaire are included in Appendix G, Questionnaire Response E.

Selected Product Specifications

Solid State Sensor Method

Compounds	Instrument responds to all VOCs and the sensor indicates total VOCs; Speciation is done separately by GC column.
Detection Limit	1 ppb, Sensors can measure long term at below 5 ppbw.
Equilibrium	A chart recording indicates equilibrium by a constant reading.
Critical Parameters	Temperature can affect reading. An air-conditioned enclosure is recommended for low ppbw samples. Readout is directly proportional to carrier flow rate. Readout is not sensitive to sample water flow rate.
Flow Rate (ml/min)	20 ml/min, normally
Temperature (°C)	Automatic control
Humidity (%)	Not specified
Sample Pressure	10 psig minimum at 20ml/min sample flow
Sampling Interval	Continuous, When a GC readout is used sampling time may vary with type of column used.
Response Time	Averages 10-15 minutes (including sample line absorption and instrument response), varies with type of compound
QA/QC, Calibration	Quality assurance/quality controls are provided by a permeation tube reference standard built into the instrument for manual or automatic operation that validates instrument operation. Reference standard is mixed and immediately used eliminating determination of sample.
Preventative Maintenance	Primary spin clean filter regeneration is automatic and secondary filter is replaced monthly. If permeation tube standard shows any change the operator checks pressure settings, flow rate, and temperature control. Once a week verification is recommended. Adjustment period is usually 3 months or longer.
Environmental Changes	Environmental conditions are provided for by final design for a job. With custom modifications there are no Environmental Limits. For ppb range analyzers, a temperature controlled building is recommended

Intrinsic Safety	Air purge is provided for hazardous locations.
Size	Stainless Steel Cabinet: 24”H x 36”W x 10”D (90 cm H x 60 cm W x 26 cm D), 200 lb. (91 kg.) Power 110/220 VAC, 50/60 Hz (please specify)
Cost	\$19,400 including membrane stripper transfer unit and solid state sensor analyzer, support gas costs and other options not included

Product Results

The manufacturer provided a case study paper that includes data obtained from operation of the analyzer in an ethylene plant. It shows a 72-hour run during which two benzene leaks were detected and corrective action taken at the 2 ppbw level. (Reference: Proceedings of the 46th Annual ISA Analysis Division Symposium, Vol. 34, April 2001, “Volatile Organic Compound (VOC) Analyzer for Cooling Tower Water”.)

On-line Process Gas Chromatograph

Product Description

A continuous sample stream is piped to the analyzer location in the form of a “Fast Loop”. From the fast loop, a continuous “Analytical Loop” provides conditioned sample to the analyzer and preferably back into the fast loop. The sample is filtered, temperature stabilized if needed, and flow and pressure stabilized if needed. The analyzer selects a fixed amount of sample from the analytical loop and injects it into the analyzer. If the sample is liquid, it is vaporized inside the analyzer prior to being flushed into the separation column. The separation system typically utilizes at least two micro-packed or capillary columns, selected according to sample matrix and targeted measuring components. Detectors are typically Thermal Conductivity (TCD) or Flame Ionization (FID) detectors. The detector signal is amplified, integrated, and compared with the calibration data from a known external standard. The results as well as status data are forwarded to a printer, a data collection system, or a process control system. The manufacturer’s responses to the questionnaire are included in Appendix G, Questionnaire Response F.

Selected Product Specifications

On-line Process Gas Chromatograph

Compounds	For cooling tower applications, the analyzer can be setup to measure Total VOC (less methane and ethane) as well as speciated individual VOCs up to C5. A second analyzer is likely required to measure benzene and other compounds of interest.
Detection Limit	< 5 ppb
Equilibrium	If used with the gas sparger, system is temperature equilibrated. Else, the water temperature is measured and included in the calculation. When used with gas sparger, the sparging gas continuously flows through the injection valve. Just prior to injecting the sample, the sample flow is momentarily stopped and the sample pressure is equilibrated to ambient pressure.
Critical Parameters	Changes in pressure and reference standard; Also, any degradation in the efficiency of the sparging system is not recognized (estimated influence is in low percentage range).
Flow Rate (ml/min)	Several L/min, depends on water pressure and distance; sample lag time less than 60 seconds typically; 50-200 ml/min gas to analyzer
Temperature (°C)	0-120 °F
Humidity (%)	0-95%, non-condensing
Sample Pressure	5-30 psi, at injection valve
Sampling Interval	Total VOC < 120 seconds Speciated VOC ~15 minutes, a column development study is needed
Response Time	Not specified
QA/QC, Calibration	Due to nature of the VOCs, it is difficult to calibrate with a liquid standard, however using a vapor standard does not account for variability in the sparging system.

	<p>Manufacturer suggests using a specific component for continuous validation. By continuously permeating small amount of component into the sparging gas and then measuring/monitoring the quantity, the efficiency of the extraction system can be determined. Manufacturer also suggests monitoring additional parameters, such as carrier gas supply pressure and sample pressure. The analytical system itself has the capability to monitor essentially every analytical parameter.</p>
Preventative Maintenance	<p>Maintenance on sample extraction system every 1-4 weeks depending on the cooling water, maintenance on the analyzer every 6-12 months. For the gas sparger, rinsing can be done frequently due to its small size and an automatic valve that permits emptying the vessel. Additional maintenance is typically only necessary every 2-3 months depending on water quality. For the analyzer, injection and column switching valves must be exchanged ~ every 12 months with a few hours offline time, also the separation columns should last ~ 2 years assuming there is no excessive water carryover.</p>
Environmental Changes	<p>Due to ambient temperature changes, it is recommended that the analyzer be installed in a climate controlled enclosure (additional cost).</p>
Intrinsic Safety	<p>As-built system is suitable for hazardous area and certified Class 1, Div 2, Group C&D. With additional cost, system can be built for Class 1, Div 1, Group B,C&D.</p>
Size	<p>39”H x 26”W x 16”D (101 cm H x 66 cm W x 45 cm D),170 lb.(77 kg.) Power 100-130/195-260 VAC, 47-63 Hz</p>
Cost	<p>Analyzer: \$55,000 Sample Conditioning: \$30,000 Enclosure: \$70,000</p>

Continuous Gas Analyzer

Product Description

A constant and continuous sample flows through the detector (FID), and the total amount of organic carbon is registered. The detector design and operation mode has to ensure that the CH₄ group is independent from the molecule from which it originates. It either consists of a single detector measuring the Total VOC including ethane and methane, or an alternative dual detector version. In this version, the first detector measures Total VOC including ethane and methane and the second detector uses a catalyst to measure methane selectively. Total VOC less methane can be determined by subtracting the detector signals from one another. The manufacturer's responses to the questionnaire are included in Appendix G, Questionnaire Response G.

Selected Product Specifications

Continuous Gas Analyzer

Compounds	Measures Total VOC (methane+) or alternatively Total VOC (ethane+).
Detection Limit	< 1 ppb (liquid)
Equilibrium	Critical to keep parameters such as sample temperature and sample flow constant.
Critical Parameters	Changes in pressure
Flow Rate (ml/min)	Several L/min, depends on water pressure and distance; sample lag time less than 60s typically; ~1 L/min gas to analyzer
Temperature (°C)	0-120 °F
Humidity (%)	0-95%, non-condensing
Sample Pressure	5-30 psi, at injection valve
Sampling Interval	Continuous
Response Time	t ₉₀ < 3 seconds
QA/QC, Calibration	Due to nature of the VOCs, it is difficult to calibrate with a liquid standard, however using a vapor standard does not account for variability in the sparging system. Manufacturer suggests using a specific component for continuous validation. By continuously permeating small amount of component into the sparging gas and then measuring/monitoring the quantity, the efficiency of the extraction system can be determined. Manufacturer also suggests monitoring additional parameters, such as carrier gas supply pressure and sample pressure. The analytical system itself has the capability to monitor essentially every analytical parameter.
Preventative Maintenance	Maintenance on sample extraction system every 1-4 weeks depending on the cooling water, maintenance on the analyzer every 6-12 months.
Environmental Changes	Due to ambient temperature changes, it is recommended that the analyzer be installed in a climate controlled enclosure (additional cost).
Intrinsic Safety	Analyzer is only available for general purpose environment

Size	29 kg. Power 115 VAC, 48-63 Hz
Cost	Single Detector: \$18,000 Dual Detector: \$23,000 Sample Conditioning: \$25,000 Enclosure: \$20-60,000 (depending on environment and configuration)

Both analyzers described above can be used with an Appendix P Sampling Method. As an alternative, the manufacturer provided information about a Gas Sparger Sampling System and a Membrane Sampling System. The Gas Sparger System provides on-line sample preparation for analysis of ppb levels of volatiles in water. The single sparger system consists of a single sample inlet, regulator, flow switch and water heater, with a backup sparger. The dual sparger system consists of two parallel sample inlets, regulators, water heaters, flow switches and spargers. The analyzer alternates between spargers. Like the analyzer, the Gas Sparger System should be protected in an enclosure. Additional technical specifications were provided in Appendix G, Questionnaire Response G, Attachment A. The Membrane Sampling System uses a membrane probe that is inserted into the cooling water stream. The manufacturer provided the following information about this system:

“In operation, a carrier gas (typically nitrogen) enters the [membrane sampler] through 1/16” tubing from a mass flow controller, flows through the permeation tubing (typically silicone rubber), and exits through a second 1/16” tube which is connected to the desired analytical instrumentation. The effectiveness of this pervaporation process is governed largely by the mass transport of the sample molecules to the tubing outer surface, the solubility of the sample molecules in the polymer, the vapor pressures of the specific molecules involved, and the temperature.”

Quantitative analysis with the Membrane Sampling System requires establishing optimum carrier gas flow as well as establishing temperature coefficients of response for each analyte. The concentration of the analyte(s) in the carrier exiting the Membrane Sampling System is determined by Henry’s Law, and Antoine’s Equations. The manufacturer also states that the “membrane sampling approach eliminates problems from dissolved solids, high levels of salts, high levels of suspended particulate, etc.”.

Product Results

No product results were obtained from the manufacturer.

Photoacoustic Spectroscopy

Product Description

The instrument uses laser-based photoacoustic spectroscopy to measure the concentration of various target species within gas-phase samples that are continuously drawn into a sample chamber from ambient conditions. This technique uses the photoacoustic effect to guarantee ultra-sensitivity, and wavelength-switching to subtract offsets and the contributions of interfering species. The manufacturer's responses to the questionnaire are included in Appendix G, Questionnaire Response H.

Selected Product Specifications

Photoacoustic Spectroscopy

Compounds	Speciated VOCs.
Detection Limit	Varies by compound as listed in Attachment L, ranges from 1 – 38 ppb (gas-phase) for compounds of high interest. Four orders of magnitude linear dynamic range is available in standard models.
Equilibrium	Because measurements are conducted over short time intervals and with a steady flowing system (i.e. there are no sudden starts or stops), equilibrium in temperature, pressure, flow rate and gas composition is achieved.
Critical Parameters	Unexpected interferences introduce the highest degree of risk.
Flow Rate (ml/min)	Samples are drawn continuously at 400 ml/min
Temperature (°C)	The instrument is currently designed to analyze gas samples with a temperature of –40 to 40 °C, but can be designed to handle a wider temperature range.
Humidity (%)	0-95%, non-condensing
Sample Pressure	~ 600-1000 Torr (~ 11.6-19.3 psi)
Sampling Interval	Continuous, with updates every few minutes.
Response Time	Gas transit time < 10 seconds
QA/QC, Calibration	Calibration is recommended every 6 months with varying gas-phase concentrations of the target species in scrubbed, moist room air. Calibration does not depend on any factors other than the concentration of the target species. Zero and span checks can be performed biweekly.
Preventative Maintenance	Yearly preventative maintenance is recommended. Maintenance includes: transducer batteries (every 6 months); vacuum pump, water pump, particulate filters, water reservoir (yearly); laser (every 2 years).
Environmental Changes	Environmental changes in humidity and wind should have no impact on this instrument. In its existing configuration, the instrument is designed for operating ambient temperatures of 15-35 °C (this range can be extended if necessary).
Intrinsic Safety	Automatic safety interlocks, shutoffs and fuses prevent overheating, short-circuits, and exposure to laser radiation.

Size	Approx. 10”H x 19”W x 24”D, 65 lb Power 110/220 VAC
Cost	Instrument cost for single-gas detection is \$20,000 (1 ppb sensitivity) to \$50,000 (100 ppt sensitivity) in quantity 1, with multi-gas detection available as an option. No optional equipment required. Instrument options include: graphical user interface with graphing capability and monitoring of the instrument’s internal system diagnostics, and multiplexing for analyzing multiple gas streams simultaneously.

Product Results

The Appendix G, Questionnaire Response H was provided by the manufacturer and illustrates data obtained in laboratory conditions using controlled gas mixtures as a part of final quality control for a product shipment. The specific data shown in this example is for ammonia (NH₃).

3.2.2.2 Conclusions

The results of this literature evaluation indicate that some of the reviewed instruments could potentially be used to monitor leaks of highly reactive VOCs from industrial cooling towers while still meeting the minimum requirements set forth by the TCEQ in Appendix P. This review was not exhaustive, though, and it is possible that additional instrumentation is currently available or under development that could also meet these criteria. This assessment was limited to technical information obtained from equipment manufacturers and industrial representatives. A recommendation for obtaining more detailed information would be to complete an inter-comparison study that could include testing of the instrumentation in lab or field environments.

The reviewed sampling systems can be divided into two broad categories: gas sparging systems (similar to the Modified El Paso Method) and membrane systems. The advantage of gas sparging systems is that they enable subsequent measurement of speciated strippable VOC, however general limitations include relatively longer response times and high maintenance requirements. Membrane systems rely on a selective membrane to enable compounds of interest to permeate through to a water or air matrix for subsequent analysis. General limitations of these systems include high sensitivity to changes in temperature and issues with determining suitable calibration procedures for the specific compounds of interest. Additionally, it is not directly evident how measurements from these systems correlate to the strippable VOC concentration required by the TCEQ. Because sampling is a critical step in achieving valid measurements, further detailed study of the advantages and limitations of these systems is recommended.

The reviewed online analytical systems include some instruments that measure only total VOCs and others that are able to provide online HRVOC speciation as well. Generally, the instruments capable of online speciation are two to four times more expensive than their total VOC counterparts. However, if sample speciation is required frequently, the added convenience could outweigh the higher cost and make these systems more attractive to the user. Another advantage of online speciation is the potential to minimize sample deterioration as compared to grab samples that must be transported elsewhere for analysis. One system offers a unique spectroscopic approach that is probably most useful for measuring concentrations of one particular molecular group. Although the approach seems to offer relative simplicity and speed when compared to a traditional GC, it is unclear what interferences and complexities would become evident in multi-component mixtures. In general, none of the manufacturers provided enough experimental data to enable more specific conclusions.

3.2.3 Summary of Evaluation of VOC Sampling, Measuring, Monitoring and Testing Methods

Four sampling methods were evaluated for speciation of the high interest VOCs: VOA vial, 0.5 L Tedlar bags, Summa Canister and 10 L Tedlar Bags. Of these methods, only the Summa canisters and the 10 L Tedlar bags used for analysis of gas samples from the air stripping column exhaust satisfy both the 90% speciation and accuracy criteria for the sampling system. Based on these criteria, the VOA vials and 0.5 L Tedlar bags used for water sampling can be eliminated since they provided unacceptable accuracy, as high as -78% for the VOA vial and -60% for the 0.5 L Tedlar bag.

One continuous monitoring method was evaluated, an FID TVOC analyzer. This instrument does not provide speciation and when compared to total VOC concentration in the water flow for the composition of organic chemicals used in the lab test series, the accuracy of the instrument decreased to -72% at 1000 ppbw VOC concentration.

Therefore, the test series conducted illustrated that for batch samples, both the Summa canister and the 10 L Tedlar bags can provide acceptable accuracy and 90% speciation of gas samples, if the VOC stripping system has efficiencies of at least 96%.

There were no readily available commercial continuous monitoring systems that had been used to measure the high interest VOCs in cooling water. Of the equipment available, there are many instruments that measure TVOC using FID technology. These instruments of course do not provide speciation and will vary in accuracy depending on the composition of VOCs in the cooling water and the concentration. The cost for the FID analyzer alone starts at approximately \$15,000.

There are available on line GC systems which must be used with either an FID or PID and which can provide acceptable speciation. On-line continuous GC systems are limited however in the specific chemicals that can be detected, compounds up to C5 being possible. For benzene and other compounds, a second analyzer would be required. These systems also require a VOC stripping system. These systems start at \$55,000 and can easily double in cost if an intrinsically safe system is required.

The most important aspect of sampling is preservation of the sample, i.e., elimination of any possible losses of the VOCs before analysis of the sample. This requires proper design of the sampling system, the sample collection procedure and conditions, the sample collection device, storage and handling of the sample prior to analysis, and similar preparation (dilution) of the samples prior to analysis. Each of these factors can adversely affect the accuracy of the results, the accuracy being as far off as 75% at low concentrations, where the specification is 10 ppbw below 50 ppbw. At these levels, sample collection, the air stripping system, and detection limit of the analytical system are critical and their impacts on the overall accuracy must all be considered.

There are also mass spectrometry systems that can provide direct speciation of VOCs from water samples. These systems can meet the accuracy and speciation requirements but are susceptible to changes in sample temperature. It is unclear how water matrix effects affect the accuracy of

the measurement. Additionally, it is not directly evident how measurements from these systems correlate to the strippable VOC concentration required by the TCEQ. These systems are \$75,000 for units that are intrinsically safe and \$65,000 for those that are not.

This project did not study the impact of matrix effects related to water quality on the data quality objectives. Clearly some water constituents like chlorine will react with the VOCs considered in this study. Therefore, any system that is considered should assess the impact of the matrix effects on both the presence/concentration of the VOCs in the water and on the accuracy of the measurements made by the system.

3.3 Evaluation of Instruments for Continuous Measurement of Cooling Water Flow Rate

3.3.1 Selection of and General Information on Flow Meter Types

There are many types of flow meters that may be used in cooling water applications. They include coriolis, pitot tube, vortex, magnetic, turbine, v-cone, orifice/venturi, impellar, ultrasonic, positive displacement, and variable area (CTI, 2003). However, not all types are applicable to all flow measurement applications. Such factors as the range of velocity or flow rate of the cooling water, typical constituents and their concentrations found in the cooling water, pipe geometry and the proximity of flow interferences/disturbances (valves, pipe fittings and equipment) upstream and downstream of the location where the flow is to be measured, constraints on the types of measurement principles that can be employed (intrusive versus non-intrusive), initial cost and maintenance costs, and accuracy desired and calibration required to maintain this accuracy eliminate some types from consideration. Consequently some meters that may be very accurate in a lab setting, such as a turbine meter, where flow conditioners are employed in conjunction with the meter, degrade in accuracy in the field if flow disturbances cannot be controlled.

It was not within the budget of this task to conduct an exhaustive review of every possible flow meter type. It was determined that up to five commonly used flow meter types could be evaluated within the schedule and budget for this project. For this cooling water application, the following typical cooling water characteristics were used in considering the selection flow measurement devices for this evaluation.

Velocity (Average) Range:	3 to 12fps
TSS:	Up to 25ppm
TDS:	Up to 5000ppm
pH:	5.5 to 9.5
Temperature:	60 to 130°F
Accuracy (Flow Rate):	±5%
Possible Water Constituents:	Ammonia Chlorine Iron Manganese Silica Sulfates Calcium

VOCs
Oil
Grease
Biological growth

In a study conducted for the Cooling Technology Institute (CTI, 2003), the performance of five flow meter types were selected and examined for their accuracy. Based on the results of that study and the above typical cooling water characteristics, the following major types of flow meters remained as commonly used and viable candidates for use in this application: electromagnetic, ultrasonic, impellar, calorimetric and multi-port averaging pitot tube type flow meters. Therefore, these five types of flow meters were selected for evaluation. A brief description of and typical performance characteristics for each of these flow meter types are described and summarized in this section.

It should also be emphasized at this point that there can be many factors that affect the measurement and, therefore, the accuracy of these instruments. Two that will be most important in this application are 1) location of the flow meter with respect to upstream and downstream pipe fittings and geometry changes, including elevation, and 2) the number of pipe diameters of straight pipe length from these flow interferences/disturbances. Ideally, every meter should be installed with 10 to 15 pipe diameters of straight horizontal continuous pipe upstream of the meter and 5 pipe diameters of straight horizontal continuous pipe downstream of the meter (CTI, 2003, Marley, 1999). Consequently, some meter types may require field calibration after installation to attempt to “correct” for specific flow disturbances in the proximity of the meter. Additionally, those meters that can be inserted through a hot tap or that are of the non-intrusive type will usually offer the greatest convenience and will likely be preferred for this application.

3.3.1.1 Electromagnetic Flow Meters

This type of flow meter has a probe with a sensor that is inserted into the water flow through the wall of the pipe. They use electromagnetic technology, i.e., Faraday’s law of electromagnetic induction, to measure water velocity. Faraday’s Law (Bueche, 1969) states “that the electromotive force (emf) induced in a circuit by a changing magnetic field is equal to the negative of the rate of change of the magnetic flux linking the circuit.” The meter’s sensor generates a magnetic field in the pipe. As the water moves through the electromagnetic field, the electromagnetic field in the water changes from zero to the maximum value of the field strength. Because water is a conductor, the magnetic field induces a voltage in the water as it moves through the magnetic field. Two electrodes in the sensor, along with a ground button, measure this voltage. The magnitude of the voltage produced is directly proportional to the velocity of the water. A faster water velocity produces a greater voltage. Flow is then calculated in the instrument by multiplying the average velocity by the cross-sectional area of the pipe. These meters can have a single pair of electrodes or multiple pairs of electrodes that would be positioned along the probe at different radii of the pipe. The position along the pipe diameter would correspond to an equal cross-sectional area of the flow, for which that sensor is measuring a velocity. The greater the number of sensors, the finer the velocity profile that can be measured, allowing for asymmetric velocity profiles due to flow disturbances in the pipe. The greater the number of sensors, the more expensive the meter.

At the point where the velocity measurement is made, the pipe must be completely filled with the liquid flow being measured and can not involve two-phase fluids. Anything other than a homogeneous liquid flow will introduce inaccuracies in the calculated flow rate as the electronics of the instrument are programmed for the specific diameter of the pipe to calculate the flow area assuming a completely filled pipe. Since this instrument operates on the principles of Faraday's law, the substance being measured must be conductive. Any non-conducting liquids in the flow will produce errors in the measurement.

Installation, Maintenance and Calibration

These types of flow meters must be inserted in the flow to establish the magnetic field. Therefore some accommodation must be made to penetrate the pipe wall to allow insertion of the meter's probe into the flow stream. This can usually be accomplished using a saddle with 2" NPT connection or a 2" NPT fitting welded in the pipe wall.

Maintenance of these flow meters requires periodic removal and cleaning of the sensor to remove any build-up on the sensor. Field calibration of these sensors should be performed per the manufacturer's detailed procedure upon initial calibration and at least once a year.

Selected performance specifications of this flow meter follow.

Local Velocity Measurement

Range: -5 to +40 ft/s (-1.5 to +12.2 m/s)

Zero Stability: ± 0.03 ft/s (± 0.009 m/s)

Accuracy: $\pm 1\%$ of reading, from 0 to 20 ft/s add zero stability

Precision: Not Available

Repeatability: 0.20% of range

Estimate of Installed Cost: (personal contact with Macaulay Controls Co.)

Labor: \$1,280 (based on 16 hours labor at \$80/hr. If a 2" NPT fitting is already present in the pipe wall, it may take only 8 hours to install.)

Materials: Meter- Depending on the pipe diameter, number of electrodes in the sensor model selected, and material of the sensor, the price of the meter will range from \$3,750 to about \$18,200.

Total: Approximately \$5,030 - \$19,480

3.3.1.2 Ultrasonic Flow Meters

Ultrasonic flow meters are non-intrusive clamp-on instruments that measure flow by sending sonic pulses through the pipe and the liquid. Sonic pulses are sent both upstream and downstream between the clamp-on, sonic transducer pairs that are mounted on the side of the pipe. The transducers are matched to the pipe's sonic properties to produce a wide sonic beam. The beam travels axially through the pipe wall, transmitting a precise, stable wave shape into the liquid.

The pulses travel between the transducers through two separate paths. The first measurement

path travels through the pipe wall and diagonally through the liquid, reflecting off the far pipe wall to the other transducer as shown in Figure 1. Liquid flow causes a proportional time difference between upstream and downstream transmissions. The system measures this time difference and converts it to volumetric or mass flow rate. The second sonic path passes between the transducers through the pipe wall only. Since liquid flow does not affect the timing of the pulses in the pipe wall, this path serves as a stable zero flow reference. It eliminates zero drift and allows the zero to be set without the need to stop flow.

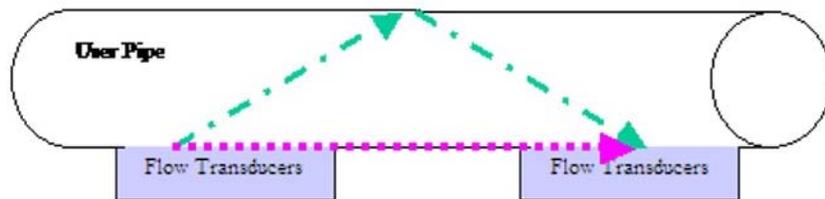


Figure 1. Principle of the ultrasonic flow meter (Controlotron, 2003)

Temperature and pressure can also be monitored. This enables the flow meter to detect and report liquid changes or interfaces, to optimize its performance and calibration for each liquid, and to compute the mass flow rate of the liquid. Installation can be made at any location, even with a minimum available straight run, with a choice of 2, 4, 6, or 8 path flow profile accommodation systems (two paths per beam with reflect mode).

The meter is calibrated upon installation per the manufacturer's manual. Since the transducers are mounted externally to the pipe, installation is straightforward and minimal installation cost is incurred. A location for installation should be selected such that the liquid flow completely fills the pipe at zero flow. The condition of the pipe surface should be corrosion free, coating free and heavy paint free to properly install the transducers.

Maintenance for the meter requires addition of pipe couplant on the transducers, every few months or so, depending on the ambient environment surrounding the application. The couplant is a synthetic grease with Teflon that is installed on the emitting surface of the transducer prior to mounting on the pipe. The couplant helps attenuate the signal through the pipe.

The meters measure the average velocity of the fluid. Therefore the pipe must be full to most accurately measure flow rate, which is calculated by multiplying the cross-sectional area of the pipe time the velocity measured. Since the substances being measured have to be sonically conductive liquids, air (a non-conductive fluid) in the pipe can be problematic and introduce errors in the flow rate calculated.

Selected performance specifications of this flow meter follow.

Local Velocity Measurement

Velocity Range: -60 to +60ft/sec (-18 to +18m/s)

Calibratable Accuracy: 2% of rate, as low as 0.2% with special order

Precision: Not available

Repeatability: 0.25%, 0.15% on high precision calibration

Estimate of Installed Cost: (personal contact with Controlotron)

Labor: \$240 (Based on 3 hrs labor at \$80/hr)

Materials: Meter and accessories - \$4,665 to \$14,000

Total: Approximately \$4,905 to \$9,125 for 12" pipe, depending on number of transducer pairs.

3.3.1.3 Calorimetric Meters

This type of meter involves the insertion of the meter's sensor into the flow stream. The sensor head of this meter contains two positive-temperature coefficient (PTC) resistors. One of them measures the temperature of the media, while the other is heated by an attached heating resistor. The temperature difference between the two PTC-resistors is predetermined and a control circuit increases power to the heating resistor to maintain a constant temperature difference.

The flow of the media (e.g., the cooling water) cools the heated PTC-resistor proportional to the speed of the flow. The heating power provided by the control circuit to keep the temperature difference constant between the two PTC-resistors is equivalent to the heat dissipation by the flow of the media. This results in a linear output signal proportional to the flow rate of the fluid.

The nature of the flow profile (laminar or turbulent) in the pipe will vary depending upon the flow rate. The probe is inserted a depth of 1/7-th (0.1429) of the pipe diameter to measure the flow velocity. For both laminar and turbulent flow, the velocity at this pipe diameter is approximately equal to the average flow velocity (Potter, 1975). It is this velocity that is used to calculate the flow rate based on the area of the pipe.

The sensor is installed through the pipe wall in a female 1-1/2" NPT fitting or into the threaded pipe itself, or into a tee. The flow meters have a male 1-1/2" NPT threaded fitting and are inserted to the proper depth.

Recalibration of this flow meter should be performed on an annual basis. Calibration may be performed in the field, if a reference flow meter is available.

Selected performance specifications of this flow meter follow.

Local Velocity Measurement

Velocity range: 0 to 6.6 ft/s (0 to 2 m/s)

Accuracy: <3%

Precision: Not available

Repeatability: <1%

Estimate of Installed Cost: (personal contact with Weber Sensors Inc.)

Labor: \$80 (Based on 1 hr labor at \$80/hr if a female 1-1/2 NPT fitting is available)

Materials: Meter - \$995

Total: Approximately \$1,075

3.3.1.4 Multi-Port Averaging Pitot Tubes Meters

Pitot tube meters must be inserted in to the flow stream to measure the velocity of the flow and may be single or multi-port in design. The ports on these meters are connected to manometers that measure the pressure of the flow stream at the port. The inlet to the port is aimed upstream and must be oriented along a line coincident with the axis of flow in the pipe. This port allows a measurement of the total velocity pressure, i.e., the kinetic energy velocity of the flow plus the static pressure in the line at this point in the flow. A separate port in the sensor is oriented perpendicular to the flow and measures only the static pressure in the flow at this point. The difference between the total pressure and static pressure measurements is the velocity pressure and is proportional to the velocity of the flow at the location in the flow stream where the total pressure was measured. These meters require pressure transducers to measure both pressures or the differential between the two.

Multi-port probes measure the total pressure at multiple insertion depths in the pipe to provide greater information about the velocity profile and hence greater accuracy in determining the average velocity in the pipe. The average velocity is then used to calculate the flow rate in the pipe using the cross-section area of the pipe at the location of the sensor. Alternatively, as with the multi-sensor electromagnetic probe, the position of the ports can be selected to measure equal flow areas and the flow rate of the pipe can be calculated summing the products of the individual cross-sectional areas of the pipe and their respective velocities.

These sensors are extremely sensitive to alignment of the port with the flowstream lines of the flow and to turbulence in the flow, due to both upstream and downstream changes in pipe geometry and pipe fittings.

To insert these flow meters, an accommodation must be made to penetrate the pipe wall. This can usually be accomplished using a saddle with 2" NPT connection or a 2" NPT fitting welded in the pipe wall.

Maintenance of these flow meters requires periodic removal and cleaning of the sensor to remove any build-up on the sensor. The differential pressure transducers that are used with the meter to measure the difference between total pressure and static pressure should be calibrated once a year. The calibration of these transducers can usually be performed on-site with the proper reference standards.

Selected performance specifications of this flow meter follow.

Local Velocity Measurement

Range: 0 to 165 ft/s (0 to 50 m/s)

Accuracy: +/- 1% of Reading

Repeatability: +/- 0.1% of Reading

Precision: Not Available

Estimate of Installed Cost:

Labor: \$1,280 (based on 16 hours labor at \$80/hr. If a 2" NPT fitting is already present in the pipe wall, it may take only 8 hours to install.)
 Materials: Meter - \$600 for 10" line plus \$300 up to \$1,800 for square root extractor and differential pressure transducer depending on model selected.

Total: Approximately \$2,180 up to \$3,680 for a 10" pipe

3.3.2 Summary of Evaluation of Flow Meters

From Section 7.3 of Appendix P, calculation of the HRVOC mass emission rate from the concentration of strippable HRVOCs in the water and the cooling water circulation rate is shown in Equation (1).

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

(1)

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

It can be seen in Equation (1) that any error (%) in the water flow rate will produce a similar error (%) in the calculated mass emission rate. Therefore, one of the primary factors to assess in selection of a flow meter is how accurate will these meters be in the field? And how easy will it be to maintain this accuracy in use?

Each type of flow meter considered in this study will have velocity ranges in which that instrument will be most accurate. Hence some will be more accurate than others in different velocity ranges. There is no one type of meter that will be the most accurate across the entire velocity spectrum and conditions that will be present for this application.

In a presentation of results of a study funded by the Cooling Technology Institute (Huber, 2003), the accuracy of three types of pitot tubes, an ultrasonic, a magnetic, and a turbine type meter were measured. Each was tested under controlled conditions that simulated pipe flow conditions that ranged from somewhat ideal (from a flow measurement standpoint) to less than ideal conditions. The conditions were however flow conditions that could be encountered in the field. With regard to accuracy, the study concluded that "Practically speaking, accuracies on the order of ±3% are the best that can be expected with the field type measurement typically encountered in cooling tower applications." This study also pointed out that this accuracy can quickly increase to ±10% or more if siting (location in the pipeline and number of pipe diameters of straight pipe upstream and downstream from fittings and bends) or application of the meter methodology (including the basis for flow rate calculation) is compromised.

For flow measurements, the true accuracy of a flow measurement can only be determined after a meter has been installed and its measurement verified. Equally important to note is that the location of installation may ultimately determine the maximum accuracy of the flow measurement and should be carefully selected, considering the measuring principle of the meter

to be used.

The cost information obtained for this study does not represent the best estimate of what the actual cost to purchase and install these types of flow meters will be. Although the cost of the flow meters themselves may be representative of each type, the installation costs and the amount of ancillary equipment that will have to be purchased will have the greatest uncertainty. Until the specific cooling tower (size) and piping configuration is known, more accurate cost estimates for the most appropriate meter and the types of piping modifications needed to locate, install and field calibrate the meter cannot be developed.

3.3.3 Conclusion of Evaluation of Instruments for Continuous Measurement of Cooling Water Flow Rate

The purpose of this task was to gather information on typical flow meters used or that could be used to measure flow rates of cooling water and to assess the impact these measurements may have on the emission estimates calculated in Appendix P. The error in the calculated value of the mass emission rate will be directly related to the accuracy of the flow measurement. The accuracy of the flow measurement will not just depend on the accuracy of the meter but will also depend on siting of the meter and the principle on how the measurement is made by the meter. It is possible to achieve the required accuracy of 5% but this will require careful siting of the meter selected and consideration of the meter measure velocity and calculates flow rate.

3.4 Development of a Mass Transfer Model of VOC Emissions from Cooling Towers

The methods tested in this study are insufficient for simulating actual emissions of VOCs from industrial cooling towers or to predict the sensitivity of emissions to changes in system conditions. As such, an emissions calculator (model) was developed to predict VOC emissions from cooling towers. User documentation for the model (*CTEC: Cooling Tower Emissions Calculator*) is provided as Appendix I of this report. A brief summary of the model is described below.

It was beyond the scope of this study to develop a model that can simulate all possible cooling tower designs. As such, the model was developed for cooling towers that employ packed media with cross-flow air exchange. The cooling tower itself is treated as two major components: (1) tower with cascading cooling water, (2) underlying sump of cooling water. Component 1 is treated as a series of 10 well-mixed stages, allowing for discrete changes in temperature and water flow rates (due to evaporative losses) in each stage. Component 2 (sump) is treated as a single well-mixed continuous flow reactor with a well-ventilated overlying headspace.

Mass balances are applied to estimate VOC concentrations exiting, and emission from, each stage of the cooling tower. Liquid and gas-phase mass transfer coefficients within each stage are modeled in accordance with classical Onda correlations. The effects of temperature variations on key fluid parameters that affect mass transfer processes are accounted for in the model, with discrete values of these properties for each stage of the cooling tower.

The *CTEC* model was developed using Microsoft® EXCEL and exists as a user-friendly

worksheet. The user is required to input key model parameters as described in the user documentation. Specific unit requirements for each input are clearly specified in the model worksheet. Output includes plots and tables of VOC concentrations in cooling water at various stages of the cooling tower, the VOC emission rate at each stage of the cooling tower and sump, and a statement of the overall emission rate from the cooling tower system.

The CTEC model was not evaluated against actual field data, and the user should recognize the model as a screening tool for first estimates of emissions. The reader is referred to Appendix I for a more detailed discussion of user input requirements and key model assumptions.

4.0 Conclusions and Recommendations

4.1 VOC Leak Detection

Five methods were evaluated in this study as potential leak detection methods/approaches. These methods were hydrocarbon trap, chlorine usage, oxidation-reduction potential, total organic carbon, and pH. The evaluation of these methods/approaches was conducted by performing a review of the theoretical principle(s) on which the method/approach is based. As these methods were considered for use in VOC leak detection, the primary evaluation criteria used was the second data quality objective for the project, specifically:

Detection Limit: ≤ 10 ppbw

Accuracy: Below 50 ppbw, ± 10 ppbw, absolute difference

Equal to or above 50 ppbw, $\pm 20\%$, as relative error or % difference

The methods, individually or in combination, must be capable of providing 90% speciation of the individual compounds in the total VOC. Speciated compounds of interest to the TCEQ considered in this study were benzene, ethylene, propylene, 1,3 butadiene, and all the butene isomers.

None of the five methods evaluated met the criteria required by the TCEQ for detecting VOC leaks in cooling water, i.e., the detection limits for these methods/instruments were not sufficiently low enough to meet the detection limit specification of 10 ppbw. Additionally, they are unable to exclusively attribute changes in the parameter measured to the introduction of a VOC due to a leak. It is not recommended that these methods be used for leak detection of benzene, ethylene, propylene, 1,3 butadiene, or any of the butene isomers.

4.2 VOC Sampling, Measuring, Monitoring, and Testing Methods

Four sampling methods were evaluated for speciation of the high interest VOCs: VOA vial, 0.5 L Tedlar bags, Summa Canister and 10 L Tedlar Bags. Of these methods, only the Summa canisters and the 10 L Tedlar bags used for analysis of gas samples from the air stripping column exhaust satisfy both the 90% speciation and accuracy criteria for the sampling system. Based on these criteria, the VOA vials and 0.5 L Tedlar bags used for water sampling can be eliminated since they provided unacceptable accuracy, as high as -78% for the VOA vial and -60% for the 0.5 L Tedlar bag.

One TVOC method was evaluated, an FID TVOC analyzer. This instrument does not provide speciation and when compared to total VOC concentration in the water flow for the composition of organic chemicals used in the lab test series, the accuracy of the instrument decreased to -72% at 1000 ppbw VOC concentration.

Therefore, the test series conducted illustrated that for batch samples, both the Summa canister and the 10 L Tedlar bags can provide acceptable accuracy and 90% speciation of gas samples, if the VOC stripping system has efficiencies of at least 96%.

There were no readily available commercial continuous monitoring systems that had been used to measure the high interest VOCs in cooling water. Of the equipment available, there are many

instruments that measure TVOC using FID technology. These instruments of course do not provide speciation and will vary in accuracy depending on the composition of VOCs in the cooling water and the concentration. The cost for the FID analyzer alone starts at approximately \$15,000.

There are available on line GC systems which must be used with either an FID or PID and which can provide acceptable speciation. On-line continuous GC systems are limited however in the specific chemicals that can be detected, compounds up to C5 being possible. For benzene and other compounds, a second analyzer would be required. These systems also require a VOC stripping system. These systems start at \$55,000 and can easily double in cost if an intrinsically safe system is required.

The most important aspect of sampling is preservation of the sample, i.e., elimination of any possible losses of the VOCs before analysis of the sample. This requires proper design of the sampling system, the sample collection procedure and conditions, the sample collection device, storage and handling of the sample prior to analysis, and similar preparation (dilution) of the samples prior to analysis. Each of these factors can adversely affect the accuracy of the results, the accuracy being as far off as 75% at low concentrations, where the specification is 10 ppbw below 50 ppbw. At these levels, sample collection, the air stripping system, and detection limit of the analytical system are critical and their impacts on the overall accuracy must all be considered.

There are also mass spectrometry systems that can provide direct speciation of VOCs from water samples. These systems can meet the accuracy and speciation requirements but are susceptible to changes in sample temperature. It is unclear how water matrix effects affect the accuracy of the measurement. Additionally, it is not directly evident how measurements from these systems correlate to the strippable VOC concentration required by the TCEQ. These systems are \$75,000 for units that are intrinsically safe and \$65,000 for those that are not.

This project did not study the impact of matrix effects related to water quality on the data quality objectives. Clearly some water constituents like chlorine will react with the VOCs considered in this study. Therefore, any system that is considered should assess the impact of the matrix effects on both the presence/concentration of the VOCs in the water and on the accuracy of the measurements made by the system.

4.3 Instruments for Continuous Measurement of Cooling Water Flow Rate

The purpose of this task was to gather information on typical flow meters used or that could be used to measure flow rates of cooling water and to assess the impact these measurements may have on the emission estimates calculated in Appendix P. The error in the calculated value of the mass emission rate will be directly related to the accuracy of the flow measurement. For this cooling water application, the following typical cooling water characteristics were used in considering the selection flow measurement devices for this evaluation.

Velocity (Average) Range:	3 to 12fps
TSS:	Up to 25ppm
TDS:	Up to 5000ppm

pH:	5.5 to 9.5
Temperature:	60 to 130°F
Accuracy (Flow Rate):	±5%
Possible Water Constituents:	Ammonia
	Chlorine
	Iron
	Manganese
	Silica
	Sulfates
	Calcium
	VOCs
	Oil
	Grease
	Biological growth

Based on the results of a study (CTI 2003) performed for the Cooling Tower Institute and the above typical cooling water characteristics, the following major types of flow meters were selected as viable candidates for use in this application: electromagnetic, ultrasonic, impellar, calorimetric and multi-port averaging pitot tube type flow meters. All of these types of flow meters are capable of meeting the accuracy (±5%) required for this application. However, the accuracy of the flow measurement will not just depend on the accuracy of the meter but will also depend on siting of the meter in the flow and the principle on how the measurement is made by the meter. It is possible to achieve the required accuracy of 5% but this will require careful siting of the meter selected and consideration of how the meter measures velocity and calculates flowrate. As discussed in Section 3.3, the cost of the instrument may be quite low (\$600) but the total cost for installation can be significantly more depending on the location, whether the instrument must penetrate the pipe wall to make the measurement, and existing pipe penetrations that can be used for the instrument, if necessary.

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APPENDICES

Appendix A

**Texas Commission on Environmental Quality
Sampling and Procedures Manual
Appendix P
Cooling Tower Monitoring**

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 °F. Specific procedures for cooling tower sampling and analysis for VOCs with boiling points of 140 °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 top 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 $\pm 2\%$ 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 $\pm 2\%$ 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 each 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 $\pm 5.0\%$ 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 $\pm 5.0\%$ 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 $\pm 5\%$ of the rotameter reading, the rotameter is acceptable. If the difference between the rotameter reading and the measured calibration flow rate exceeds $\pm 5\%$, 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 $\pm 2\%$ 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 $\pm 5\%$ of the mean.

4.4.3 If the average measured calibration flow rate agrees within $\pm 5\%$ of the rotameter reading, the rotameter is acceptable. If the difference between the

rotameter reading and the calibration flow rate exceeds $\pm 5\%$, 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 $\pm 1.5\%$ 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 to 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 °C 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 °C 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 °C 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 150°C. 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 on 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

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

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, °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

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

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

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

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

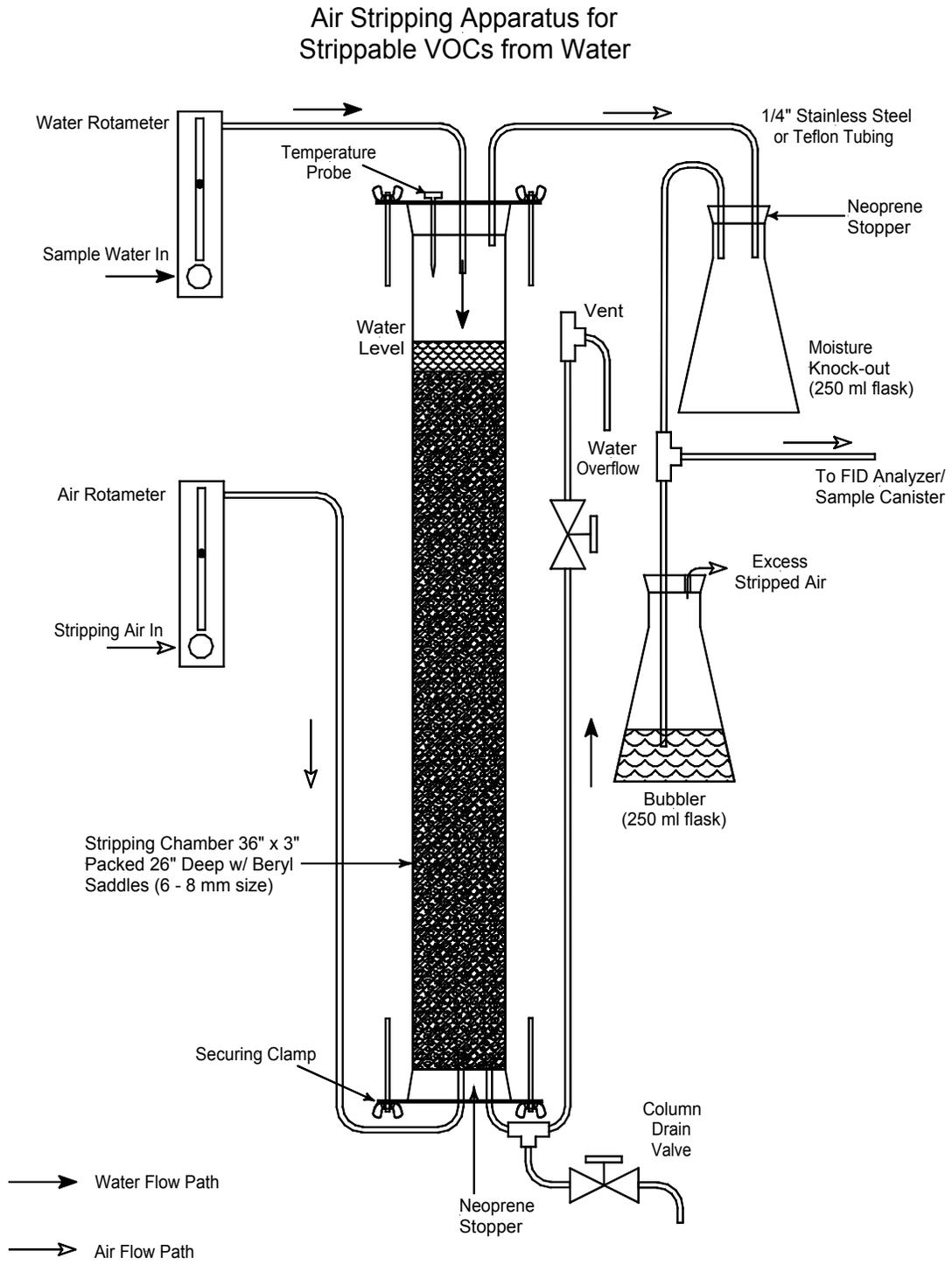
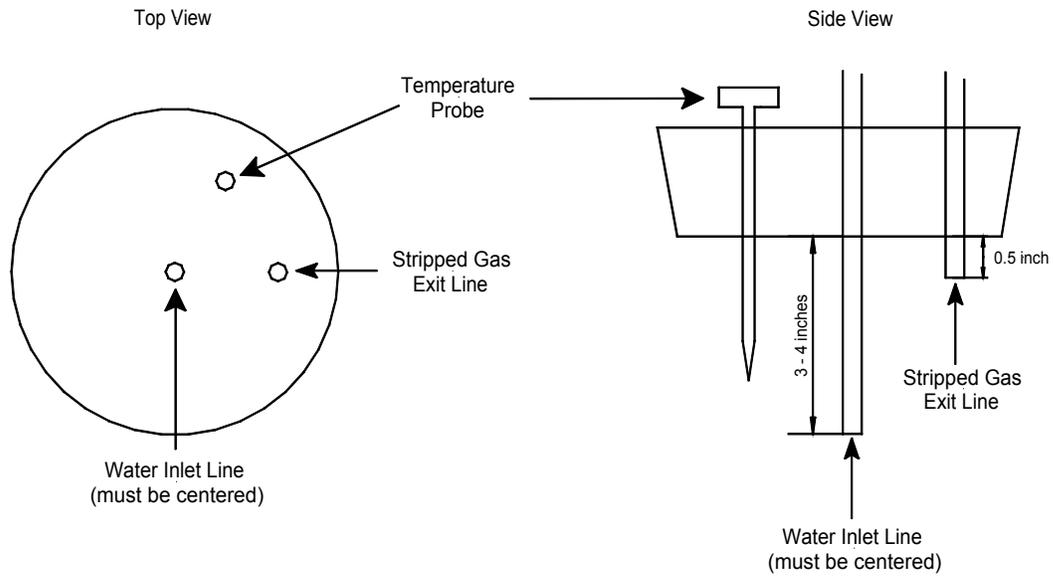


Figure 2

Air Stripping Apparatus Stripping Chamber End Cap Design

Stripping Chamber Top



Stripping Chamber Bottom

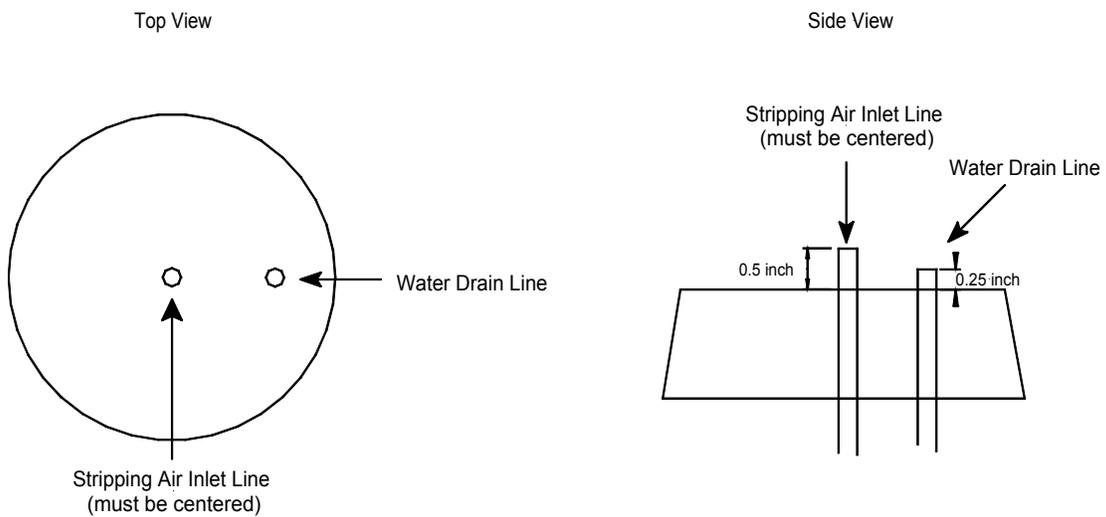


Figure 3
Air Strippable VOCs in Water
FID Analyzer Measurement Data Sheet

Regulated Entity: _____

Regulated Entity No: _____

Air Account No: _____

Instrument Model: _____

Unit Name: _____

Instrument Serial No: _____

EPN/FIN ID No: _____

Operator(s): _____

Process Description: _____

Certified Gas Value: Zero: _____

Date/Time: _____

Mid-level: _____

Barometric Pressure: _____

High-level: _____

Process Water Flow: _____

FID Response Zero: _____

Zero Air Background VOC: _____

Mid-level: _____

Zero Water Background VOC: _____

High-level: _____

Stabilization Time: _____

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: _____	Regulated Entity No: _____
Air Account No: _____	Instrument Model: _____
Unit Name: _____	Instrument Serial No: _____
EPN/FIN ID No: _____	Operator(s): _____
Process Description: _____	Certified Gas Value: Zero: _____
Date/Time: _____	High-level: _____
Canister ID: _____	FID Response Zero: _____
Sample ID: _____	High-level: _____
Barometric Pressure: _____	Zero Air Background VOC: _____

Appendix B

Chlorine Concentration Measurement Methods

As discussed in Section 3.1.1.2, measurement of both the free and total chlorine concentrations are needed to begin to assess whether changes in chlorine concentration are due to the presence of VOCs in the cooling water, because it is unknown which form of chlorine, i.e., free or compounds containing chlorine will react with the VOCs. Various methods for measurement of both total and free chlorine concentrations in water are prescribed in *Standard Methods for the Examination of Water and Wastewater* (Greenberg et al, 1992). There are eight standard methods that are appropriate to measure the free chlorine in cooling water. The eight standard methods are Iodometric Method I and II, Amperometric Titration Method, Low-level Amperometric Titration Method, DPD Ferrous Titrimetric Method, DPD Colorimetric Method, Syringaldazine (FACTS) Method, and Iodometric Electrode Technique. These standard methods for total and free chlorine measurement are described in this Appendix.

In practice, residual free and residual total (free plus combined) chlorine concentrations are typically measured to monitor water quality in cooling tower systems. The selection of the measurement method to be used will first depend on whether the free or total chlorine concentration is desired. Second, depending on the water quality and specific constituents in the water, interferences in the measurement methods should be considered before final selection of a method.

Free chlorine concentration measurement

In considering the use of the eight methods mentioned above for the measurement of free chlorine in cooling water containing significant amounts of organic matter, the amperometric method, the DPD methods, and the FACTS method are the most suitable measurement methods. Some pertinent characteristics for the use of these three methods for this application are listed below:

- The amperometric method is the method of choice because it is not subject to interference from color, turbidity, iron, manganese, or nitrogen.
- The DPD methods are subject to interference from high concentrations of monochloramine, which is avoided by adding thioacetamide immediately after addition of the reagent. Oxidized forms of manganese at all levels encountered in water will interfere in all methods except in the free chlorine measurement of amperometric titrations and FACTS, but a blank correction for manganese can be made in the DPD methods.
- The FACTS method is unaffected by concentrations of monochloramine, dichloramine, nitrite, iron, manganese, and other interfering compounds normally found in domestic wastewaters.

Total chlorine concentration measurement

For the measurement of total chlorine in cooling water containing significant amounts of organic matter, the DPD methods, amperometric and the iodometric back titration method are the most suitable measurement methods. Some pertinent characteristics of each method are listed below:

- The iodometric back titration method cannot be used if the concentration is less than 1 mg/L.
- Certain metal, surface-active agents and complex anions in some industrial wastes interfere in the amperometric titration.

- The DPD titrimetric and colorimetric methods are applicable to determining total chlorine in polluted waters. In all colorimetric procedures using color and turbidity blanks, the color and the turbidity can be compensated for by zeroing with a blank sample.

There are a number of commercially available on-line monitoring devices for chlorine. Some, like the Hach CL17, use a DPD colorimetric measurement method. Others, like the American Sigma Models 8450 and 8451 and the GLI AccuChlor, use an amperometric method.

Currently, the Public Drinking Water Program requires the use of the colorimetric method for compliance monitoring because the amperometric methods used by on-line monitors differ slightly from that described in Standard Method 4500-Cl Method D. Nevertheless, several systems are using the amperometric models for process control monitoring and seem to be satisfied with their accuracy and reliability (Schulze J.C, TCEQ, 2003).

[What is the sensitivity, accuracy and detection limits and how does this relate to VOC](#)

For both the free and total chlorine measurement, the DPD colorimetric method is the most appropriate method to use in terms of convenience, accuracy, and speed of making the measurement.

The following method description summaries are taken from *Standard Methods for the Examination of Water and Wastewater*.

Standard Method 4500-Cl B. Iodometric Method I

a. Principle: Chlorine will liberate free iodine from potassium iodide (KI) solutions at pH 8 or less. The liberated iodine is titrated with a standard solution of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) with starch as the indicator. It must be titrated at pH 3 to 4 because the reaction is not stoichiometric at neutral pH due to partial oxidation of thiosulfate to sulfate.

b. Interference: Oxidized forms of manganese and other oxidizing agents interfere. Reducing agents, such as organic sulfides, also interfere.

c. Minimum detectable concentration: The minimum detectable concentration approximates 40 $\mu\text{g Cl as Cl}_2/\text{L}$ if 0.01N $\text{Na}_2\text{S}_2\text{O}_3$ is used with a 1000-mL sample. Concentrations below 1 mg/L chlorine cannot be determined accurately by this method. Lower concentrations can be measured with the amperometric end point in Methods C and D.

Standard Method 4500-Cl C. Iodometric Method II

a. Principle: This method is used for wastewater analysis. The end-point signal is reversed because the unreacted standard reducing agent remaining in the sample is titrated with standard iodine or standard iodate, rather than the iodine released being titrated directly. This indirect procedure is necessary regardless of the method of end-point detection to avoid contact between the full concentration of liberated iodine and the wastewater.

b. Interference: Oxidized forms of manganese and other oxidizing agents give positive interferences. Reducing agents such as organic sulfides do not interfere as much as in Method B. An unusually high content of organic matter may cause some uncertainty in the end point. A larger fraction of organic chloramines will react at lower pH along with the interfering substances.

c. Minimum detectable concentration: The minimum detectable concentration is 0.2 mg/L chlorine.

Standard Method 4500-Cl D. Amperometric Titration Method

a. Principle: Chlorine residuals over 2 mg/L are measured best by means of smaller samples or by dilution with water that has neither residual chlorine nor a chlorine demand. The method can be used to determine total chlorine and can differentiate between free and combined chlorine. The amperometric method is a special adaptation of the polarographic principle. Free chlorine is titrated at a pH between 6.5 and 7.5, a range in which the combined chlorine reacts slowly. The combined chlorine, in turn, is titrated in the presence of the proper amount of KI in the pH range 3.5 to 4.5. A special amperometric cell is used to detect the end point of the residual chlorine-phenylarsine oxide titration. The cell consists of a nonpolarizable reference electrode that is immersed in a salt solution and a readily polarizable noble-metal electrode that is in contact with both the salt solution and the sample being titrated. Another approach to end-point detection uses dual platinum electrodes, a mercury cell with a voltage divider to impress a potential across the electrodes, and a microammeter.

b. Interference: Accurate determinations of free chlorine cannot be made in the presence of nitrogen trichloride, NCl_3 , or chlorine dioxide, which titrate partly as free chlorine. Some organic chloramines also can be titrated in each step. Monochloramine can intrude into the free chlorine fraction and dichloramine can interfere in the monochloramine fraction, especially at high temperatures and prolonged titration times. Free halogens other than chlorine also will titrate as free chlorine. Interference occurs in some highly colored waters and in waters containing surface-active agents. An unusually high content of organic matter may cause uncertainty in the end point.

c. Minimum detectable concentration: The minimum detectable concentration is 0.2 mg/L chlorine.

Standard Method 4500-Cl E. Low-level Amperometric Titration Method

a. Principle: This method modifies the Amperometric Titration Method by using a more dilute titrant and a graphical procedure to determine the end point. Detection and quantification of chlorine residuals below 0.2 mg/L requires special modifications to the amperometric titration procedure. It is not possible to differentiate between free and combined chlorine forms using this method.

b. Interference: Same as the Amperometric Titration Method.

c. Minimum detectable concentration: With the special modifications, chlorine concentrations at the 10 µg/L level can be measured.

Standard Method 4500-Cl F. DPD Ferrous Titrimetric Method

a. Principle: N, N-diethyl-p-phenylenediamine (DPD) is used as an indicator in the titrimetric procedure with ferrous ammonium sulfate (FAS). When complete differentiation of chlorine species is not required, the procedure may be simplified to give only free and combined chlorine or total chlorine.

In the absence of iodide ions, free chlorine reacts instantly with the DPD indicator to produce a red color. The red color indicates the existence of free chlorine in the sample or container. Concentration of monochloramine, dichloramine, and total chlorine can be measured by various DPD titrimetric methods.

b. Interference: Interferences are caused by oxidized manganese, copper and chromate. Despite the interferences caused by oxidized manganese and copper, and chromate, these interferences can be overcome by the addition of compensating solutions. High concentrations of combined chlorine can break through into the free chlorine fraction. If free chlorine is to be measured in the presence of more than 0.5 mg/L combined chlorine, the thioacetamide modification must be employed.

c. Minimum detectable concentration: Approximately 18 µg Cl as Cl₂/L. This detection limit is achievable under ideal conditions; normal working detection limits typically are higher.

Standard Method 4500-Cl G. DPD Colorimetric Method

a. Principle: This is a colorimetric version of the DPD method and is based on the same principles. Instead of titration with a standard ferrous ammonium sulfate (FAS) solution as in the titrimetric method, a colorimetric procedure is used.

b. Interference: Same as DPD ferrous titrimetric method. However, color and turbidity must be compensated for by using sample to zero photometer. Chromate interference is minimized by using the thioacetamide blank correction.

c. Minimum detectable concentration: Approximately 10 µg of Cl as Cl₂/L. This detection limit is achievable under ideal conditions; normal working detection limits typically are higher.

Standard Method 4500-Cl H. Syringaldazine (FACTS) Method

a. Principle: The free (available) chlorine test, syringaldazine (FACTS) measures free chlorine over the range of 0.1 to 10 mg/L. A saturated solution of syringaldazine in 2-propanol is used. Syringaldazine is oxidized by free chlorine on a 1:1 molar basis to produce a colored product with an absorption maximum of 530 nm. The color product is only slightly soluble in water; therefore, at chlorine concentrations greater than 1 mg/L, the final reaction mixture must contain 2-propanol to prevent product precipitation and color fading. The optimum color and solubility are obtained in a solution having a pH between 6.5 and 6.8.

b. Interference: Interferences common to other methods for determining free chlorine do not affect the FACTS procedure.

c. Minimum detectable concentration: The FACTS procedure is sensitive to free chlorine concentrations of 0.1 mg/L or less.

Standard Method 4500-Cl I: Iodometric Electrode Technique

a. Principle: This method involves the direct potentiometric measurement of iodine released on the addition of potassium iodide to an acidified sample. A platinum-iodide electrode pair is used in combination with an expanded-scale pH meter.

b. Interference: All oxidizing agents that interfere with other iodometric procedures interfere. These include oxidized manganese and iodate, bromine, and cupric ions. Silver and mercuric ions above 10 and 20 mg/L interfere.

c. Minimum detectable concentration: The minimum detectable concentration is not available in the literature. If total residual chlorine is below 0.2 mg/L, the procedure specifies that the apparent chlorine in the reagent blank should be subtracted from the calculated total residual chlorine to obtain the true total residual chlorine value. Therefore, the minimum detectable concentration should be considered to be 0.2 mg/L.

Standard Method 5310 B. High-Temperature Method

a. Principle: The sample is homogenized and diluted as necessary and a microportion is injected into a heated reaction chamber packed with an oxidative catalyst such as cobalt oxide. The water is vaporized and the organic carbon is oxidized to CO₂ and H₂O. The CO₂ from oxidation of organic and inorganic carbon is transported in the carrier-gas stream and is measured by means of a nondispersive infrared analyzer, or titrated coulometrically.

Because total carbon is measured, inorganic carbon (IC) must be removed by acidification and sparging or measured separately and TOC is obtained by subtracting IC from the total carbon. IC is measured by injecting the sample into a reaction chamber packed with phosphoric acid-coated quartz beads. Under these acidic conditions, all IC is converted to CO₂, which is transferred to the detector and measured. Under these conditions organic carbon is not oxidized and only IC is measured

Alternatively, one can convert inorganic carbonates to CO₂ with acid and remove the CO₂ by purging before sample injection. The sample then contains only the nonpurgeable organic carbon fraction of total carbon. Therefore, the purgeable fraction of TOC, is also necessary to measure true TOC.

b. Interference: Removal of carbonate and bicarbonate by acidification and purging with purified gas results in the loss of volatile organic substances. The volatiles can also be lost during sample blending, particularly if the temperature is allowed to rise. Another important loss can occur if large carbon-containing particles fail to enter the needle used for injection. Filtration, although necessary to eliminate particulate organic matter when dissolved organic carbon is determined, can result in loss or gain of dissolved organic carbon, depending on the physical properties of the carbon-containing compounds and the adsorption or desorption of carbonaceous material on the filter.

c. Minimum detectable concentration: The minimum detectable concentration is 1mg C/L. The minimum detectable concentration can be reduced if the sample can be concentrated.

Appendix C Standard Method 4500-H+ B. Electrometric Method

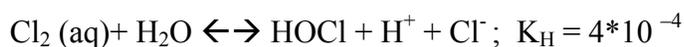
a. Principle: The basic principle of electrometric pH measurement is determination of the activity of the hydrogen ions by potentiometric measurement using a standard hydrogen electrode and a reference electrode. The hydrogen electrode consists of a platinum electrode across which hydrogen gas is bubbled at a pressure of 101 kPa. Because of difficulty in its use and the potential for poisoning the hydrogen electrode, a glass electrode is commonly used. The electromotive force (emf) produced in the glass electrode system varies linearly with pH. This linear relationship is described by plotting the measured emf against the pH of different buffers. Sample pH is determined by extrapolation.

b. Interference: Use of low sodium error electrodes can reduce sodium errors at $\text{pH} > 10$. Temperature affects the properties of the electrodes and chemical equilibrium. Electrodes should be allowed to reach thermal equilibrium and the temperature at which the pH is measured should always be recorded.

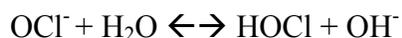
c. Method Detection Level: Minimum detection limit is 0.1 pH unit.

Discussion of Critical Parameters for VOC Leak Detection Use

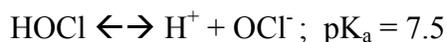
The effect on pH by the addition of the water treatment chemicals depends on the chemical and its form. As an example, the addition of chlorine gas to the water will lower its alkalinity because of the production of the strong acid and hypochlorous acid (HOCl), by the following reaction.



However, if chlorine is dosed as a salt of hypochlorous acid, then the following reactions occur



and there will be an increase in alkalinity to the extent that OCl^- reacts with H_2O . These considerations are important because they show that the form in which chlorine is added can affect the water chemistry in different ways. Additionally, the ratio of the amount of both hypochlorous acid (HOCl) and the hypochlorite ion (OCl^-) that were dissociated in the water are dependent on the pH of the water because hypochlorous acid is a weak acid, which means that it tends to undergo partial dissociation as shown below.



$\text{pK}_{\text{a}} = 3000.00/T - 10.0686 + 0.0253 T$, where T = temperature in K ($^{\circ}\text{C} + 273$)

HOCl produces a hydrogen ion and a hypochlorite ion. From the 25 °C pK_a value, it can be deduced that at pH 7.5 the activities {HOCl} and {OCl⁻} are equal. HOCl predominates at pH values below 7.5, while OCl⁻ is the predominant species at pH values above 7.5. In waters of pH between 6.5 and 8.5, the reaction is incomplete and both species are present to some degree. The table for the percent of undissociated HOCl species for the various temperature and pH values is shown in Table 1 (Daeil Aqua Co., 2003).

Table 1. Percent of Undissociated HOCl Species in Water for Various pH and Temperatures

Percent Undissociated HOCl							
Temp °C → pH ↓	0	5	10	15	20	25	30
5.0	99.85	99.83	99.80	99.77	99.74	99.71	99.68
5.5	99.53	99.75	99.36	99.27	99.18	99.09	99.01
6.0	98.53	98.28	98.01	97.73	97.45	97.18	96.92
7.0	87.05	85.08	83.11	81.17	79.23	77.53	75.90
8.0	40.19	36.32	32.98	30.12	27.62	25.65	23.95
9.0	6.30	5.40	4.69	4.13	3.68	3.34	3.05
10.0	0.67	0.57	0.49	0.43	0.38	0.34	0.31
11.0	0.067	0.057	0.049	0.043	0.038	0.034	0.031

The percent OCl⁻ ion becomes the difference between these numbers and 100. The percent distribution of the OCl⁻ ion and undissociated HOCl can be calculated for various pH values as follows:

$$\frac{HOCl}{HOCl + OCl^-} = \frac{1}{1 + \frac{OCl^-}{HOCl}} = \frac{1}{1 + \frac{K_i}{H^+}}$$

Where, K_i is a constant of HOCl ionization and is calculated from (H⁺) x (OCl⁻) / (HOCl). This constant is shown in Table 2 (Daeil Aqua Co., 2003).

Table 2. HOCl ionization constant (K_i)

HOCl Ionization Constant Table							
Temperature (°C)	0	5	10	15	20	25	30
K _i x 10 ⁻⁸ (moles/liter)	1.488	1.753	2.032	2.320	2.621	2.898	3.175

At 20°C and pH 8, the percent distribution of HOCl is obtained from

$$100 \times [1 + (K_i / H^+)]^{-1} = 100 \times [1 + (2.621 \times 10^{-8} / 10^{-8})]^{-1} = 100 / 3.61 = 27.65\%$$

The germicidal efficiency of a free available chlorine residual is a function of the pH, which establishes the amount of dissociation of HOCl to H⁺ and OCl⁻ ions. Table 1 shows the percentage of undissociated HOCl in a chlorine solution for various pH values and temperatures. Lowering the temperature of the reacting solution suppresses the dissociation; conversely, raising the temperature increases the amount of dissociation.

The rate of dissociation of HOCl is so rapid that equilibrium between HOCl and OCl⁻ ion is maintained, even though the HOCl is being continuously used. For example, if water containing 1 mg/l of titable free available chlorine residual has been dosed with a reducing agent that consumes 50 percent of the hypochlorous acid, the remaining residual will redistribute itself between the HOCl and OCl⁻ ion according to the values shown in Table 1. This is commonly referred to as the “reservoir” effect.

If a known amount of chlorine were added, and then after a time interval the cooling water was analyzed for chlorine concentration, we would find less chlorine present than the amount added. The water has a “chlorine demand”, which is the difference in chlorine concentration between the initial chlorine addition (chlorine dose) to the cooling tower water and the residual chlorine concentration measured after allowing suitable time for reaction. The chlorine demand is the result of a variety of reactions in which chlorine is consumed by various constituents of the water and decomposition of the chlorine (Snoeyink and Jenkins, 1980) .

The reactions of chlorine with the water constituents can be conveniently grouped into

1. those promoted by sunlight,
2. those with inorganic compounds
3. those with ammonia
4. those with organic compounds.

If there was a VOC leak into the cooling water, the chlorine would be consumed by reacting with the VOCs. The form of chlorine used would determine how the pH is changed, i.e., increased or decreased. The changed pH affects the extent of dissociation of hypochlorous acid. The remaining residual chlorine will redistribute itself between the HOCl and OCl⁻ ion by the reservoir effect. Reactions of chlorine with water constituents would be factors that may also change the pH of the cooling water.

Appendix D. Laboratory Test Procedure for Modified El Paso System Tests

D1.0 Purpose of the Laboratory System for Appendix P Tests

The purpose of the Laboratory System for Appendix P Tests (LS-AP) is to conduct a series of tests that require delivery of water containing a mixture of volatile organic compounds (VOCs) of known flow rate, composition and concentration of the components to an El Paso Method continuous monitoring instrument that has been modified by the TCEQ to be in compliance with TCEQ Source Sampling Procedures Manual, Appendix P: Cooling Tower Monitoring. The series of tests were designed to obtain data on the accuracy of three sample collection methods (See Section 2.2.1) and the FID analyzer when employed in accordance with the Appendix P protocol and how water matrix effects might impact the accuracy of the measurements and the performance of the modified El Paso system. The LS-AP was designed specifically for use with the high interest VOCs specified in TCEQ Work Order No. 55078-03-07.

D2.0 Description of the LS-AP

A schematic drawing of the LS-AP is shown in Figure D-1. The LS-AP is designed to be used in a ventilated walk-in chemical hood. The system is composed of three water supply reservoirs and associated pumps to move the water through the test system, an inline mixer, a 4.6-m length of 1.91-cm outside/1.59-cm inside diameter Teflon tubing to ensure a minimum of 5 minutes contact time between the water containing the VOCs and the background water, chilled coils for collection of water samples at the entry to and exit from the El Paso method column, pressure and temperature instrumentation, and the El Paso method column with modifications as specified in Appendix P. Each of these major components is described in detail in the following sections.

Water Reservoirs The LS-AP can supply water from any one of three water reservoirs individually or as mixture of the dionized (DI) water containing VOCs and the background water simulating the cooling water matrix characteristic being studied. The flow rate from each reservoir is controlled by separate variable flow pumps (each a Cole-Parmer Masterflex Controller and PTFE Diaphragm Pump) and calibrated water flow meters. The reservoirs are Tedlar™ bags, 10-L for the DI water containing VOCs and 40-L for the background and DI water supplies of sufficient quantity to conduct one test. Preparation of the DI water containing VOCs is described in Section D4.1.7. All tubing and fittings used in the system are Teflon (PTFE) or stainless steel. All DI water used in the LS-AP was obtained from a Modulab Water Purification System made by Water and Power Technology, Inc. The system produces ASTM Type II water (resistance > 1 M⁻¹·cm).

In-line Mixer Immediately after exiting the tee in the line where the water containing VOCs and the background water flow together, is an inline flow mixer. The purpose of the flow mixer is to promote mixing of the water containing VOCs and the background water to promote a homogeneous mixture. The flow mixer is 0.64-cm diameter stainless steel tubing, 23.5-cm long, with 27 internal right- and left-hand helical elements running the length of the mixer to mix the flow.

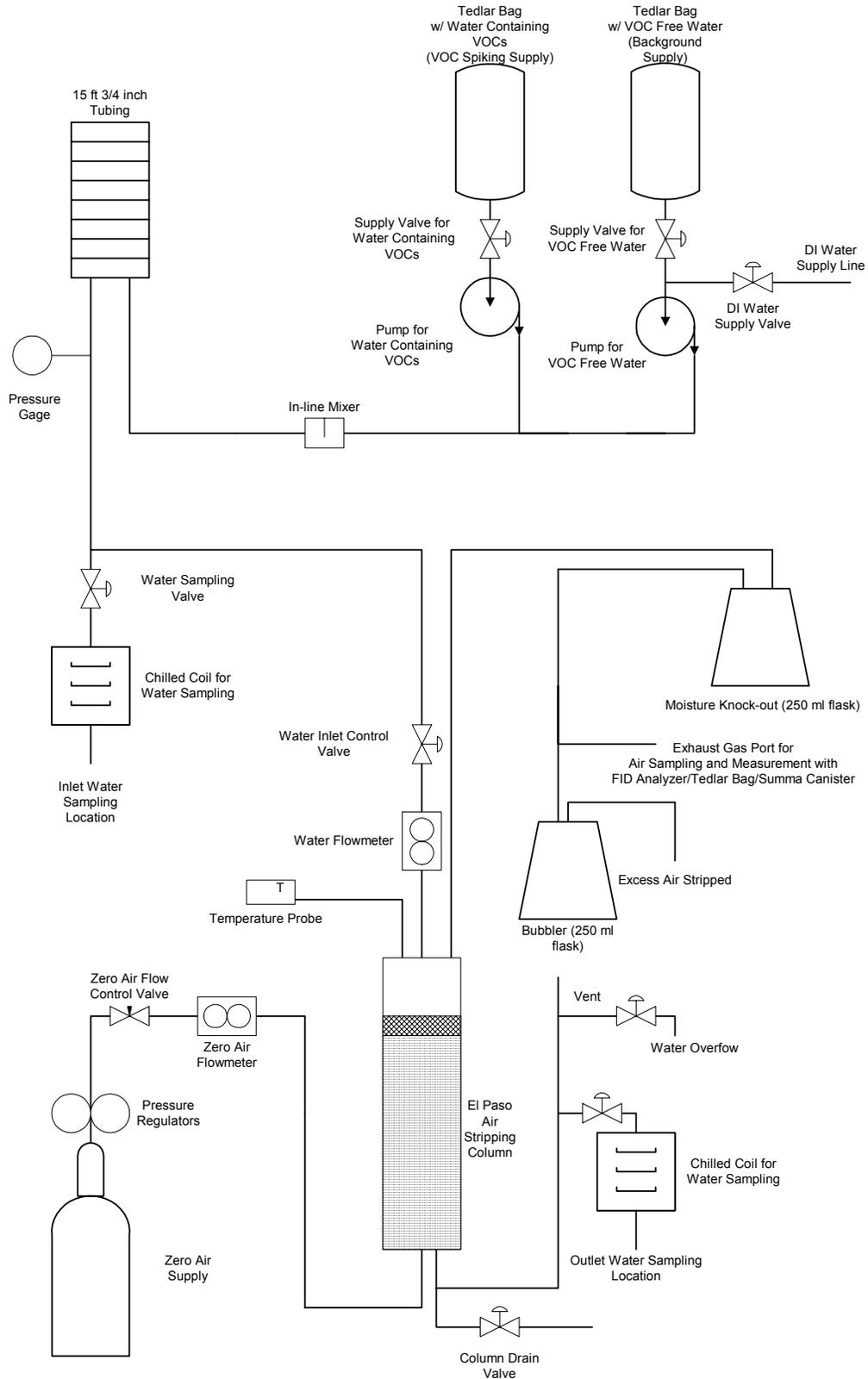


Figure D-1: Schematic Diagram of the Laboratory System for Appendix P Tests

Chilled Coil for Water Sampling At the entrance and exit to the modified El Paso method column are tees with valves that lead to a 3.0-m length of 0.68-cm diameter stainless steel tubing in an ice bath. The purpose of the tubing is to chill the water flow in this line to provide an exit water temperature at the sample collection point of less than 10°C to minimize flashing of the VOCs during sample collection.

El Paso Method System with Appendix P Modifications The El Paso Method system used in this test series was provided by the TCEQ and included modifications specified in Appendix P. All equipment and materials used during the experiments satisfied the equipment and materials requirements of Appendix P, Section 3.

D3.0 Matrix of Tests to be Conducted

A total of 4 tests were conducted. These tests are summarized in Table D-1.

Table D-1. Matrix of Appendix P Tests Conducted

Background Water Quality	VOC Concentration in Background Water Entering Air Stripping Column			
	Detection Limit (D) 10 ppbw Test ID: A-DI-D	Low Level (L) 50 ppbw Test ID: A-DI-L	Medium Level (M) 100 ppbw Test ID: A-DI-M	High Level (H) 1000 ppbw Test ID: A-DI-H
Dionized Water (Chlorine = 0 ppmw, TDS = CT TDS*)	•	•	•	•

* TDS = total dissolved solids, CT TDS = cooling tower total dissolved solids (nominal value)

The VOC mixture that was used for all tests to prepare source water samples contained propylene, 1,3 butadiene, isobutene, 1-butene, cis-2-butene, trans-2-butene and ethylene. The actual concentration of the individual species varied slightly from one test to another depending on the total target concentration desired (See Section 3.2). The nominal value for total dissolved solids that was used for the background water was selected based on that value that might be a typical value for a petrochemical plant cooling tower in the Houston-Galveston area.

Each test consisted of three runs at the same set of operating conditions, e.g., water flow rate, zero air flow rate, VOC concentration in the water flow, water matrix characteristics (TDS, pH and chlorine concentration), and sample collection methods except where specified differently in the following sections. For each test except the detection limit (D) test, data on three sample collection methods was obtained. The sample collection methods were volatile organic analysis (VOA) vials for collection of water samples from the water flow immediately prior to entering the air stripping column and Summa canisters and Tedlar bags for collection of air samples from the exhaust air of the air stripping chamber. For tall tests, FID analyzer measurements were made of the air flow at the same location that the Summa canister and Tedlar bag samples were collected, i.e., at the exit (air flow) of the air stripping column.

D4.0 Procedure for Conducting Tests

The procedure for conducting a test consisted of pretest procedures and activities, those test procedures and activities that were repeated during the individual runs of a test, and post test activities.

D4.1 Pretest Preparations

D4.1.1 Cleaning of Air Stripping Chamber

Initially, and as required during the course of any testing, the air stripping chamber was cleaned per the TCEQ Sampling and Procedures Manual, Appendix P, Section 5.5.3.

D4.1.2 Leveling of the Air Stripping Chamber

The air stripping chamber was leveled per Appendix P, Section 5.3 and checked before each test. Adjustments were made as necessary.

D4.1.3 Summa Canister Cleaning & VOC & Leak Checks

When Summa canisters were used for sample collection, only 6 liter passivated stainless steel canisters with a vacuum gauge and an automated flow regulator were used. Each canister was evacuated to less than 0.05 mm Hg pressure at least 24 hours prior to sample collection. Sample canisters were cleaned and prepared before each use according to procedures described in Section 11.1 of US EPA Test Method TO-14a. A schematic of the cleaning apparatus used for the canister cleaning is shown in Figure D-2. The apparatus can accommodate up to sixteen canisters at one time. Cleaning takes approximately 3 hours to complete. Prior to cleaning, the canisters were emptied of their sample contents and 100 microliters of deionized water was injected into each canister. The cleaning procedure consisted of four fill and purge cycles. The canisters were filled with nitrogen gas to 20 psi and heated for 10 minutes. After heating, the canisters were vented to atmospheric pressure and evacuated to 29.4 inches Hg using a Varian SD200 vacuum pump for 30 minutes. In the second cycle, the canisters were filled to 30 psi followed by immediate venting of the canisters to 5 psi three times. In the third cycle, the canisters were filled to 30 psi, vented to 5 psi and then evacuated to 29.4 inches of Hg for 30 minutes. The fourth cycle was a repeat of the third cycle. After the last evacuation, at least two of every sixteen canisters cleaned were picked at random for a cleaning check using a GC/FID analyzer (discussed later). The canisters were considered clean, when the GC/FID analysis showed that all of the target compounds were present at less than 0.2 ppbv.

D4.1.4 Tedlar Bag Purging, VOC Check & Leak Check

When Tedlar bags were used for sample collection of exhaust air from the air stripping chamber, only new and unused bags (10-L) were used. Tedlar bags were checked for leaks and contamination as described in US EPA Test Method 18, Section 16.1.3.2.

D4.1.5 Tedlar Bag Recovery Study

A recovery study for bag sampling as specified in US EPA Test Method 18, Section 8.4.2, was performed for all target compounds. The recovery study was 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 a known quantity of the target compounds. This step checks not only the potential loss of compounds due to the permeability of the Tedlar™ bag, but also loss due to condensed moisture in the bag. The percent recovery for each target compound must be between 70 - 130% for Tedlar™ bags to be acceptable for sample collection. When Tedlar™ bags are

acceptable, analysis results for the target compounds will be corrected for the percent recoveries. Recovery study bags were stored for the same period of time as the sample bags, i.e., 68 to 72 hours.

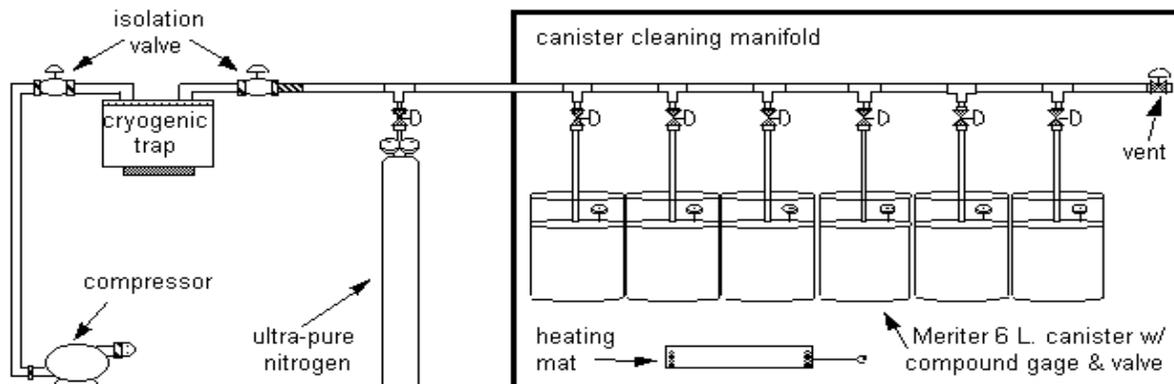


Figure D-2. Schematic of Canister Cleaning Apparatus

D4.1.6 Equipment Calibration

D4.1.6.1 FID Analyzer

The calibration precision and response time tests of the FID analyzer were performed as described in Sections 8.1.2 and 8.1.3 of US EPA Test Method 21 in 40 CFR 60, Appendix A. The precision test was completed prior to placing the analyzer into service.

Precision was defined as the degree of agreement between measurements of a known concentration, expressed as the relative percentage of the average difference between the meter readings and the known concentration. A total of three measurements are made by alternately using zero gas and the specified calibration gas. The analyzer readings were recorded. The average algebraic difference between the analyzer readings and the known calibration gas value was then calculated. This average difference was divided by the known calibration gas value and multiplied by 100 to express the resulting calibration precision as a percentage. The calibration precision was considered acceptable if it was equal to or less than 10 percent of the calibration gas value.

The response time test was performed before placing the instrument into service. Response time was defined as the time interval from a step change in VOC concentration at the input of the sampling system to the time at which 90 percent of the corresponding final value is reached as displayed on the instrument readout meter. Zero gas was introduced into the instrument sample probe. When the analyzer reading had stabilized, it was switched quickly to the specified calibration gas. After switching, the time required to attain 90 percent of the final stable reading was then measured. This test sequence was performed three times and the results recorded. The average response time was then calculated. The instrument response time was considered

acceptable if it was equal to or less than 30 seconds. The instrument pump, sample probe, and probe filter that were used during testing were all in place during the response time test.

The FID analyzer was calibrated using zero, mid-level, and high-level gases before each experiment (three runs). Zero calibration was performed by introducing the zero gas to the FID analyzer and calibrating the analyzer to read 0.0 ± 0.2 ppmv. The high-level calibration was performed by introducing the high-level calibration gas to the FID analyzer. The analyzer was calibrated to read the concentration to within $\pm 5.0\%$ of the calibration gas certified value. The high-level concentration was selected such that the measured sample concentrations were between 10% and 100% of the high-level calibration gas concentration. The mid-level calibration was performed by introducing the mid-level calibration gas to the FID analyzer. The FID analyzer response using the mid-level calibration gas had to agree within $\pm 5.0\%$ of the calibration gas certified value to be acceptable. The mid-level calibration gas concentration was selected to be between 20% and 50% of the high-level calibration gas concentration. Only zero air, certified to contain less than or equal to 0.1 ppmv of total hydrocarbon (THC) was used. Gas standards of methane in air, certified by the manufacturer to be within $\pm 2\%$ of the specified concentration, were used for mid and high level calibrations. The actual concentrations of the gas standards used for calibration were recorded on the test data sheet. Certified gases were used within the manufacturer's specified shelf life.

D4.1.6.2 GC Calibration

First Method

A seven-point calibration was performed on the GC/FID system using a certified gas standard. To develop the calibration, a precise volume of the gas standard was injected and diluted with nitrogen in a 6 liter Summa® passivated stainless steel canister at 30 psi. The final concentration in the canister after such dilution was approximately 10 ppbv for each compound. Seven different volumes, between 20 and 500 cm³, representing seven different masses of the standard, were drawn from this canister by the Entech 7000 preconcentrator and injected into the GC/FID. The instrument response was correlated with the injected volume of each VOC compound in the standard. A calibration curve was determined using the seven points for each VOC compound. The correlation coefficient for each calibration curve had to be greater than 0.99 for the calibration curve to be considered acceptable. A new calibration curve was developed for each batch of samples analyzed.

Second Method

Before beginning any experiments, a second calibration of the GC/FID analysis system was performed by injecting the same volume from seven different known gas standards. To develop this calibration, seven different known volumes of a certified gas standard were injected and diluted with nitrogen in a 6 liter Summa® passivated stainless steel canister at 30 psi. The final concentrations in the canister were calculated after this dilution for each compound. Equal volumes of these known standards, representing seven different masses of the gas standard, were drawn from this canister by the Entech 7000 preconcentrator and injected into the GC/FID analysis system. The instrument response was correlated with the injected concentration for each VOC compound in the standard. A calibration curve was determined using the seven points for each VOC compound. The calibration was considered acceptable if the correlation coefficient for the calibration curve was greater than 0.99. This calibration was compared to the calibration

prepared by the first method. The purpose of this second calibration method is to evaluate the acceptability of the first calibration method. Calibration by the second method was performed only once before beginning any tests.

D4.1.6.3 Air Rotameter Calibration

The air supply rotameter system was calibrated initially using a primary gas flow calibrator (SKC, Ultraflo™, Model 709). The calibration of the rotameter consisted of operating the rotameter at 2,500 ml/min for at least three calibration runs of 10 minute duration. When three consecutive calibration flow rates agreed within ± 5 percent of the average of the three flow rates, the rotameter calibration was considered acceptable. If the difference between the rotameter reading and the measured calibration flow rate exceeded $\pm 5\%$, then the rotameter was remarked to the calibrated flow rate. The air supply rotameter system was calibrated before beginning any tests and scheduled for recalibration semiannually.

D4.1.6.4 Water Rotameter Calibration

The water rotameter was calibrated initially using a graduated cylinder with a $\pm 2\%$ accuracy 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). The graduated cylinder used had a volume of 1000 ml. The water rotameter was operated at 125 ml/min, while filling the container. The time required to fill the container will be recorded and the actual flow rate was calculated based on the container volume and time required to fill the container. The procedure was repeated until three consecutive flow rates agreed within $\pm 5\%$ of the mean value of the flow rates. When the average calculated flow rate of three consecutive repetitions agreed within $\pm 5\%$ of the rotameter reading, the rotameter calibration was considered acceptable. If the difference between the rotameter reading and the calibration flow rate exceeded $\pm 5\%$, then the rotameter was remarked to the calibrated flow rate. The water rotameter system was calibrated before beginning any tests and scheduled for recalibration semiannually.

D4.1.6.5 Temperature Probe Calibration

The air stripping chamber temperature probe was calibrated against an ASTM mercury thermometer. The calibration was performed at or near 0 °C, 20 °C, and 40 °C. If the absolute temperature (in degrees Kelvin) measured by the temperature probe agreed within $\pm 1.5\%$ of each reference point, the temperature probe was considered acceptable. The stripping chamber temperature probe was calibrated before beginning any tests and scheduled for recalibration semiannually.

D4.1.7 Preparation of DI Water with VOC Mixture for Spiking of Background Water During Experiments

Preparation of the water containing the VOC mixtures, which were used for spiking of the background water, was a two step process. The first step involved preparing a deionized water solution with a high concentration of VOCs. This solution was prepared and analyzed per Section D4.1.7.1. Once the analysis results from this solution were obtained and considered acceptable, a second water solution containing VOCs, but at a lower concentration, was prepared using a known quantity of water from the deionized water solution with the high concentration of VOCs and diluting it with deionized water to the value desired for spiking of the background water during the tests. This second solution was analyzed prior to its use in testing to determine

the actual VOC concentration in the water. This two step process was needed to meet the criterion of using water containing VOCs during a test with a total VOC concentration that was within 10% of the target VOC concentration desired for a test.

D4.1.7.1 Preparation of Water Solution with High Concentration of VOCs

All of the high interest compounds except benzene remain in gas phase at room temperature (nominally 22 °C) and pressure. To provide an initial estimate of the quantity of a gas phase VOC mixture that should be added to water to achieve a desired VOC concentration in the water, Henry's Law constants were used to determine how much gas phase VOC mixture should be added to a known quantity of water. Additionally, to overcome the heat of mixing and to ensure that equilibrium had been established, the following process included an equilibration period of 24 hours during which the water solution was agitated using a mechanical shaker.

Equilibrium VOC concentrations in water can be estimated from the following equation (1):

$$C_1 = \frac{m_1}{V_1} = \frac{m_T}{H_c V_g + V_1} \quad (\text{Eq. D-1})$$

where, C_1 is the equilibrium VOC concentration in water, m_1 is the mass of VOC in water, V_1 is the volume of water, m_T is the mass of total gaseous VOC introduced into the Tedlar™ bag, H_c is Henry's law constant for the specific VOC, and V_g is the volume of total gaseous VOC injected into the Tedlar™ bag. The derivation of the equation is presented in Section D4.9 of this Appendix.

The following example is provided to illustrate the procedure used for preparation of the water solution containing a high concentration of VOCs. A Tedlar™ bag was completely evacuated using a low pressure suction pump. Then 5 liters of deionized water would be introduced into the 10 liter Tedlar™ bag ($V_1 = 5$ liter). A gas phase mixture (certified gas cylinder) of ethylene, propylene, 1,3-butadiene, isobutene, 1-butene, c-2-butene, and t-2-butene was used as the VOCs supply source. For purposes of this example, it will be assumed that the concentration of each of these compounds is 10,000 ppmv in the gas mixture. Two hundred fifty (250) milliliters (ml) of the gaseous VOC from the cylinder was then injected into the 10-L Tedlar™ bag containing 5 liters of water ($V_g = 0.25$ liter). The Tedlar™ bag was then placed on a mechanical shaker to apply agitation for 24 hours. The resulting equilibrium VOC concentrations in water as predicted using Henry's Law constants using Equation D-1 are shown in Table D-2. The Henry's Law constants for these compounds were obtained from the United States Environmental Protection Agency's Estimation Program Interface Suite™ (United States Environmental Protection Agency, 2000).

Table D-2: Estimation for VOC Concentration in Water

	MW	HLC @ 25C	HLC @ 25C	Volume of Gas Injected	gas conc (cyl)	Total VOC mass	VOC Conc in water
compounds	gm/mol	atm-m ³ /mol	[m ³ /m ³ g]	Liter	gm/L	gm	ppbw
			H _c	V _g		m _T	C ₁

Ethylene	28	0.2280	9.33	0.25	0.01145	0.00286	390
Propylene	42	0.1960	8.02	0.25	0.01718	0.00430	614
1,3 butadiene	54	0.0736	3.01	0.25	0.02208	0.00552	960
1-butene	56	0.2330	9.54	0.25	0.02290	0.00573	776
isobutene	56	0.2180	8.92	0.25	0.02290	0.00573	793
c-2-butene	56	0.2300	9.41	0.25	0.02290	0.00573	779
t-2-butene	56	0.2240	9.17	0.25	0.02290	0.00573	786
Total							5,098

The Tedlar™ bags used had a sampling port equipped with a septum. After 24 hours of agitation, water samples were extracted by inserting a gas-tight syringe through the sampling port of the Tedlar™ bag. The valve on the gas-tight syringe was immediately closed after drawing the water sample and stored in a refrigerator (temperature of less than 10 °C) until the sample was purged.

Water from the gas-tight syringe was transferred into a purge and trap vessel via injection through a septum cap (See Section D4.8.3) for a detailed explanation of this system) and purged with ultra high purity zero air. The purged air containing the stripped VOCs was collected directly into a stainless steel passivated Summa canister with a mass flow controller on the inlet port and analyzed for the target compounds using US EPA Test Method TO-14a. The VOC concentration in the water sample was then be determined from a mass balance analysis of the water and the volume of air used for stripping the VOCs from the water. Analysis of the canister samples containing the purged air and VOCs were completed within 24 hours after sample collection.

After obtaining reasonable agreement (<5%) between the duplicate sample results, an average value was calculated. The average value of the VOC analyses of the duplicate water samples was compared to the expected VOC concentration. The average value was compared to the theoretical values obtained from equation (1). If measured values were significantly lower than the expected results, then the contact period between the gas phase VOCs and the deionized water was increased. Duplicate water samples were again collected using gas tight syringes on the following day and analyzed using the procedure just described. The average results were compared to the expected value using equation (1). Only after obtaining reasonable agreement between expected and measured results, was water containing VOCs used for preparation of the

D4.2 Procedure for Conducting Tests with DI Water, VOC Target Concentration in Water of 10 ppbw (Detection Limit Concentration)

D4.2.1 First Run

D4.2.1.1 FID Analyzer Calibration

The FID analyzer shall be calibrated before each test (three runs). The FID analyzer shall also be checked with zero air and a gas of 10 ppm methane in air before each run. The FID analyzer shall be challenged with zero air and the response shall be recorded. If the FID analyzer response is not within ± 0.2 ppmv of the FID reading for zero air during calibration, then the FID shall be re-calibrated before further proceeding with any experiments. The FID analyzer shall then be challenged with a gas of 10 ppm methane in air and the response shall be recorded. If

the FID analyzer response is not within $\pm 5\%$ of the gas concentration, then the FID shall be recalibrated before further proceeding with any experiments.

D4.2.1.2 Zero Air Check

A zero air check on the modified El Paso System shall be performed before each run. The high purity zero air shall flow through the column at an air flow rate of 2,500 ml/min. Air effluent from the apparatus shall be monitored with the FID analyzer to determine the baseline reading of the empty stripping chamber and apparatus. The stripping apparatus system and the FID readings will be allowed to stabilize. The analyzer reading shall be recorded on the data sheet. If the zero air check indicates a concentration ≥ 1.0 ppmv as methane in the stripped gas, then the apparatus should be purged thoroughly to remove the contamination until an acceptable concentration is measured (< 1.0 ppmv as methane).

D4.2.1.3 DI Water Check

A water blank check shall be performed on the air stripping apparatus before each run. A Tedlar™ bag shall be filled with deionized water and connected to the Air Stripping Unit. The valve shall be opened and the water flow rate shall be adjusted to 125 ml/min. The air supply shall then be started and adjusted to 2,500 ml/min. The air effluent from the apparatus shall be monitored using the FID analyzer to determine the reading of the apparatus while the system is flowing with clean water. The stripping apparatus system and the FID readings will be allowed to stabilize. The total strippable VOC concentration in the air will be measured and recorded using the FID analyzer. If the water blank check indicates a concentration ≥ 1.0 ppmv as methane in the stripped gas, then the apparatus should be purged thoroughly to remove the contamination until an acceptable concentration is measured (< 1.0 ppmv as methane).

An outlet water blank sample shall be collected in a clean glass vial at the exit of the Air Stripping System for further verification of contamination. The valve on the sampling line shall be opened to allow blank water to flush through the sample line for at least 5 sample line volumes (about 10 minutes) and to achieve a steady flow condition. The cooling coil shall be operated to maintain an exit temperature of the water to be sampled to less than 10 °C. A "blank" water sample shall be collected in a clean glass vial (40-ml) at a sufficiently slow rate to maintain the water exit temperature below 10 °C and to prevent the formation of turbulence. The glass vial shall be cleaned using the procedures under Quality Assurance Procedures. The tip of the sampling tube shall be kept below the surface of the water during sampling to minimize contact with the atmosphere. After sampling, the glass vial shall be immediately capped (a septum cap) to leave a zero headspace in the vial and immediately stored in a refrigerator until analyzed for target VOC compounds. The valve on the sampling line shall be closed. The blank water supply line shall be closed.

D4.2.1.4 Background Water Flow

The valve on the large Tedlar™ bag containing deionized water (VOC free water with the TDS content adjusted to that approximating the value of cooling tower water, i.e., 1,500 +/- 150 ppmw) shall be opened and the water flow rate shall be adjusted to 125 ml/min. The valve on the sampling line shall be opened to allow water to flush through the sample line for at least 5 sample line volumes (about 10 minutes) and to achieve a steady flow condition. A cooling coil shall be installed on the water sampling line to achieve an exit sample temperature of the water

to be sampled of less than 10 °C. Water (background) samples shall be collected in clean glass vials (40 ml) at a sufficiently slow rate to maintain the water exit temperature below 10 °C and to prevent the formation of turbulence. The tip of the sampling tube shall be kept below the surface of the water during sample collection to minimize contact with the atmosphere. After sampling, the glass vial shall be immediately capped (a septum cap) to leave a zero headspace in the vial. One water sample (one glass vial) shall be collected for each of the following parameters: VOC, TDS, total residual chlorine, free residual chlorine, and pH of the water. All water samples (except VOC content in water) shall be analyzed immediately. The water sample for VOC contents shall be stored in a refrigerator at a temperature of less than 10 °C and analyzed for VOC content within 5 days using the procedures under the Sample Analysis Procedure Section D4.8.3. The free and total residual chlorine content of the water shall be measured using the DPD Colorimetric method (SM 4500-Cl G) using a Hach DR/2010 spectrometer. The conductivity and pH shall be measured using a Hach SensION™378 Bechtol Multi-Parameter Meter. The TDS content of the water shall be estimated from the measured water conductivity. Each background water sample shall be analyzed in duplicate per Section D4.8.2. All instruments will be calibrated according to the manufacturer's specifications.

The valve on the water sampling line shall be closed and the valve on the water inlet of the Air Stripping System shall be opened. If needed, the zero air flow rate shall be adjusted to 2,500 ml/min to the column. Air effluent from the apparatus shall be monitored with the FID analyzer while VOC free water passes through the system. The stripping apparatus system will be allowed to stabilize before making any measurements. Before starting the test, the time required for stabilization, the barometric pressure, and the ambient temperature will be recorded. The VOC free water flow rate, air flow rate, and stripping chamber temperature, and the FID readings shall be monitored and recorded at 2 minute intervals.

The FID will then be disconnected from the Air Stripping Unit and a sample canister will be connected to the air outlet of the air stripping apparatus. At first, the stripping air will remain flowing while the sample canister valve is shut, and excess air flow will be vented through the bubbler. Then, the sample canister valve will be opened to begin sampling. The VOC free water flow rate, and stripping chamber temperature will be monitored and recorded at 2 minute intervals. The air and water flows shall be adjusted as necessary to maintain the target flows of 2,500 ml/min and 125 ml/min, respectively. An automated flow controller will be used to regulate the flow rate to achieve a flow rate of approximately 1/10th the canister volume per minute or less. The canister will be only partially filled to help prevent condensation in the canister. Once sample collection is complete, the final sample canister vacuum, sample collection time, and sample ID will be recorded on the data sheet. An example datasheet is attached. The canister shall then be disconnected from the Air Stripping Unit. Upon receipt of the samples and prior to analysis, the vacuum gauge of the canisters will be checked and recorded to determine if any leakage has occurred.

D4.2.1.5 VOC Spike, Target Concentration 10 ppbw

The valve on the water containing VOC shall then be opened. The flow rates of the water containing VOC from 10-L Tedlar™ bag and the VOC free water from the large (40-L) Tedlar™ bag shall be adjusted to achieve the target VOC concentration in the resulting water at 125 ml/min. The resulting water mixture shall pass through the water sampling line and will be

allowed to achieve a steady-state condition. The valve on the sampling line shall be opened to allow water to flush through the sample line for at least 5 sample line volumes (about 10 minutes) and to achieve a steady flow condition. The cooling coil shall be operated to maintain an exit temperature of the water to be sampled to less than 10 °C. "Spiked" water samples shall be collected in clean glass vials (40-ml) at a sufficiently slow rate to maintain the water exit temperature below 10 °C and to prevent the formation of turbulence. Each glass vial shall be cleaned per the Quality Assurance Procedures. The tip of the sampling tube shall be kept below the surface of the water during sampling to minimize contact with the atmosphere. After sampling, the glass vial shall be immediately capped (a septum cap) to leave a zero headspace in the vial. One water sample (one glass vial) shall be collected for each of the following parameters: VOC, TDS, total residual chlorine, free residual chlorine, and pH of the water. "Spiked" water samples shall be analyzed by the same methods as blank water samples as discussed earlier. The sample collection time and sample ID will be recorded on the data sheet. An example datasheet is attached. Relevant experimental data shall be recorded on a log sheet. The valve on the sampling line shall be closed and water will be allowed to pass through the Stripping Chamber.

The effluent from the stripping apparatus system shall be connected to the FID. The stripping apparatus system and the FID readings will be allowed to stabilize for a minimum of 10 minutes or longer before making any measurements or sample collection. Before starting the test, the time required for stabilization, the barometric pressure, and the ambient temperature will be recorded. The total strippable VOC concentration in the air will be measured using the FID analyzer for 10 minutes. The FID analyzer measurement, water containing VOC flow rate, VOC free water flow rate, air flow rate, and stripping chamber temperature will be recorded every two minutes. An example datasheet is attached. The air and water flows will be adjusted as necessary to maintain the target flows of 2,500 and 125 ml/min, respectively.

The FID will then be disconnected from the Air Stripping Unit and a sample canister will be connected to the air outlet of the air stripping apparatus. At first, the stripping air will remain flowing while the sample canister valve is shut, and excess air flow will be vented through the bubbler. Then, the sample canister valve will be opened to begin sampling. The water containing VOC flow rate, VOC free water flow rate, air flow rate, and stripping chamber temperature will be monitored and recorded at 2 minute intervals. The air and water flows shall be adjusted as necessary to maintain the target flows of 2,500 ml/min and 125 ml/min, respectively. An automated flow controller will be used to regulate the flow rate to achieve a flow rate of approximately 1/10th the canister volume per minute or less. The canister will be only partially filled to help prevent condensation in the canister. Once sample collection is complete, the final sample canister vacuum, sample collection time, and sample ID will be recorded on the data sheet. An example datasheet is attached. The canister shall then be disconnected from the Air Stripping Unit. Upon receipt of the samples and prior to analysis, the vacuum gauge of the canisters will be checked and recorded to determine if any leakage has occurred.

D4.2.1.6 Drain and DI Water Flush of Air Stripping Column

The flow of water containing VOCs shall be stopped and the flow of background water shall be stopped. The flow of air through the stripping column shall be stopped. The drain valve at the

bottom of the air stripping column shall be opened and the column drained of all water present. Once emptied, the drain valve at the bottom of the air stripping column shall be closed. The flow of dionized water shall be started and the air stripping column flushed with dionized water for one hour. The zero air supply through the air stripping column shall the be started and the TVOC concentration in the air effluent measured with the FID analyzer. When the TVOC concentration is less than 1.0 ppmv, the air stripping column has been flushed sufficiently and the zero air and dionized water flows shall be turned off if no other runs are to be conducted that day.

D4.2.2 Second Run

D4.2.2.1 FID Analyzer Calibration

Repeat D4.2.1.1

D4.2.2.2 Zero Air Check

Repeat D4.2.1.2

D4.2.2.3 DI Water Check

Repeat D4.2.1.3

D4.2.2.4 Background Water Flow

Repeat D4.2.1.4

D4.2.2.5 VOC Spike, Target Concentration 10 ppbw

Repeat D4.2.1.5

D4.2.2.6 Drain and DI Water Flush of Air Stripping Column

Repeat D4.2.1.6

D4.2.3 Third Run

D4.2.3.1 FID Analyzer Calibration

Repeat D4.2.1.1

D4.2.3.2 Zero Air Check

Repeat D4.2.1.2

D4.2.3.3 DI Water Check

Repeat D4.2.1.3

D4.2.3.4 Background Water Flow

Repeat D4.2.1.4

D4.2.3.5 VOC Spike, Target Concentration 10 ppbw

Repeat D4.2.1.5

D4.2.3.6 Drain and DI Water Flush of Air Stripping Column

Repeat D4.2.1.6

D4.3 Conducting Experiments with DI Water, VOC Target Concentration in Water of 50 ppbw (Low Level Concentration)

D4.3.1 First Run

D4.3.1.1 FID Analyzer Calibration

Repeat D4.2.1.1

D4.3.1.2 Zero Air Check

Repeat D4.2.1.2

D4.3.1.3 DI Water Check

Repeat D4.2.1.3

D4.3.1.4 Background Water Flow

Repeat D4.2.1.4

D4.3.1.5 VOC Spike, Target Concentration 50 ppbw

Repeat D4.2.1.5 with the VOC spiking supply containing a sufficiently high enough VOC concentration to achieve a VOC concentration in the water entering the El Paso column of 50+/- 5ppbw.

D4.3.1.6 Drain and DI Water Flush of Air Stripping Column

Repeat D4.2.1.6

D4.3.2 Second Run

D4.3.2.1 FID Analyzer Calibration

Repeat D4.2.1.1

D4.3.2.2 Zero Air Check

Repeat D4.2.1.2

D4.3.2.3 DI Water Check

Repeat D4.2.1.3

D4.3.2.4 Background Water Flow

Repeat D4.2.1.4

D4.3.2.5 VOC Spike, Target Concentration 50 ppbw

Repeat D4.2.1.5 with the VOC spiking supply containing a sufficiently high enough VOC concentration to achieve a VOC concentration in the water entering the El Paso column of 50+/- 5ppbw.

D4.3.2.6 Drain and DI Water Flush of Air Stripping Column

Repeat D4.2.1.6

D4.3.3 Third Run
D4.3.3.1 FID Analyzer Calibration
Repeat D4.2.1.1

D4.3.3.2 Zero Air Check
Repeat D4.2.1.2

D4.3.3.3 DI Water Check
Repeat D4.2.1.3

D4.3.3.4 Background Water Flow
Repeat D4.2.1.4

D4.3.3.5 VOC Spike, Target Concentration 50 ppbw
Repeat D4.2.1.5 with the VOC spiking supply containing a sufficiently high enough VOC concentration to achieve a VOC concentration in the water entering the El Paso column of 50+/-5ppbw.

D4.3.3.6 Drain and DI Water Flush of Air Stripping Column
Repeat D4.2.1.6

D4.4 Conducting Experiments with DI Water, VOC Target Concentration in Water of 100 ppbw (Mid Level Concentration)

D4.4.1 First Run
D4.4.1.1 FID Analyzer Calibration
Repeat D4.2.1.1

D4.4.1.2 Zero Air Check
Repeat D4.2.1.2

D4.4.1.3 DI Water Check
Repeat D4.2.1.3

D4.4.1.4 Background Water Flow
Repeat D4.2.1.4

D4.4.1.5 VOC Spike, Target Concentration 100 ppbw
Repeat D4.2.1.5 with the VOC spiking supply containing a sufficiently high enough VOC concentration to achieve a VOC concentration in the water entering the El Paso column of 100+/-10ppbw.

D4.4.1.6 Drain and DI Water Flush of Air Stripping Column

D4.4.2 Second Run
D4.4.2.1 FID Analyzer Calibration
Repeat D4.2.1.1

D4.4.2.2 Zero Air Check

Repeat D4.2.1.2

D4.4.2.3 DI Water Check

Repeat D4.2.1.3

D4.4.2.4 Background Water Flow

Repeat D4.2.1.4

D4.4.2.5 VOC Spike, Target Concentration 100 ppbw

Repeat D4.2.1.5 with the VOC spiking supply containing a sufficiently high enough VOC concentration to achieve a VOC concentration in the water entering the El Paso column of 100+/-10ppbw.

D4.4.2.6 Drain and DI Water Flush of Air Stripping Column

Repeat D4.2.1.6

D4.4.3 Third Run

D4.4.3.1 FID Analyzer Calibration

Repeat D4.2.1.1

D4.4.3.2 Zero Air Check

Repeat D4.2.1.2

D4.4.3.3 DI Water Check

Repeat D4.2.1.3

D4.4.3.4 Background Water Flow

Repeat D4.2.1.4

D4.4.3.5 VOC Spike, Target Concentration 100 ppbw

Repeat D4.2.1.5 with the VOC spiking supply containing a sufficiently high enough VOC concentration to achieve a VOC concentration in the water entering the El Paso column of 100+/-10ppbw.

D4.4.3.6 Drain and DI Water Flush of Air Stripping Column

Repeat D4.2.1.6

D4.5 Conducting Experiments with DI Water, VOC Target Concentration in Water of 1000 ppbw (High Level Concentration)

D4.5.1 First Run

D4.5.1.1 FID Analyzer Calibration

Repeat D4.2.1.1

D4.5.1.2 Zero Air Check

Repeat D4.2.1.2

D4.5.1.3 DI Water Check

Repeat D4.2.1.3

D4.5.1.4 Background Water Flow

Repeat D4.2.1.4

D4.5.1.5 VOC Spike, Target Concentration 1000 ppbw

Repeat D4.2.1.5 with the VOC spiking supply containing a sufficiently high enough VOC concentration to achieve a VOC concentration in the water entering the El Paso column of 1000+/-100ppbw.

D4.5.1.6 Drain and DI Water Flush of Air Stripping Column

Repeat D4.2.1.6

D4.5.2 Second Run

D4.5.2.1 FID Analyzer Calibration

Repeat D4.2.1.1

D4.5.2.2 Zero Air Check

Repeat D4.2.1.2

D4.5.2.3 DI Water Check

Repeat D4.2.1.3

D4.5.2.4 Background Water Flow

Repeat D4.2.1.4

D4.5.2.5 VOC Spike, Target Concentration 1000 ppbw

Repeat D4.2.1.5 with the VOC spiking supply containing a sufficiently high enough VOC concentration to achieve a VOC concentration in the water entering the El Paso column of 1000+/-100ppbw.

D4.5.2.6 Drain and DI Water Flush of Air Stripping Column

Repeat D4.2.1.6

D4.5.3 Third Run

D4.5.3.1 FID Analyzer Calibration

Repeat D4.2.1.1

D4.5.3.2 Zero Air Check

Repeat D4.2.1.2

D4.5.3.3 DI Water Check

Repeat D4.2.1.3

D4.5.3.4 Background Water Flow

Repeat D4.2.1.4

D4.5.3.5 VOC Spike, Target Concentration 1000 ppbw

Repeat D4.2.1.5 with the VOC spiking supply containing a sufficiently high enough VOC concentration to achieve a VOC concentration in the water entering the El Paso column of 1000+/-100ppbw.

D4.5.3.6 Drain and DI Water Flush of Air Stripping Column

Repeat D4.2.1.6

D4.6 Quality Assurance Procedures

Glass Vials

Only EPA VOA glass vials that are new and certified to be clean by the manufacturer shall be used for collecting water samples. Only one sample shall be collected per vial. The cap on each vial shall remain on until the sample is to be collected and shall be replaced immediately after the sample is collected. All samples shall be labeled with the test ID number, run number and the sample description.

FID Analyzer

The FID analyzer shall be calibrated by using zero, mid-level, and high-level gases before each test run. The FID analyzer shall be challenged with zero air and the response shall be recorded. If the FID analyzer response is not within ± 0.2 ppmv of the FID reading for zero air during calibration, then the FID shall be re-calibrated before proceeding any further with the test run. The FID analyzer shall then be challenged with a gas of 10 ppm methane in air and the response shall be recorded. If the FID analyzer response is not within $\pm 5\%$ of the gas concentration, then the FID shall be re-calibrated before proceeding further with test run. The FID analyzer shall then be challenged with a gas of 50 ppm methane in air and the response shall be recorded. If the FID analyzer response is not within $\pm 5\%$ of the gas concentration, then the FID shall be re-calibrated before proceeding further with test run. The zero air, 10 ppm and 50 ppm challenges shall be repeated three times and high and low readings of the FID analyzer recorded on the lab data sheet.

Zero Air Check (Air Blank Check)

A zero air check shall be performed before every run. The zero air supply to the apparatus shall be opened and the rotameter shall be adjusted to read 2,500 ml/min. Air effluent from the apparatus shall be monitored with the FID analyzer to determine the baseline reading of the empty stripping chamber and apparatus. The analyzer reading shall be recorded on the data sheet. If the zero air check indicates a background concentration ≥ 1.0 ppmv as methane in the stripped gas, then the apparatus should be purged thoroughly to remove the contamination until an acceptable background concentration is measured (< 1.0 ppmv as methane).

Water Blank Check

A water blank check shall be performed on the air stripping apparatus before each run. The large Tedlar bag shall be filled with deionized water and be connected to the Air Stripping Unit. The

valve shall be opened and the water flow rate shall be adjusted to 125 ml/min. The air supply shall then be started and adjusted to 2,500 ml/min. The air effluent from the apparatus shall be monitored using the FID analyzer to determine the baseline reading of the apparatus while the system is flowing with clean water. The analyzer reading shall be recorded on the data sheet. If the water blank check indicates a background concentration ≥ 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).

Triplicate Runs

Each experiment shall consist of triplicate identical runs. The purpose of triplicate runs is to evaluate the reproducibility of these methods.

Tedlar Bag Leak and Contamination Check

Only new Tedlar™ bags shall be purchased and used in these tests. Three new Tedlar™ bags shall be randomly chosen and checked for contamination as described in USEPA Method 18, Section 16.1.3.2. According to manufacturer's (SKC, Inc.) suggestion, all new Tedlar™ bags shall be flushed with zero air at least 3 times before use. Three of the Tedlar bags (that have been flushed with zero air at least 3 times) shall be filled with zero air and stored in the laboratory for 24 hours or longer to check for leaks and to evaluate the possibility of desorption of organic compounds from the bag. For leak check, the bags shall be visually observed for deflation. Sample from each Tedlar bag shall then be analyzed in triplicate using the GC/FID system and evaluated for the presence of the target organic compounds. If target organic compounds are detected, then these bags shall be further flushed with zero air and re-analyzed in triplicate using the GC/FID system and evaluated for the presence of the target organic compounds. The numbers of flushing that produce the no-detectable concentration in these Tedlar bags shall be recorded and will be used to flush all new bags for removing any possible trace contaminants.

Recovery Study for Tedlar bag

A recovery study shall be performed on Tedlar bag to determine an average recovery factor. The recovery study shall be 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 a known quantity of 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. The percent recovery for each target compound must be between 70 - 130% for Tedlar™ bags to be acceptable for sample collection. When Tedlar™ bags are acceptable, analysis results for target compounds will be corrected for the percent recoveries. Recovery study bags will be stored for the same period of time as the sample bags. Recovery study shall be completed at three VOC concentrations: low, medium and high levels. The low, medium, and high VOC concentrations in the Tedlar bags will be approximately equal to the VOC concentrations in the stripped air corresponding to the low, medium, and high VOC concentrations in water. As shown in Table D-3, a total of six recovery experiments shall be completed. Three of the recovery experiments shall be completed with benzene only and the other three experiments shall be completed with gaseous mixture mentioned earlier. The first experiment shall be completed at low VOC concentration, the second experiment shall be completed at medium VOC concentration, and the third experiment shall be completed at high VOC concentration. Each experiment shall include

three triplicate runs in which the Tedlar bag shall be filled with known volumes of zero air and the target compounds to achieve low, medium or high level VOC concentration. An average recovery factor shall be determined from the results of the triplicate runs and will be used to correct the sample analysis results.

Table D-3: Number of Experiments for Recovery Study

Compounds	Low Level VOC in Water (50 ppbw)	Low Level VOC in Water (100 ppbw)	Low Level VOC in Water (1000 ppbw)
A mixture of ethylene, propylene, 1,3-butadiene, 1-butene, isobutene, c-2-butene, and t-2-butene	1 expt (1 Tedlar bags)	1 expt (1 Tedlar bags)	1 expt (1 Tedlar bags)

Results of Tedlar Bag Recovery Study

A summary of the results of the Tedlar Bag Recovery study are presented in Tables D-4a, b, c and d. It can be seen that the average recovery factor for the compounds studied varied from 88% to 96% as shown in Table D4d. These recovery factors were then applied to the GC analysis for each compound.

Table D-4a
 Recovery Factor Study for Tedlar Bag at Low (50 ppbw) VOC Concentration
 GC Analysis Performed Directly from 1st Tedlar Bag after 72 Hours

VOC Spiked Water

Sample ID	A-DI-L-1RA-VOC-SP-TB	
Date Sample Collected	10/14/2003	
Temperature	70	Deg F
Temperature	21	Deg C
Date GC Analysis Performed (From TB)	10/17/2003	
Time GC Analysis Performed (From TB)	11:45 - 18:15	

Sample Collection Data

Sample ID	VOC Free Water Flow Rate	Total Water Flow rate	Water Containing VOCs Flow Rate	Air Flow Rate	Tedlar Bag Flow Rate
A-DI-L-1RA-VOC-SP-TB					
Time	ml/min	ml/min	ml/min	LPM	LPM
14:34	112	125	13	2.5	0.6
14:36	112	125	13	2.5	0.6
14:38	112	125	13	2.5	0.6
14:40	112	125	13	2.5	0.6
14:42	112	125	13	2.5	0.6
14:44	112	125	13	2.5	0.6
Average	112	125	13	2.5	0.6

Initial VOC Concentrations in Tedlar Bag

Sample ID	Water Containing VOCs Conc (ppbw)	Conc in Water at EPC Inlet (ppbw)	Compound MW	Conc in Tedlar Bag (ppbv)
A-DI-L-1RA-VOC-SP-TB				
Ethylene	26	2.7	28	117
Propylene	43	4.5	42	129
t-Butene	57	5.9	56	128
1-Butene	54	5.7	56	122
iso-Butene	170	17.7	56	381
cis-Butene	68	7.0	56	151
1,3-Butadiene	72	7.5	54	167
Total	491	51.1		1196

VOC Concentration Measured in Tedlar Bag After 72 Hours

Compounds	1st Analysis ppbv	2nd Analysis ppbv	3rd Analysis ppbv
Ethylene	115	116	114
Propylene	122	122	121
t-Butene	108	109	108
1-Butene	112	113	111
iso-Butene	349	351	345
cis-Butene	135	136	134
1,3-Butadiene	150	151	149

Recovery Factor Analysis

	Initial Conc	Final Avg Conc	Recovery
Compounds	ppbv	ppbv	Factor
Ethylene	117	115	0.98
Propylene	129	122	0.94
t-Butene	128	108	0.84
1-Butene	122	112	0.92
iso-Butene	381	348	0.91
cis-Butene	151	135	0.89
1,3-Butadiene	167	150	0.90

GC Analysis

% Difference from Average
1st
0.3
0.2
-0.1
0.1
0.2
0.1
0.1

Table D-4b
Recovery Factor Study for Tedlar Bag at Low (50 ppbw) VOC Concentration
GC Analysis Performed Directly from 2nd Tedlar Bag after 72 Hours

Spiked Water

Sample ID	A-DI-L-2RA-VOC-SP-TB	
Date Sample Collected	10/14/2003	
Temperature	70	Deg F
Temperature	21	Deg C
Date GC Analysis Performed (From TB)	10/17/2003	
Time GC Analysis Performed (From TB)	12:22 - 18:52	

Sample Collection Data

Sample ID	VOC Free Water Flow Rate	Total Water Flow rate	Water Containing VOCs Flow Rate	Air Flow Rate	Tedlar Bag Flow Rate
A-DI-L-2RA-VOC-SP-TB					
Time	ml/min	ml/min	ml/min	LPM	LPM
14:45	112	125	13	2.5	0.6
14:47	112	125	13	2.5	0.6
14:49	112	125	13	2.5	0.6
14:51	112	125	13	2.5	0.6
14:53	112	125	13	2.5	0.6
14:55	112	125	13	2.5	0.6
Average	112	125	13	2.5	0.6

Initial VOC Concentrations in Tedlar Bag

Sample ID	Water Containing VOCs Conc (ppbw)	Conc in Water at EPC Inlet (ppbw)	Compound MW	Conc in Tedlar Bag (ppbv)
A-DI-L-2RA-VOC-SP-TB				
Ethylene	26	2.7	28	117
Propylene	43	4.5	42	129
t-Butene	57	5.9	56	128
1-Butene	54	5.7	56	122
iso-Butene	170	17.7	56	381
cis-Butene	68	7.0	56	151
1,3-Butadiene	72	7.5	54	167
Total	491	51.1		1196

VOC Concentrations Measured in Tedlar Bag After 72 Hours

Compounds	1st Analysis ppbv	2nd Analysis ppbv	3rd Analysis ppbv
Ethylene	115	116	114
Propylene	123	123	121
t-Butene	109	109	108
1-Butene	112	113	112
iso-Butene	350	351	347
cis-Butene	136	136	135
1,3-Butadiene	151	152	150

Recovery Factor Analysis

	Initial Conc	Final Avg Conc	Recovery
Compounds	ppbv	ppbv	Factor
Ethylene	117	115	0.98
Propylene	129	122	0.95
t-Butene	128	109	0.85
1-Butene	122	112	0.92
iso-Butene	381	349	0.92
cis-Butene	151	136	0.90
1,3-Butadiene	167	151	0.90

GC Analysis

% Difference from Average
1st
0.2
0.3
0.0
0.1
0.1
0.1
0.2

Table D-4c
Recovery Factor Study for Tedlar Bag at Low (50 ppbw) VOC Concentration
GC Analysis Performed Directly from 3rd Tedlar Bag after 72 Hours

Spiked Water

Sample ID	A-DI-L-3RA-VOC-SP-TB	
Date Sample Collected	10/14/2003	
Temperature	70	Deg F
Temperature	21	Deg C
Date GC Analysis Performed (From TB)	10/17/2003	
Time GC Analysis Performed (From TB)	12:59 - 19:28	

Sample Collection Data

Sample ID	VOC Free Water Flow Rate	Total Water Flow rate	Water Containing VOCs Flow Rate	Air Flow Rate	Tedlar Bag Flow Rate
A-DI-L-3RA-VOC-SP-TB					
Time	ml/min	ml/min	ml/min	LPM	LPM
14:56	112	125	13	2.5	0.6
14:58	112	125	13	2.5	0.6
15:00	112	125	13	2.5	0.6
15:02	112	125	13	2.5	0.6
15:04	112	125	13	2.5	0.6
15:06	112	125	13	2.5	0.6
Average	112	125	13	2.5	0.6

Initial VOC Concentrations in Tedlar Bag

Sample ID	Water Containing VOCs Conc (ppbw)	Conc in Water at EPC Inlet (ppbw)	Compound MW	Conc in Tedlar Bag (ppbv)
A-DI-L-3RA-VOC-SP-TB				
Ethylene	26	2.7	28	117
Propylene	43	4.5	42	129
t-Butene	57	5.9	56	128
1-Butene	54	5.7	56	122
iso-Butene	170	17.7	56	381
cis-Butene	68	7.0	56	151
1,3-Butadiene	72	7.5	54	167
Total	491	51.1		1196

VOC Concentrations Measured in Tedlar Bag After 72 Hours

Compounds	1st Analysis ppbv	2nd Analysis ppbv	3rd Analysis ppbv
Ethylene	108	109	109
Propylene	115	116	116
t-Butene	102	102	103
1-Butene	105	106	106
iso-Butene	328	330	330
cis-Butene	127	128	128
1,3-Butadiene	142	143	143

Recovery Factor Analysis

	Initial Conc	Final Avg Conc	Recovery
Compounds	ppbv	ppbv	Factor
Ethylene	117	109	0.93
Propylene	129	116	0.89
t-Butene	128	103	0.80
1-Butene	122	106	0.87
iso-Butene	381	329	0.86
cis-Butene	151	128	0.85
1,3-Butadiene	167	143	0.85

GC Analysis

% Difference from Average
1st
-0.6
-0.3
-0.3
-0.5
-0.4
-0.5
-0.5

Table D-4d
 Recovery Factor Study for Tedlar Bag at Low (50 ppbw) VOC Concentration
 GC Analysis Performed Directly from Tedlar Bag after 72 Hours
 Recovery Factor Analysis Summary

	First	Second	Third	
	Tedlar Bag	Tedlar Bag	Tedlar Bag	Average
Compounds	Recovery Factor	Recovery Factor	Recovery Factor	Recovery Factor
Ethylene	0.98	0.98	0.93	0.96
Propylene	0.94	0.95	0.89	0.93
t-Butene	0.84	0.85	0.80	0.83
1-Butene	0.92	0.92	0.87	0.90
iso-Butene	0.91	0.92	0.86	0.90
cis-Butene	0.89	0.90	0.85	0.88
1,3-Butadiene	0.90	0.90	0.85	0.88

Replicate Sample Analysis

Each water sample shall be analyzed in duplicate for pH, TDS, residual free chlorine, and residual total chlorine contents. An average value shall be calculated and used in the data analysis. All Summa canister samples shall be analyzed in duplicate using the procedures of EPA Test Method TO-14A. If individual sample result differ by greater than 5% compared to the averaged value, then each sample shall be analyzed in triplicate using the procedures of EPA Test Method TO-14A. All Summa canister samples shall also be analyzed in triplicate using the procedures of EPA Test Method 18. All Tedlar™ bag samples shall be analyzed in triplicate using the procedures of EPA Test Method 18.

One field (experimental) blank Summa canister. The field blank Summa canister sample shall be analyzed in duplicate using the procedures of EPA Test Method TO-14A. The field blank Summa canister sample shall also be analyzed in triplicate using the procedures of Method-18. One laboratory (analytical) blank Summa canister shall also be analyzed in duplicate with each batch of samples using the procedures of EPA Test Method TO-14A. One laboratory (analytical) blank Summa canister shall also be analyzed in triplicate with each batch of samples using the procedures of Method 18.

El Paso System Cleaning Procedure

If air and water blanks are not sufficient to remove contamination from the system, the system shall be disassembled and the components shall be cleaned thoroughly. The stripping chamber shall be cleaned per TCEQ Sampling and Procedures Manual, Appendix P, Section 5.5.3.

Teflon™ and stainless steel tubing, unions, and valves that contact water or the stripped air sample shall be cleaned with hot soapy water, rinsed by flushing with 5 volumes of tap water and 5 volumes of deionized water, and then purged with zero air. These shall then be baked at 150 °C in an oven for at least 1 hour. Stainless steel tubing too long to fit inside the oven without bending will just be purged with zero air after cleaning.

The water rotameter will be cleaned according to the manufacturer's recommendations, followed by flushing with deionized water and purging with zero air. 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 150°C. Such components shall be baked at a lower temperature for longer periods, purged with zero air without heating, or simply air dried, as appropriate.

- D4.7 Post Test Procedures
- D4.7.1 GC Analysis Procedures for Air Samples
- D4.7.1.1 Summa Canisters
- D4.7.1.1.1 EPA Test Method TO14a

Canister samples shall be analyzed using the general procedures outlined in the “Determination of Volatile Organic Compounds in Ambient Air using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography” (USEPA, 1999) (Test Method TO-14A) and “Measurement of Gaseous Organic Compound Emissions by Gas Chromatography” (USEPA, 2000) (Method 18). Samples shall be stored in the laboratory and analyzed within 72 hours of

collection. The room temperature in the laboratory is maintained around 75 °F. The sample analysis date and time shall also be recorded.

Dilution

After sample collections, canisters will be transported to the laboratory and prepared for chemical analysis. The canister pressure will be increased to above atmospheric pressure using nitrogen as a diluent to allow for optimum functioning of the downstream cryofocuser. A mass flow controller will be used to control the volume of nitrogen drawn into each canister. A pressure transducer will indicate the precise pressure in the canister prior to and during the dilution. A datalogger will control the total volume of nitrogen drawn into the canister, based on the pressure transducer readings.

Cryofocusing and Data Collection

After dilution, the canisters will be connected to the chemical analysis system, which consists of a cryofocuser, a gas chromatograph and a data acquisition system. An Entech 7000 (connected to GC/FID) preconcentrator will draw a predetermined amount of sample from the canister, and will mix the sample of known volume of an internal standard at 4 ppbv per standard. The internal standard will be added to the sample to assist in the identification of the unknown components present in the sample. The instrument will sequentially cool the mixture to -185°C , draw off the overhead gases, and reheat the mixture. By repeating this sequence three times, the preconcentrator will substantially decrease the volume of the original mixture and will increase the concentration of the VOCs in the sample.

A Hewlett Packard 5890A gas chromatograph (GC) equipped with a Flame Ionization Detector (FID) will be used to measure VOC concentrations in the sample. The mixture from the cryofocuser will be automatically desorbed onto the GC column and the GC oven will follow a prescribed temperature ramping program. Chromatograms of the samples shall be generated using the EZ-Chrom V4.0 software for GC/FID. These chromatograms will be analyzed and converted into VOC concentrations using the calibration methods outlined below. Detailed laboratory procedures for this project shall be included in the final report to be submitted to TCEQ. Detailed analytical procedures that will be followed in this project can be obtained upon request.

D4.7.1.1.2 EPA Reference Method 18

D4.7.1.2 TEDLAR Bags

After sample collections, Tedlar™ bags shall be transported to the laboratory for storage at 24 °C (75 °F). Tedlar™ bag samples shall be analyzed within 72 hours of collection using the general procedures outlined in the “Measurement of Gaseous Organic Compound Emissions by Gas Chromatography” (USEPA, 2000) (Reference Method 18). A multi-point calibration shall be performed on the GC/FID system using known standards before analyzing every batch of samples. Each sample shall be analyzed in triplicate using the calibrated GC/FID system. After analyzing every batch of samples, a mid-point calibration check shall be performed on the GC/FID system. The average response factors of the pre and post calibration checks shall be compared. If the pre and post calibration response factors differ by less than 5% from the mean value, then the pre-test calibration curve shall be used to determine sample concentrations. If the

pre and post-test calibration response factors differ by more than 5% from the mean value, then other calibration standards shall be analyzed by the GC/FID system and a new calibration shall be developed using the average of the pre and post-test calibration values. The new calibration curve shall be used to determine sample concentrations. A corrected sample concentration shall be determined by dividing the measured concentration by the sample recovery factor.

With every new batch of sample, a mid-level certified gas shall be directly introduced and analyzed by the GC/FID in triplicate. The average difference of the GC response and the certified gas value shall be less than $\pm 5\%$. A certified gas cylinder of benzene and propylene mixture (200 ppb of benzene, 200 ppb propylene, and the balance nitrogen) shall be used for this purpose.

For some Tedlar™ bag samples, dilution may be necessary before analysis can be performed using the GC/FID system. If dilution is needed, a known volume of the sample gas from the Tedlar™ bag shall be extracted using a gas-tight syringe and will be injected to another new Tedlar™ bag. The sample in the new Tedlar™ bag shall be diluted with a known volume of zero air. A 1-liter syringe shall be used to transfer the known volume of zero air into the Tedlar bag.

Alternately, a flow meter can be used to transfer the known volume of zero air into the Tedlar bag. The flow meter shall be operated at a flow rate of approximately 100-200 ml/min until the desired amount of zero air is transferred into the Tedlar bag. The duration of the transfer shall be measured using a stop watch and the total volume of zero air transferred into the Tedlar bag shall be estimated by multiplying the flow rate with the measured duration of the transfer. A corrected sample concentration shall be determined by dividing the measured concentration by the dilution factor and the sample recovery factor. The sample analysis date and time shall also be recorded

D4.8 Analysis Procedures for Water Samples Collected in VOA Vials

D4.8.1 Free and Total Chlorine Concentrations

The free and total residual chlorine concentrations the water samples shall be measured using the DPD Colorimetric method (SM 4500-Cl G) using a Hach DR/2010 spectrometer. Each water sample shall be analyzed in duplicate.

D4.8.2 Total Dissolved Solids (TDS) and pH Concentrations

The conductivity and pH shall be measured using a Hach SensION™378 Bench-top Multi-Parameter Meter. The TDS content of the water shall be estimated from the measured water conductivity. Each water sample shall be analyzed in duplicate.

D4.8.3 VOC Concentration

Glass vials containing water samples shall be stored in a laboratory refrigerator at a temperature of less than 10 °C and analysis shall be completed for target compounds using the following procedures within 5 days. 5ml of water from the glass vial shall be drawn into a gas tight syringe and directly injected into a purge and trap vessel. The vessel shall then be purged with ultra high purity zero air at 35ml/min for 20 min, minimum. The actual air flow and the actual purging time shall be recorded on the data sheet/log. The off-gas from the purge and trap vessel shall be collected in a clean Summa canister, cleaned per Section D4.1.3. A mass flow controller located at the inlet to the Summa canister shall be used to control the amount of purged gas that

passes through the vessel. The Summa canister shall be under vacuum and care shall be taken not to draw any water into the canister. The Summa canister will then be analyzed for the target compounds using the generalized procedures of EPA Method TO-14A. The VOC concentration in water shall then be determined from a mass balance analysis using the volume of water sample and total quantity of zero air used to purge the water sample based on the actual time and actual zero air flow rate. The Summa canister containing purged off-gas from the vessel shall be analyzed within 24 hours after collection. The sample analysis temperature, date and time shall also be recorded.

D4.9 Calculations

Derivation of the Equation to Estimate Equilibrium VOC Concentrations in Water

Assume that a Tedlar™ bag is completely evacuated and is free of water and air. A known volume (V_1) of VOC free water is introduced in the Tedlar™ Bag. A known volume (V_g) of gaseous VOC is then introduced in the Tedlar™ Bag. The total mass of VOC introduced in the Tedlar™ bag is m_T . The gaseous VOC and water are allowed to contact for a period of time to overcome the heat of mixing and to assure that equilibrium has been reached. Henry's Law constant for the VOC is H_c . The equilibrium VOC concentration in water is C_1 and in gas is C_g . At equilibrium, m_1 is the mass of VOC in water and m_g is the mass of VOC in gas. At equilibrium:

$$H_C = \frac{C_g}{C_1} \qquad C_g = \frac{m_g}{V_g} \qquad C_1 = \frac{m_1}{V_1}$$

$$H_C = \frac{C_g}{C_1} \qquad C_g = \frac{m_g}{V_g} \qquad C_1 = \frac{m_1}{V_1}$$

$$H_C = \frac{C_g}{C_1} = \frac{m_g V_1}{m_1 V_g}$$

$$m_T = m_g + m_1 \qquad m_g = m_T - m_1$$

$$\frac{m_1 H_c}{V_1} = \frac{m_T - m_1}{V_g}$$

$$m_1 \left(\frac{H_C}{V_1} + \frac{1}{V_g} \right) = \frac{m_T}{V_g}$$

$$m_1 = \frac{m_T}{V_g \left(\frac{H_c}{V_1} + \frac{1}{V_g} \right)} = \frac{m_T}{\left(1 + \frac{H_c V_g}{V_1} \right)}$$

$$C_1 = \frac{m_1}{V_1} = \frac{m_T}{H_c V_g + V_1}$$

Appendix E

Test Data for Appendix P Tests

This appendix contains the paper copies of all data sheets from the four VOC concentration test series conducted with the test system described in Appendix D. It is organized into three volumes. Volume 1 contains the laboratory data sheets for each of the four test series. Volume 2 contains the chain-of-custody forms for the Summa canisters used to collect samples directly from the test system and to collect exhaust air from the purge and trap system used to strip water samples collected at the inlet to the El Paso column. Volume 3 contains copies the results of the GC/FID analysis for each of the Summa canisters in Volume 2. For a given test series, the sample analysis data would be obtained by obtaining the sample collection date and Summa canister ID from the Volume 1 test data sheets, which are organized by test series. Then, GC/FID analysis date and analysis data file name is then obtained from Volume 2 (organized chronologically by sample collection date) based on the canister and sample ID and the date the test series was conducted. Using the GC/FID analysis date and the file name, Volume 3 (organized chronologically by analysis date) is used to view a copy of the GC/FID analysis data.

Also included in Volume 1 is the Laboratory Review Checklist (LRC) with Exception Reports (ERs) as required in the data quality objectives. The Data Usability Summary follows.

Data Usability Summary

Vincent M. Torres reviewed four packages of data from the Cooling Tower Project tests and sample analysis of samples collected June 1 to November 30, 2003 at the Center for Energy and Environmental Resources. Data were reviewed for conformance with TCEQ Work Order 55078-03-07, the Project Work Plan, and adherence to project objectives.

Intended Use of Data: To evaluate test methodologies that will be used to identify leaks into cooling water as soon as possible.

Analysis Used include:

EPA Method TO14a

EPA Method 18

Data were reviewed and validated as described in *Review and Reporting of COC Concentration Data* (RG-366/TRRP-13) and the results of the review/validation are discussed in this Data Usability Summary (DUS). The following laboratory submittals and test data were examined:

- the reportable data,
- the laboratory review checklists and associated exception reports, and
- the test notes with respect to test system calibrations, sampling procedures and sample preservation procedures prior to laboratory analysis.

The results of supporting review checklists (LRCs), Exception Reports (ERs), and the case narratives, all of which were included in this review.

The LRCs, associated ERs and reportable data included in this review are included in Volume 1 of this Appendix.

Four test series were conducted using the TCEQ *Source Sampling Procedures Manual, Appendix P*, each test performed at different concentrations of a mixture of ethylene, propylene, t-butene, 1-butene, iso-butene, cis-butene, and 1,3-butadiene in the water, nominally detection limit (10 ppbw), low (50 ppbw), medium (100 ppbw), and high (1000 ppbw) values. Each test consisted of three runs at the same conditions.

Project Objectives

Detection Limit: ≤ 10 ppbw

Accuracy: Below 50 ppbw, ± 10 ppbw, absolute difference

Equal to or above 50 ppbw, $\pm 20\%$, as relative error or percent difference

A method must be capable of providing 90% speciation of the individual compounds in the total mixture.

Analytical Results

All GC/FID analysis results are ultimately reported as concentrations of the VOC in the water per the procedure of Appendix P. Any non-detected results are reported as BDL, below the detection limit in the data.

Preservation and Holding Times

Samples were evaluated for agreement with the chain-of-custody (C-O-C). All samples were collected in appropriate containers and stored at designated temperatures per the Work Plan. Samples were analyzed within the time specified in the Work Plan.

Calibrations

According to the LRC, initial and continuing calibration of the test systems was performed per Appendix P. The LRC also documents satisfactory instrument performance calibrations per Appendix P and EPA Methods TO 14a and 18.

Blanks

Test system blanks were used to provide repeatable and quality controlled test data per the procedure in the Work Plan.

Matrix Spikes/Matrix Spike Duplicates

MS/MSD precision and accuracy were with the Work Plan QC acceptance criteria.

Test Procedures

Samples were collected using the specially designed test system described in Work Plan. This system was designed and procedures followed to ensure repeatability and comparability of the data.

Summary

Test data are usable for the purpose of evaluating performance of the El Paso column Appendix P test system for the range of VOC concentrations and the composition (a mixture of ethylene, propylene, t-butene, 1-butene, iso-butene, cis-butene, and 1,3-butadiene in the water) used in these four test series.

Appendix E

Laboratory Data for Appendix P Tests

Volume 1a

Detection Limit (10 ppbw) A-DI-D Test Series Data Sheets

Appendix E

Laboratory Data for Appendix P Tests

Volume 1b

Low VOC Concentration (50 ppbw) A-DI-L Test Series Data Sheets

Appendix E

Laboratory Data for Appendix P Tests

Volume 1c

Medium VOC Concentration (100 ppbw) A-DI-M Test Series Data Sheets

Appendix E

Laboratory Data for Appendix P Tests

Volume 1d

High VOC Concentration (1000 ppbw) A-DI-H Test Series Data Sheets

Appendix E

Test Data for Appendix P Tests

Volume 2

Summa Canister Chain-of-Custody Forms for Lab Samples

Appendix E
Test Data for Appendix P Tests

Volume 3a
GC/FID Analysis Data
for
Samples Analyzed During the Period
July 8 to July 31, 2003

Appendix E
Test Data for Appendix P Tests

Volume 3b
GC/FID Analysis Data
for
Samples Analyzed During the Period
August 1 to August 31, 2003

Appendix E
Test Data for Appendix P Tests

Volume 3c
GC/FID Analysis Data
for
Samples Analyzed During the Period
September 1 to September 30, 2003

Appendix E
Test Data for Appendix P Tests

Volume 3d
GC/FID Analysis Data
for
Samples Analyzed During the Period
October 1 to October 20, 2003

Appendix E
Test Data for Appendix P Tests

Volume 3e
GC/FID Analysis Data
for
Samples Analyzed During the Period
October 21 to October 30, 2003

Appendix E
Test Data for Appendix P Tests

Volume 3f
GC/FID Analysis Data
for
Samples Analyzed During the Period
November 1 to November 10, 2003

Appendix E
Test Data for Appendix P Tests

Volume 3g
GC/FID Analysis Data
for
Samples Analyzed During the Period
November 11 to November 27, 2003

Appendix F Questionnaire for Continuous VOC Monitoring/Sampling Methods

The University of Texas at Austin (UT) under contract to the Texas Commission on Environmental Quality (TCEQ) is performing an assessment of continuous VOC monitoring/sampling methods that can be used to analyze leaks of highly reactive VOCs from industrial cooling towers. Providing the information requested in this questionnaire will enable UT to include your system in our evaluation. It is important that we receive correct and detailed technical information about the operation and performance of this equipment so that an accurate evaluation can be made. If you have more than one instrument that can be used for this type of application, please submit a separate questionnaire for each one.

1. What is the manufacturer's name and model number for the instrument being described?
2. Provide a brief description of how the instrument operates and the principles on which it is based (sampling system, sample media, detector/analyzer, data collection/analysis/reporting, etc.).
3. Does the instrument measure total volatile organic compounds (VOCs)? Speciated VOCs? What VOCs can be detected/quantified with this instrument and in what concentration range (ppm)? A list of compounds of special interest is provided below for reference.

High interest: benzene; ethylene; propylene; 1,3-butadiene; all butene (butylene) isomers

Medium interest: acetaldehyde; formaldehyde; all hexene isomers; isoprene; all pentene isomers; all trimethylbenzene isomers; m-,o-xylene

Moderate interest: n-,iso-butane; n-,iso-pentane, toluene

4. What is the range of operation for the following parameters: flow rate (ml/min), temperature (°C), humidity (%), and pressure (kPa)? Identify any other critical parameters and their operating range.
5. Does the instrument provide continuous measurements? Semi-continuous? For this purpose, continuous is defined as a minimum of one sample every 15 minutes. Identify the sampling interval. What is the response time associated with these measurements?
6. How does the instrument achieve, determine, and assure equilibrium (steady state) during measurements?
7. Identify the parameters at most risk of affecting the accuracy of measurements obtained with this instrument (if possible, quantify the effect on accuracy).
8. How is the accuracy of the method affected by environmental changes in ambient temperature, humidity, and wind? What are the environmental limitations of this equipment?

9. What are the quality assurance/quality control requirements for this instrument? What calibration frequency is needed and for what parameters (e.g., flow rate, temperature, pressure, detector, etc.)? Describe the calibration method (calibration phase: air, water)?
10. Identify a recommended preventative maintenance schedule for this instrument.
11. Is the instrument intrinsically safe? Describe any safety features of the equipment.
12. What is the cost of this instrument including any optional equipment that may be needed for this application?
13. How many instruments are installed and currently operating (and for how long)? How many are in Texas?
14. If possible, provide samples of actual data obtained from the use of this equipment and describe actual conditions under which these data were collected (controlled laboratory experiments, field testing, etc.)
15. If possible, provide two references of customers who currently use this equipment in the laboratory or in the field and whom we may contact regarding the use of this equipment. Please provide name of contact, company, phone number, and email address for each reference.
16. Additional relevant technical literature/information/comments are welcome.

Alba Webb
The University of Texas at Austin
Center for Energy and Environmental Resources
10100 Burnet Road, Bldg. 133, R7100
Austin, TX 78758

Phone: (512) 232-4808
Fax: (512) 471-1720
Email: alba@mail.utexas.edu

Appendix G

Disclaimer

Information presented in this Appendix of the report pertaining to the performance characteristics of the equipment identified in this Appendix has been obtained directly from those manufactures of the equipment referenced in this Appendix. The inclusion of such information does not constitute an endorsement of the performance characteristics stated in this Report. Neither The University of Texas at Austin nor the Texas Commission on Environmental Quality can provide a warranty or guarantee, expressed or implied, as to the accuracy, reliability or completeness of the data furnished by other organizations.

Responses to Continuous VOC Monitoring/Sampling Methods

Questionnaire Response A

From: Chuck Slicker e-Mail chuck.slicker@baselineindustries.com
Baseline-MOCON
PO Box 649
Lyons, CO 80540
Phone: 800-321-4665

Questionnaire for Continuous VOC Monitoring/Sampling Methods:

The University of Texas at Austin (UT) under contract to the Texas Commission on Environmental Quality (TCEQ) is performing an assessment of continuous VOC monitoring/sampling methods that can be used to analyze leaks of highly reactive VOCs from industrial cooling towers. Providing the information requested in this questionnaire will enable UT to include your system in our evaluation. It is important that we receive correct and detailed technical information about the operation and performance of this equipment so that an accurate evaluation can be made. If you have more than one instrument that can be used for this type of application, please submit a separate questionnaire for each one.

A second application is submitted for Baseline's Model 8900 GC

1. What is the manufacturer's name and model number for the instrument being described?

Baseline -MOCON, Inc
19661 Highway 36
Lyons, CO 80540 (USA)

2011 A Lamar Drive
Round Rock, TX 78664

10 Bearfoot Rd
Northborough, MA 01532

7500 Boone Ave. N.
Suite 111
Minneapolis, MN 55428

Baseline recommends as an option our Model 8800H/ FID (Heated Total Hydrocarbon

Analyzer). The data sheet for this model is attached.

2. Provide a brief description of how the instrument operates and the principles on which it is based (sampling system, sample media, detector/analyzer, data collection/analysis/reporting, etc.).

The 8800H is an on-line total hydrocarbon analyzer based on an electronically flow controlled microprocessor based flame ionization detector (FID). A small portion of the gas sample is introduced directly to the detector flame. During the combustion process organic or hydrocarbon-based gases in the sample are ionized to a point where they can be detected and reported as concentration. The VOC air pollutants can be stripped from the water matrix into an air matrix for monitoring by the 8800H/ FID using an El Paso style sparging system, permeation device, or a proprietary (patent pending) Gas Stripper Assembly. Data can then be transferred to the appropriate collection system by means of a digital RS-485/232 signal or 4 -20 mA output.

3. Does the instrument measure total volatile organic compounds (VOCs)? Speciated VOCs? What VOCs can be detected/quantified with this instrument and in what concentration range (ppm)? A list of compounds of special interest is provided below for reference.

High interest: benzene; ethylene; propylene; 1,3-butadiene; all butene (butylene) isomers

Medium interest: acetaldehyde; formaldehyde; all hexene isomers; isoprene; all pentene isomers; all trimethylbenzene isomers; m-,o-xylene

Moderate interest: n-,iso-butane; n-,iso-pentane, toluene

The 8800H/ FID directly measures total volatile organic compounds or the listed compounds above. The Lower Detectable Limit (LDL) is 0.1 ppm as propane in air matrix. The exception to the list is Formaldehyde that can be done indirectly on an FID if converted to Methane using a catalyst.

4. What is the range of operation for the following parameters: flow rate (ml/min), temperature (°C), humidity (%), and pressure (kPa)? Identify any other critical parameters and their operating range.

The 8800H can handle sample flow rates of < 2000ml/min, temperatures to 200 ° C, Humidity of 95% or Dew Points to 195 ° C, and pressures 206 kPa (30 psi). An internal heated sample pump is optional on the 8800H for lower pressures.

5. Does the instrument provide continuous measurements? Semi-continuous? For this purpose, continuous is defined as a minimum of one sample every 15 minutes. Identify the sampling interval. What is the response time associated with these measurements/

The Model 8800 H is considered continuous analyzers. The analyzer is constantly sampling and disregarding transport time from the sampling point to the analyzer; the 8800H's internal response time is <5 seconds to 90% full scale.

6. How does the instrument achieve, determine, and assure equilibrium (steady state) during

measurements?

The Model 8800H uses a back pressure regulation system to assure that sample is being supplied to the detector in a stable and steady state.

7. Identify the parameters at most risk of affecting the accuracy of measurements obtained with this instrument (if possible, quantify the effect on accuracy).

The sample system, particularly the El Paso style sparging system, is most at risk especially for continuous and uninterrupted service. High maintenance will be the key to keeping molds and mildews from forming in the stripping chamber. Buildup of these residues will effect the measurement, and accuracy

8. How is the accuracy of the method affected by environmental changes in ambient temperature, humidity, and wind? What are the environmental limitations of this equipment?

The standard 8800H comes in a general-purpose wall or 19" rack mount configurations. Typical environmental changes will not affect the analyzer, however the analyzer should be protected from harsh outdoor weather. The analyzer can be enclosed in a cabinet to control environmental limits and area classification concerns. Operation conditions are temperature of 32 to 104° F and humidity of 0 to 95% non-condensing.

9. What are the quality assurance/quality control requirements for this instrument? What calibration frequency is needed and for what parameters (e.g., flow rate, temperature, pressure, detector, etc.)? Describe the calibration method (calibration phase: air, water)?

The 8800H drift is +/- 1% of Full Scale over a 24 hour. The 8800H can be calibrated either manually or automatically according to requirements TCEQ appendix P section 4.0. The zero and span parameters are stored internal and are used for reference during the continuous monitoring process. Procedure for calibration would be in accordance to TCEQ Appendix P section 4.1

10. Identify a recommended preventative maintenance schedule for this instrument.

Maintaining air and fuel sources for the FID as well as zero and span calibration gases. See the data sheet for support gas consumption. Diagnostic alarms can be viewed from the front panel display or transmitted back to the control room.

11. Is the instrument intrinsically safe? Describe any safety features of the equipment.

The 8800H can be manufactured using purge controls to be located in classified area. Besides the digital output that reports status of instrument as well as concentration levels and programmable averages, there is the front panel display that shows at a glance the instrument status. Programmable relays can be selected for calibration, fault, and threshold alarms. The electronically flow controlled FID will automatically re-light if flame-out takes place, and if unsuccessfully will shut off fuel, air and sample to the

instrument. This makes the instrument safe and with shutdown of the sample pump also limits instrument harm when the unit is brought back on line.

12. What is the cost of this instrument including any optional equipment that may be needed for this application?

The Model 8800H wall mount or panel mount enclosure with Baseline's proprietary gas stripping system would list for < \$15,000. I have not included sample lines or support gas costs. The 8800H with the El Paso style sparging system would be < \$20,000

13. How many instruments are installed and currently operating (and for how long)? How many are in Texas?

There are approximately 15 to 20 series 8800 analyzers working in the Texas environmental applications. The oldest have been in place and running continuously for 4 years. Baseline has over 100 units a large majority for EPA Method 25A applications. Baseline also sells this series of analyzer into the specialty gas markets (Air Liquide, Air Products, Linde/BOC) for quality control of very low-level impurities in their ultra pure gas product.

14. If possible, provide samples of actual data obtained from the use of this equipment and describe actual conditions under which these data were collected (controlled laboratory experiments, field testing, etc.)

Baseline will provide data for the system in the next few days showing efficiency of the total analyzer and sample systems. These results will be gathered from our laboratory.

15. If possible, provide two references of customers who currently use this equipment in the laboratory or in the field and whom we may contact regarding the use of this equipment. Please provide name of contact, company, phone number, and email address for each reference.

Both contacts are using the analyzer in the field (on line).

**Al Spivey (I&E Technician)- Arch Chemical, Beaumont, TX. 409-835-6641ext.152
Russell Fuller (Project Engineer)-Bayer Corp., Orange, TX. 409-882-2414**

Arch Chemical is burning hazardous waste as a fuel and must maintain levels not to exceed levels of hydrocarbons allowed on their permit. Bayer Polymer is using the analyzer to monitor their flare to maintain hydrocarbon levels for complete combustion.

Please contact me if you have any further questions, and thank you for the opportunity

Chuck Slicker
Baseline Industries
Direct phone: 970-203-0880

Questionnaire Response B

From: Chuck Slicker e-Mail chuck.slicker@baselineindustries.com
Baseline-MOCON
PO Box 649
Lyons, CO 80540
Phone: 800-321-4665

Questionnaire for Continuous VOC Monitoring/Sampling Methods:

The University of Texas at Austin (UT) under contract to the Texas Commission on Environmental Quality (TCEQ) is performing an assessment of continuous VOC monitoring/sampling methods that can be used to analyze leaks of highly reactive VOCs from industrial cooling towers. Providing the information requested in this questionnaire will enable UT to include your system in our evaluation. It is important that we receive correct and detailed technical information about the operation and performance of this equipment so that an accurate evaluation can be made. If you have more than one instrument that can be used for this type of application, please submit a separate questionnaire for each one.

A second application is submitted for Baseline's Model 8800 Total Hydrocarbon Analyzer

1. What is the manufacturer's name and model number for the instrument being described?

Baseline -MOCON, Inc
19661 Highway 36
Lyons, CO 80540 (USA)

2011 A Lamar Drive
Round Rock, TX 78664

10 Bearfoot Rd
Northborough, MA 01532

7500 Boone Ave. N.
Suite 111
Minneapolis, MN 55428

Baseline recommends as an option our Model 8900 Gas Chromatograph. The data sheet for this model is attached. Depending on preference the 8900 can be plumbed with either the Flame Ionization Detector (FID) or Photo Ionization Detector (PID).

2. Provide a brief description of how the instrument operates and the principles on which it is based (sampling system, sample media, detector/analyzer, data collection/analysis/reporting, etc.).

The 8800GC is an on-line field gas chromatograph based on a microprocessor controlled based (FID) or (PID). A small portion of the gas sample is automatically introduced into the appropriate column configuration via a sample loop and switching valves. No pre-concentration should be necessary for the levels requested in TCEQ appendix P. Separation of the compounds takes place in the column(s). The speciated VOCs are then passed to the detector, where they are converted to concentration. The VOC air pollutants can be stripped from the water matrix into an air matrix for monitoring by the 8900GC using an El Paso style sparging system, permeation device, or a proprietary

(patent pending) Gas Stripper Assembly. Data can then be transferred to the appropriate collection system by means of a digital RS-485/232 signal or 4 -20 mA output. Sky-Chrom (Baseline's proprietary software) can be used to add, modify, and delete GC methods.

3. Does the instrument measure total volatile organic compounds (VOCs)? Speciated VOCs? What VOCs can be detected/quantified with this instrument and in what concentration range (ppm)? A list of compounds of special interest is provided below for reference.

High interest: benzene; ethylene; propylene; 1,3-butadiene; all butene (butylene) isomers

Medium interest: acetaldehyde; formaldehyde; all hexene isomers; isoprene; all pentene isomers; all trimethylbenzene isomers; m-,o-xylene

Moderate interest: n-,iso-butane; n-,iso-pentane, toluene

The 8900GC directly measures total volatile organic compounds or those chemicals listed above. The Lower Detectable Limit (LDL) is approx 0.01 ppm in the air matrix for both the FID and PID. The exception to the list is Formaldehyde that can be done indirectly on an FID when converted to Methane using a catalyst.

4. What is the range of operation for the following parameters: flow rate (ml/min), temperature (°C), humidity (%), and pressure (kPa)? Identify any other critical parameters and their operating range.

The 8900GC can handle sample flow rates of < 2000ml/min, temperatures to 150 ° C, Humidity of 95% or Dew Points to 145 ° C, and pressures 206 kPa (30 psi). A sample pump is optional on the 8900GC for lower pressures.

5. Does the instrument provide continuous measurements? Semi-continuous? For this purpose, continuous is defined as a minimum of one sample every 15 minutes. Identify the sampling interval. What is the response time associated with these measurements/

The Model 8900GC is considered continuous analyzers. The analyzer is constantly sampling and disregarding transport time from the sampling point to the analyzer; the 8800GC internal response time is less than the 15 minutes. For example the analyzer completes a C1 through C5 analysis (7 compounds) in 45 seconds, start time to start time.

6. How does the instrument achieve, determine, and assure equilibrium (steady state) during measurements?

The Model 8900 uses a traditional sample loop with baseline being established at the beginning and end of each sample run.

7. Identify the parameters at most risk of affecting the accuracy of measurements obtained with this instrument (if possible, quantify the effect on accuracy).

The sample system, particularly the El Paso style sparging system, is most at risk especially for continuous and uninterrupted service. High maintenance will be the key to

keeping molds and mildews from forming in the stripping chamber. Buildup of these residues will effect the measurement, and accuracy. They can also contaminate the analyzer. The permeation and Baseline's gas stripper assembly are less susceptible to the mold and mildew due to the manufactured materials.

8. How is the accuracy of the method affected by environmental changes in ambient temperature, humidity, and wind? What are the environmental limitations of this equipment?

The standard 8900GC comes in a general-purpose wall or 19" rack mount configurations. Typical environmental changes will not affect the analyzer, however the analyzer should be protected from harsh outdoor weather. The analyzer can be enclosed in a cabinet to control environmental limits and area classification concerns. Operation conditions are temperature of 32 to 104° F and humidity of 0 to 95% non-condensing.

9. What are the quality assurance/quality control requirements for this instrument? What calibration frequency is needed and for what parameters (e.g., flow rate, temperature, pressure, detector, etc.)? Describe the calibration method (calibration phase: air, water)?

The 8900GC drift is less than +/- 1% of Full Scale over a 24 hour. The 8900GC can be calibrated either manually or automatically according to requirements TCEQ appendix P section 4.0. The zero and span parameters are stored internal and are used for reference during the monitoring process. Multi-point calibration is available through Sky-Chrom Software. Procedure for calibration would be in accordance to TCEQ Appendix P section 4.1

10. Identify a recommended preventative maintenance schedule for this instrument.

Maintaining air and fuel sources for the FID as well as zero and span calibration gases. The PID would need cleaned, although the detector in the GC mode is less susceptible to contamination. Diagnostic alarms can be viewed from the front panel display or transmitted back to the control room.

11. Is the instrument intrinsically safe? Describe any safety features of the equipment.

The 8900GC can be manufactured using purge controls to be located in classified area and be made intrinsically safe. Besides the digital output that reports status of instrument as well as concentration levels, there is the front panel display that shows at a glance the instrument status. Programmable relays can be selected for calibration, faults, and alarms. The electronically flow controlled FID will automatically re-light if flame-out takes place, and if unsuccessfully will shut off fuel, air and sample to the instrument. This makes the instrument safe and with shutdown of the sample pump also limits instrument harm when the unit is brought back on line.

12. What is the cost of this instrument including any optional equipment that may be needed for this application?

The Model 8900GC wall mount or panel mount enclosure with Baseline's proprietary gas

stripping system would list for < \$23,000. I have not included sample lines or support gas costs. The 8900GC with the El Paso style sparging system would be < \$28,000.

13. How many instruments are installed and currently operating (and for how long)? How many are in Texas?

There are currently around one hundred Series 8900 GC analyzers working throughout the world. Baseline's largest market since the inception of the 8900 has been in the oil and gas exploration where the product is placed in some of the more harsh environments. It is required to be easy to use and maintain as well as accurate, as locations are remote but precise data retrieval critical. The oldest have been in place and running continuously for 4 years. Baseline has over 20 units in environmental applications. We currently have several units in the oil patch in West Texas.

14. If possible, provide samples of actual data obtained from the use of this equipment and describe actual conditions under which these data were collected (controlled laboratory experiments, field testing, etc.)

Baseline will provide data for the system in the next few days showing efficiency of the total analyzer and sample systems. These results will be gathered from our laboratory.

15. If possible, provide two references of customers who currently use this equipment in the laboratory or in the field and whom we may contact regarding the use of this equipment. Please provide name of contact, company, phone number, and email address for each reference.

**Todd Harbage of GeoSyntec Consultants; Atlanta GA 404-705-9500
Adam Fasano of GZA GeoEnvironmental. Inc.; Norwood, MA 781-278-3700**

GeoSyntec is sparging ground water for trace TCE. They have been running an EPA site for over a year and a half.

Please contact me if you have any further questions, and thank you for the opportunity

Chuck Slicker
Baseline Industries
Direct phone: 970-203-0880

Questionnaire Response C

Evaluation of Two Air Stripping Methods for the Determination of Volatile Organic Compounds from Water Sources

Thomas Pietrykowski
Applications Chemist
Baseline-Mocon, Inc.

Background

Cooling tower monitoring describes the characterization of volatile organic air pollutants that are capable of being air-stripped from a water matrix. Historically, a method utilizing a dynamic or flowthrough system for air stripping a sample of cooling tower water has been used that was developed for use by El Paso Products in the early 70's (2). The purpose of this experiment is to empirically evaluate the effectiveness of both the traditional El Paso method, and an alternative method.

Objective

Evaluate and compare two methods for air stripping highly reactive volatile organic compounds (HRVOC) from water. Evaluation will be based on, response, response time, minimum detectable quantity (MDQ), and stability. Both methods will use a Baseline 8800 H Flame Ionization Detector (FID) to analyze the effluent from the stripper column.

Method Descriptions

El Paso Method

The El Paso Method uses an air stripping apparatus to air-strip HRVOC's from a water matrix. The main chamber is a 36" chamber with an internal diameter of 3", which is constructed of clear, heavywalled glass. This chamber is packed with berl saddles between 6-8 mm in size to a height of 26 inches, and capped with non-reactive end caps. Stainless steel and Teflon tubing is used to transport gas and water throughout the system. Following the main air stripping column, a glass knock-out filter is used to prevent any liquid from entering the analyzer, and a bubbler is used to visually display an excess amount of stripped gas supply to the analyzer. To prevent problems caused by condensing water in the sample lines, a Baseline series 8800 H Total Hydrocarbon Analyzer (Heated FID) was used. (2)

Air Stripper Method

The air stripping apparatus gives similar results to those obtained with the classic trickling tower, one form of which is known as the El Paso Tower. This is because both approaches use the gas-liquid partitioning phenomenon generally known and expressed as Henry's law. Our apparatus uses a nozzle instead of a trickling tower to strip the dissolved and entrained gases and volatiles from the water. The small nozzle creates a continuous stream of fine droplets, which releases gas

from water in an enclosed headspace. The general technique can also be used for stripping volatiles and gases from drinking water and wastewater. Our apparatus is compact, reliable, fast response and low in cost. The apparatus is the subject of a patent applied for and so a more detailed disclosure cannot be made at this time. Manufacturing of instruments using this apparatus for the Texas Cooling Tower Project is restricted to Baseline-Mocon, Inc.

Model 8800 H – Heated Total Hydrocarbon Analyzer

The analyzer is based on an electronically flow controlled flame ionization detector (FID) that delivers a small portion of the sample gas to the detector flame. During the combustion process, organic or hydrocarbon-based gases in the sample are ionized to a point where they can be detected by the instrument and reported as a concentration. The Model 8800 H is configured for a single point analysis of samples heated up to 200 °C, and supports external valves for automatic calibration or an internal automatic calibration valve option.

Procedure

Air Stripper Method Test Procedure

A fluid pump was connected to the water inlet port using 0.25 inch Teflon tubing. The inlet to the pump was placed in a 20 L carboy filled with deionized water. The pump was turned on, and the flow was adjusted to approximately 150 mL/min. Pressurized hydrocarbon free air was connected to a needle valve, and then to the air inlet of the mini-sparger. The flow was then adjusted to 2000 mL/min. The outlet of the air stripper was then connected to a knock out filter, and then a stainless steel tee with one end connected to a rotameter (to verify a positive and excess flow to the analyzer), and the other end connected to the analyzer. The system was then allowed to purge overnight (16 hours), to allow the system to fully equilibrate, and prevent drift from contamination in the system.

The following day, the same 20 L carboy was rinsed and re-filled with fresh deionized water, and then the system was allowed to sample the deionized water for 2 hours while data was collected from the instrument digitally using the instruments RS-485 output. Specifically, the date, time, and detector current were recorded to quantify the background and noise of the system.

Next, a concentrated standard (1 g/L) was generated by adding 2.000 g of benzene to a 2 L volumetric flask, and diluting to a volume of exactly 2 L with deionized water. Standards with concentrations of 0.02, 0.10, 0.25, and 0.50 mg/L were then mixed using aliquots of this concentrated standard. Standards having concentrations of 2.00, 5.00, and 10.00 mg/L were generated using direct micro liter injections of benzene in deionized water. All standards were mixed immediately before use to ensure accuracy and to prevent any losses of the analyte. These standards were then run through the system and the data was recorded using the 8800 H RS-485 output. Between each standard, the instrument was purged with deionized water.

El Paso Method Test Procedure

A fluid pump was connected to the water inlet rotameter using 0.25 inch Teflon tubing. The inlet to the pump was placed in a 20 L carboy filled with deionized water. The pump was turned on, and the flow was adjusted to approximately 150 mL/min. Pressurized hydrocarbon free air was connected to the sparging air inlet rotameter. The flow was then adjusted to 2500 mL/min. The outlet of the stripping tower was then connected to the analyzer. The system was then allowed to purge overnight (16 hours), to allow the system to fully equilibrate, and prevent drift from contamination in the system.

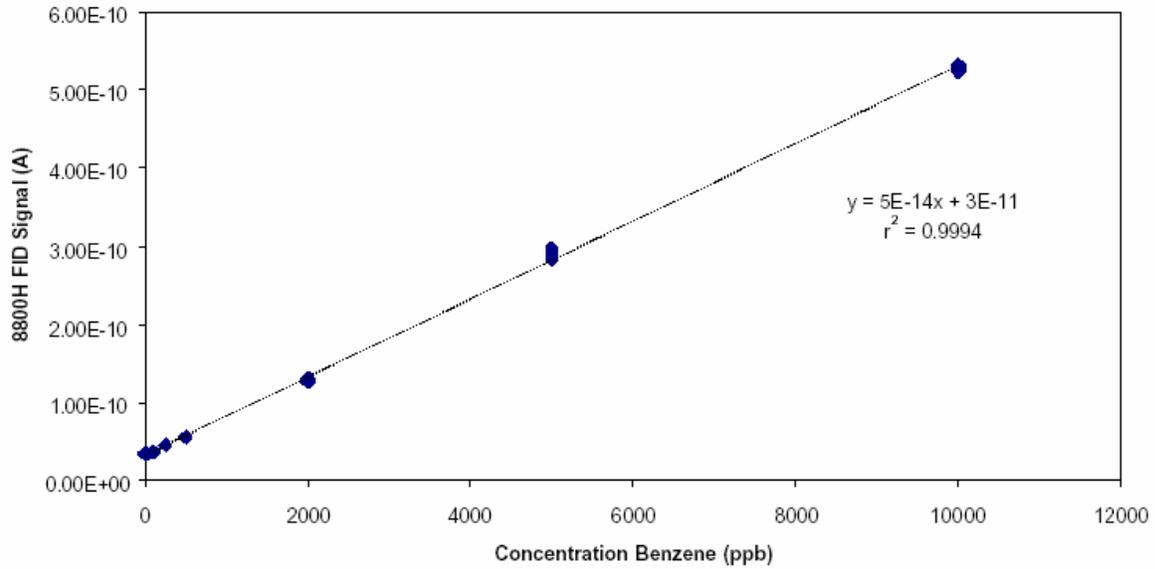
The following day, the same 20 L carboy was rinsed and re-filled with fresh deionized water, and then the system was allowed to sample the deionized water for 2 hours while data was collected from the instrument digitally using the instruments RS-485 output. Specifically, the date, time, and detector current were recorded to quantify the background and noise of the system.

Next, a concentrated standard (1 g/L) was generated by adding 2.000 g of benzene to a 2 L volumetric flask, and diluting to a volume of exactly 2 L with deionized water. Standards with concentrations of 0.10, 0.25, and 0.50 mg/L were then mixed using aliquots of this concentrated standard. Standards having concentrations of 1.00, 2.00, 5.00, and 10.00 mg/L were generated using direct micro liter injections of benzene in deionized water. All standards were mixed immediately before use to ensure accuracy and to prevent any losses of the analyte. These standards were then run through the system and the data was recorded using the 8800 H RS-485 output. Between each standard, the instrument was purged with deionized water.

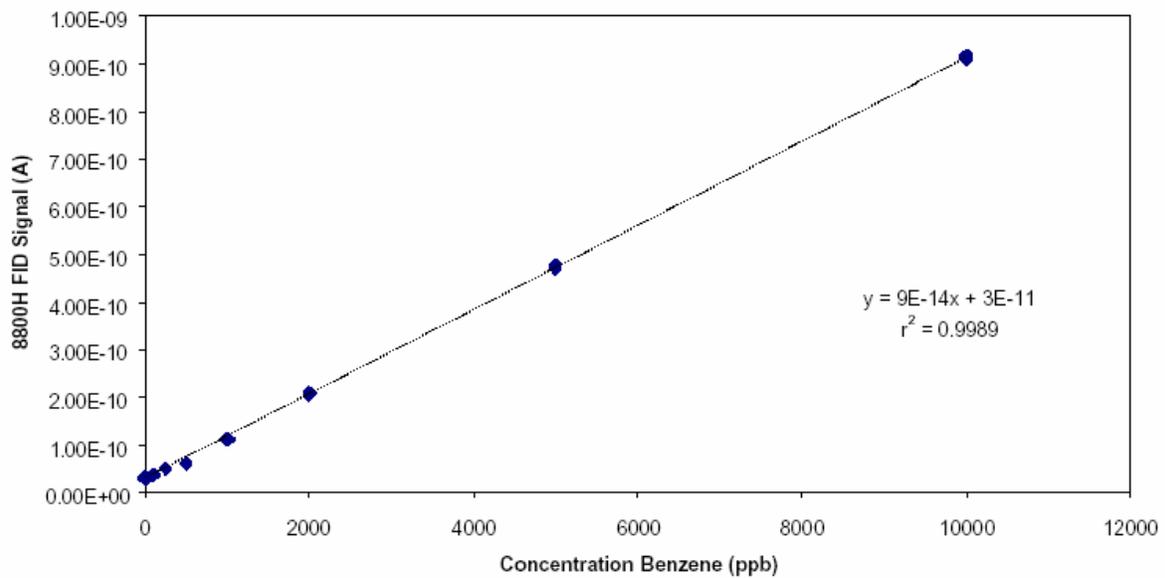
Results

A calibration curve was generated for each system as shown in figures 1 and 2.

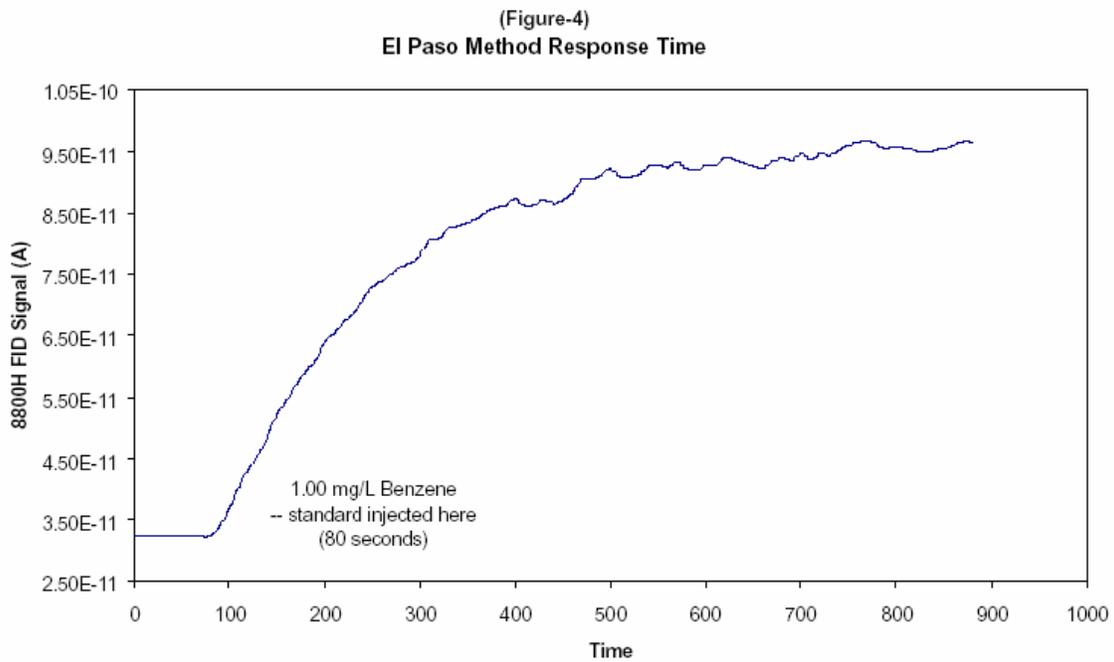
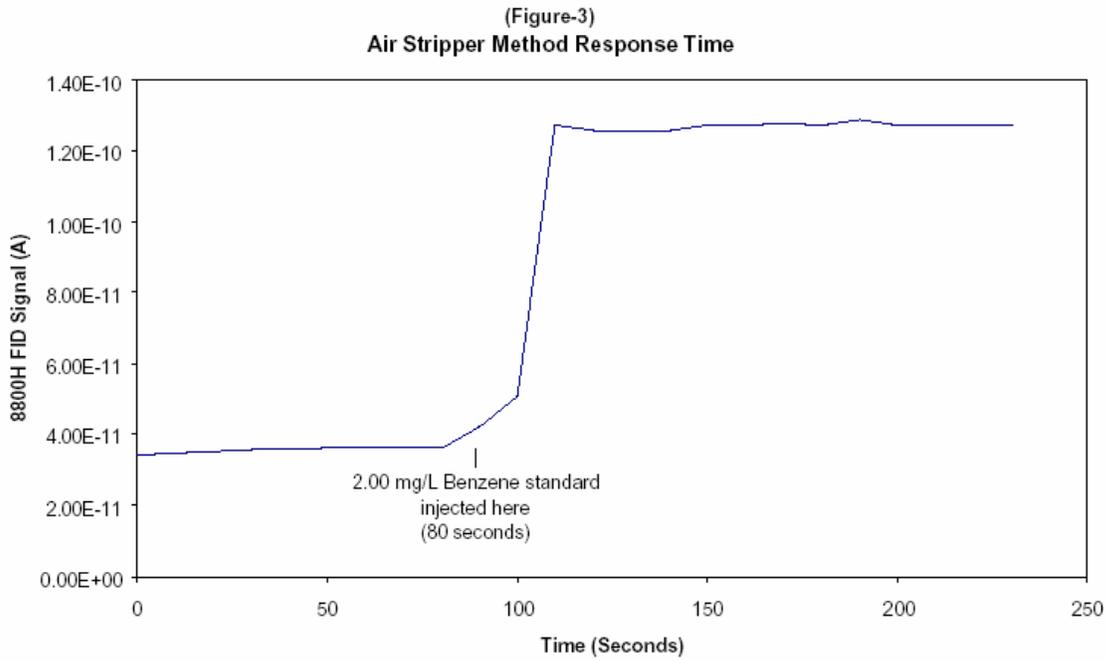
(Figure-1)
Air Stripper Method Calibration Curve



(Figure-2)
El Paso Method Calibration Curve



A curve showing the FID response over time after the addition of a known standard was generated for each system, as shown in figures 3 and 4.



(Table-1)
Analytical Parameters

	Mini Sparger	El Paso Tower
Background	29.7 pA	31.2 pA
Gain	64 pA/ppm	89 pA/ppm
Noise (Ten minutes)	1.57 ppb	3.39 ppb
MDQ (3 * Noise)	4.71 ppb	10.16 ppb
Response Time (90% span signal)	29 seconds	300 seconds
Stability (% RSD)	0.46%	1.49%

Calculations

Background – The background was calculated by determining the mean value of 10 minutes of data (FID signal) from the analysis of deionized water.

Gain – The gain was calculated by taking the mean value of the detector current from an equilibrated 2-ppm standard, subtracting the background, and dividing by the concentration.

Noise – The system noise was quantified recording 10 minutes of data (concentration) from the analysis of a blank (deionized water), and subtracting the minimum concentration from the maximum reported during that time period.

MDQ – Minimum detectable quantity was quantified by multiplying 3 times the noise. This is the minimum value that can be distinguished from the noise.

Response Time – The response time was calculated by running a blank, and then injecting a known standard and recording the data until equilibrium has been reached. The response time is the time it takes to reach 90% of the equilibrium value.

Stability – The stability of the signal was quantified by injecting a known standard, allowing the reading to equilibrate, and then recording the data every 10 seconds for 5 minutes. The standard deviation is divided by the mean. This is the coefficient of variation of the data set, and is a measure of the precision.

Discussion

For this experiment, an analyte that would challenge both systems was required. Benzene was chosen for a few main reasons. First, because of its slight water solubility (0.18 g/100 mL), the generation of known standards was a simple dilution. Benzene was also attractive because it was of high interest from the list of VOCs. Finally, because of its relatively low dimensionless Henry's Law Constant ($k_{H\text{ inv}} = 0.227 \text{ gas/aq}$); benzene would tend to stay in the aqueous phase more so than the other VOCs of high interest such as propylene, 1,3-butadiene, and butene isomers ($1.022 \leq k_{H\text{ inv}} \leq 9.732$) (1).

In comparing the two methods, it can be seen that the El Paso Method is more efficient, more analyte is stripped out of the water, as shown both by a higher gain, 89 pA/ppm compared to 64 pA/ppm, and a steeper calibration curve. However, this higher efficiency does not translate to a

more sensitive system. This is because of a slightly higher background signal, and a higher noise value (See Table-1).

The largest difference between the two systems is the stability of the signal, and the response time. This can be seen both visually in Figures 2 and 3, and is also reflected by the coefficient of variation for the equilibrated systems (Table-1). The major variables that determine the response time are the volume of water in each system, and the Henry's Law constant of the analyte in question. The air stripping method contains less than 100 mL of water at any given time in the stripping chamber, while the El Paso method contains over 2 L of water. Therefore, for any given analyte, the air-stripping chamber will respond significantly quicker than the El Paso tower, in the case of this experiment, it was a factor of 10.

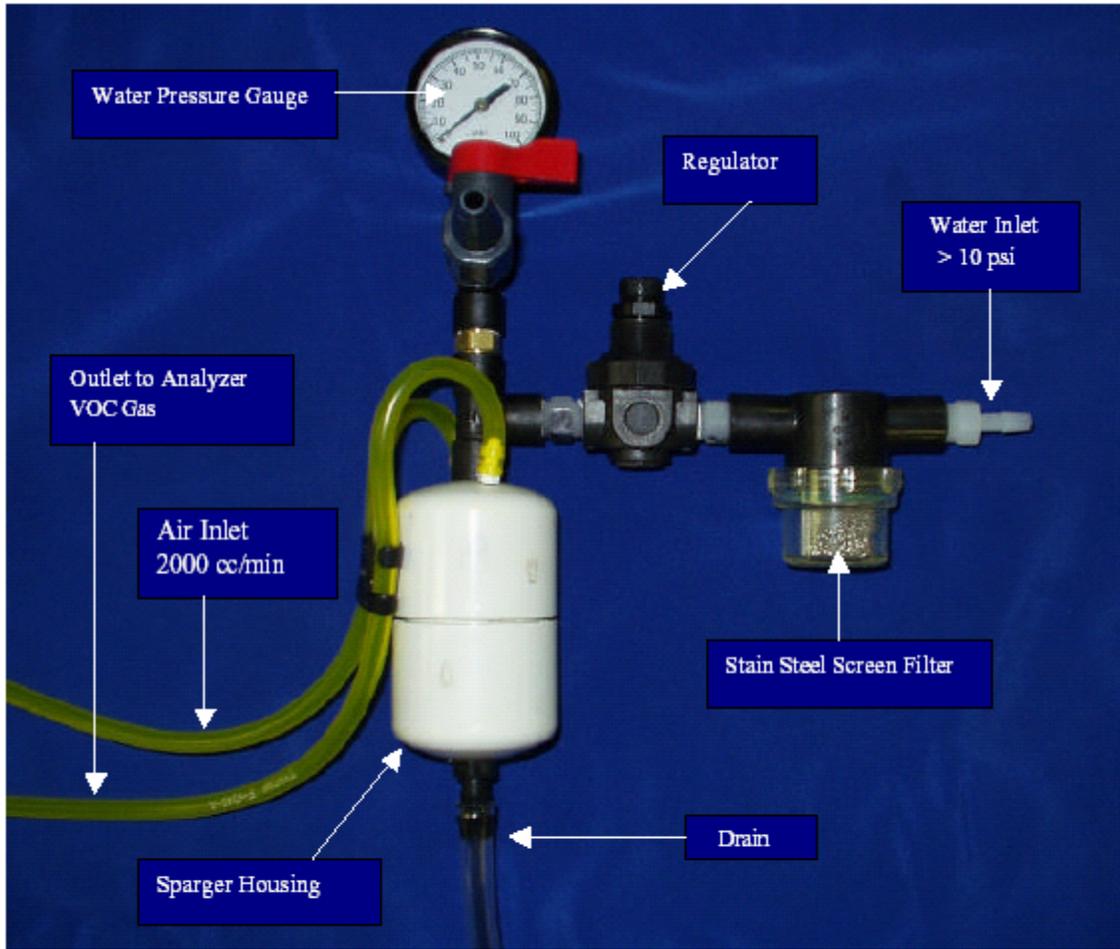
Conclusions

The air stripping method used in this study has many advantages over the traditional El Paso method. The most significant is the response time. Due to the large volumes of water in the El Paso tower, it is slow to respond to volatiles that do not readily transfer to the gas phase. The alternative air stripping method overcomes this by minimizing the amount of water in the air-stripping chamber. The air stripping method was also much more stable than the El Paso method, which made the air stripping method more sensitive despite being slightly less efficient. Another advantage of the air stripping method is its size; it is much smaller than the El Paso Tower, which also translates to a more cost effective system. The set-up and use of the systems was equal, neither presented a significant problem.

Some major factors not specifically evaluated by this study, but of importance to the long-term use of the equipment, are long-term maintenance and ruggedness of the system. The El Paso method, if contaminated, must be broken down and cleaned. This would expose the glass components of the system to possible breakage. Also, the packing material in the main stripper column (berl saddles) may need to be periodically replaced as they become contaminated. The clear glass may also allow the growth of algae and bacteria, which may compromise the accuracy of the system. The alternative air stripping method uses rugged components, which should not break unless severely mishandled. The stripping chamber is made of an opaque material, which would prevent algal growth. And the design of the system would allow quick and easy cleaning and maintenance compared to the El Paso method.

References

- (1) R. Sander (1999) Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry (Version 3) <http://www.mpchmainz.mpg.de/~sander/res/henry.html>
- (2) 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.



Baseline – MOCON mini-Sparger

Patent pending

Questionnaire Response D

Please find our response to your technical questionnaire.

1. The proposed instrument is the Ametek ProLine process mass spectrometer. There is no specific model number for this version. The ProLine is a general-purpose instrument intended for installation in some environmentally controlled area. We also offer the ProMaxion for this application. The ProMaxion is the industrially hardened version of the ProLine and carries its own environmentally controlled enclosure. The ProMaxion can be used in hazardous area classifications up to and including Class I, Division 1.
2. The instrument is a quadrupole-based mass spectrometer using a membrane introduction interface for direct liquid sampling. The attachment (MIMS Texas Cooling Towers.DOC) is an in-depth look at how the instrument operates.
3. The instrument is capable of speciated, on-line determination of VOC's in water.

The determination of which VOC's can be measured depends on the what the combination of VOC's would be in a given stream. The attached Table 1 (TCEQ Mass Assignments.XLS) shows the interaction of ALL identified species. Any component highlighted in red would be able to be measured regardless of the stream mixture. Those components that are not highlighted would require further applications work to determine just how well those components could be measured.

Isomers cannot be measured by quadrupole mass spectrometry since the fragmentation patterns of the various isomers are, for all practical purposes, identical. All xylenes, for example would be measured at a single mass and reported as a totalized xylene concentration.

For this application, we assume that a given cooling tower will have a high probability of a **group** of the targeted components being present at any time but not **all** of the targeted components due to the nature of the given tower being tied to a specific process. Knowing which of the targeted components have the highest probability of presence in the stream allows us select appropriate analysis masses for each of the components.

In general, the targeted components will have detection limits of 1 ppb as shown in the performance data included in Attachment A (MIMS Texas Cooling Towers.DOC).

4. Assuming that these operating parameters pertain to the actual sample, there are few limitations to the sample condition. The mass spectrometer uses a bypass flow sampling arrangement and uses only 50-100mL/Min of sample flow. Likewise, the pressure and the temperature of the sample are controlled at the mass spectrometer interface. Sample pressure could be as low as 2 psig or as high as 50 psig. Sample temperature can be up to 150 degrees C.

5. The instrument provides continuous, on-line analysis. Sampling interval is somewhat dependent on the stream composition but averages 2 minutes per analysis if one were switching between several sample streams. The majority of this time is spent in assuring that the sample has equilibrated. The actual mass spectrometric measurements take a few seconds. The sample concentration will have reached 100% of its calibrated value during the sampling interval.
6. During the calibration cycle (which is set up to duplicate the actual stream sampling conditions) all of the targeted component data is preserved in raw form. We use the raw form data to actually see when equilibrium has occurred and time the actual stream sampling sequences accordingly. There is always a little extra time dialed in to the sampling sequence to guarantee that equilibrium has been reached. If the instrument will be used as a single-stream device, there is, essentially, no time required for equilibration. In single stream operation, the instrument is capable of providing a typical analysis at a rate of 200 mSec per measured component. That is to say that if the instrument was being used to monitor all of the high interest targets, fresh data would be presented to the operator every second. The data acquisition time can be varied from 3 mSec/component up to 16 sec/component.
7. The single biggest hurdle in obtaining reliable data from aqueous streams is maintaining the consistency of the sample from the extraction point to the analyzer. With the idea of using a single analyzer for a single cooling tower and minimizing both the number and the length of individual sample lines, a much higher degree of control is brought to bear on the actual sample. Using short, heated sample transfer lines guarantees sample preservation.

The condition of the membrane itself can lead to analytical inconsistencies. Membrane faults lead to varying high vacuum conditions in the mass spectrometer vacuum system. The system vacuum is monitored and any abnormalities are logged and brought to the operators' attention for correction.

8. The analysis method can be affected by changes in sample and/or membrane interface temperatures. The use of short, heated sample lines minimizes the risk of changing sample temperatures. The membrane interface is temperature controlled to a high degree as part of the instrument itself. Membrane temperature is a monitored value and changes or failure of the membrane temperature is logged and brought to the operators' attention.

The ProLine instrument, as a general-purpose unit, is subject to constraints on ambient temperature and humidity levels. As such, this unit must be housed in an environmentally controlled enclosure (instrument shack or cabinet.)

The ProMaxion comes complete in an environmentally controlled enclosure and is immune from the ambient conditions in the Houston-Galveston area.

9. Measurement quality is checked against a certified standard. Periodically (and under operator control in terms of frequency) the system performs a validation check by

sampling the calibration standard. A window of acceptance is specified by the operator and upon passing the calibration verification test, the system returns to online sampling with the calibration verification details logged in a calibration file. Should the instrument fail the calibration verification test, the failure is logged and a new calibration is performed prior to retuning to on-line sampling. Since all other operating parameters are fixed, detector calibration to a standard is all that is required.

Calibration is done with in liquid phase using commercially available standards at equivalent flows, pressures, and temperatures to the actual sample.

10. Preventative maintenance is a once-yearly event consisting of routine vacuum system servicing. This servicing requires no specialized training and will consume approximately 8 hours of on-site time.
11. The ProLine is not intrinsically safe and must be housed in an appropriate non-classified area. The ProMaxion is equipped with an X-purged, environmentally controlled housing to allow operation in hazardous areas up to and including Class 1, Division 1.
12. The ProLine, equipped for single line sampling, has an installed cost of \$65,000.00. The ProMaxion, configured for hazardous area location service and single line sampling, has an installed cost of \$75,000.00
13. Ametek has been manufacturing mass spectrometers since 1986 and has over 6,000 units in worldwide operation. The analysis of VOC's in water is a new application. There are no current users of the instrument at present.
14. The data included in the Attachment A (MIMS Texas Cooling Towers.DOC) illustrates data obtained in a laboratory environment.
15. We can provide names of customers that are using our instruments in process environments. However, we cannot provide a user list for this specific application.

Should you have any further questions or need clarification on any points, please feel free to contact me a 412-826-2452.

Sincerely,

Anthony L. Slapikas
Ametek Process Instruments

Questionnaire Response D, Table 1

Shows the interaction of ALL identified species.

Any component highlighted in red would be able to be measured regardless of the stream mixture.

Those components that are not highlighted would require further applications work to determine just how well those components could be measured.

Mass	High Interest Components					Medium Interest Components					Moderate Interest Comp				
	Benzene	Ethylene	Propylene	1,3 Buta	Butene	Acetaldehyde	Formaldehyde	Hexene	Isoprene	Pentene	TMB	Xylene	Butane	Pentane	Toluene
15						X									
26		X													
27		X		X								X		X	
28		X										X			
29						X						X			
30												X			
39			X	X	X										
41			X		X			X						X	
42			X											X	
43						X		X				X		X	
44						X								X	
50	X														
51	X														
52	X														
53				X					X						
54				X											
55					X			X							
56					X			X							
67									X	X					
68									X	X					
77	X										X				
78	X														
91												X			X
92															X
93															
105										X		X			
106											X	X			
119											X				
120											X				

Questionnaire Response D, Attachment A

Membrane Interface Mass Spectrometry for the Analysis of VOC's in Water

Membrane interface mass spectrometry (MIMS) has been used successfully for a number of years in the analysis of volatile organic compounds (VOC's) in water. Any number of references to the technique can be found via the Internet. Proprietary MIMS systems have been used for over a decade to monitor cooling tower leaks to satisfy regulatory requirements. Long-term use of the technique at these sites has proven the efficacy and robustness of on-line MIMS. Ametek's commercially available ProLine process mass spectrometer, outfitted with a MIMS interface, is used for continuous, on-line analysis of VOC's in water.

The Technique

At the heart of the MIMS technique is the ability of various membrane materials to selectively block polar compounds (e.g. water) while allowing the non-polar species to migrate through the membrane. Typically, the membrane is a thin sheet, or tube, of dimethylsilicone. Other membranes are available and vary typically in their ability to enhance, or retard, the migration of specific compounds through the membrane. The VOC's called out in the Texas regulations have all been proven to work well with standard membranes.

It must also be understood that the selective extraction of an analyte from the bulk matrix represents an enrichment of that analyte. If one were tasked, for example, with detecting a few black marbles in the presence of a large number of white marbles, it would be advantageous to remove all of the white marbles prior to the analysis. In the bulk matrix, the ratio of white to black marbles may be on the order of 10,000:1. Thus, the analysis tool is faced with the relatively daunting task of separating a small piece from a large whole. Removing all, or mostly all, of the white marbles lets the instrument see only the black marble as the target.

MIMS provides analyte enrichment in a similar manner. Since the analysis of any VOC in any matrix requires an instrument with low detection limits, the ability to provide the instrument with a sample that is comprised almost completely of the analytes of interest leads to startlingly low limits of detection due to the reduction of bulk matrix interferences and the subsequent rise in signal-to-noise ratio of the instrument. It is common for MIMS instruments to provide lower limits of detection of 1 ppb with some reports of low ppt detection for specific VOC's coupled to specific membranes.

The actual process of analyte transmission through the membrane is known as pervaporation and consists of three phases:

- a. Adsorption of the analyte of interest on the surface of the membrane material
- b. Passage of the analyte of interest through the lattice structure of the membrane

c. Evolution of the analyte into the analysis instrument

In our case, the membrane is providing the highly enriched sample directly into the ion source of the mass spectrometer.

The attached data file shows the performance Ametek ProLine process mass spectrometer equipped with a MIMS sample introduction system. The system was challenged with various concentrations of methylene chloride in water. A lower limit of detection of 1 ppb is clearly seen with quantifiable concentrations starting at 10 ppb. Both of these benchmarks fall clearly within the guidelines of the proposed Texas regulations for detection.

It is also important to note the speed of response of the system. Transitions from one concentration level to the next are very clean and exhibit a fast equilibrium response.

Physical Instrument Characteristics

When equipped for MIMS operation, the ProLine process mass spectrometer uses a dimethylsilicone membrane coupled directly to the ion source of the instrument. A rotary valve assembly is used for multiple sample stream selection and the introduction of calibration standards. A small peristaltic pump is used at the “bottom” of the sample inlet to ensure constant sample flow across the membrane.

It is our intent to offer the instrument with two sample entry points (although more are certainly possible). While the regulations currently call for the analysis of the exit flow from the cooling tower, it seems obvious that a differential measurement obtained across the cooling tower will provide a far more accurate look at the VOC concentrations in the stream. Minimizing the number of sample streams will also provide the user with a high integrity sampling system to guarantee sample preservation from the tower to the instrument. As an added benefit, the idea of a close-coupled instrument (as opposed to a centrally located, high stream count, multiple sampling instrument) will significantly reduce initial capital outlay and long-term cost of ownership due to the reduction in total length of the heated sample lines necessary to move sample to the instrument.

Data can be moved from the instrument in a variety of ways. All common industrial protocols are available as are dedicated analog lines to bring the data to a common point for collection. Alarms are available for every stream along with an “on the fly” mathematics package that will allow the data to be presented in any appropriate way to the user (mole %, lbs/hour, etc.)

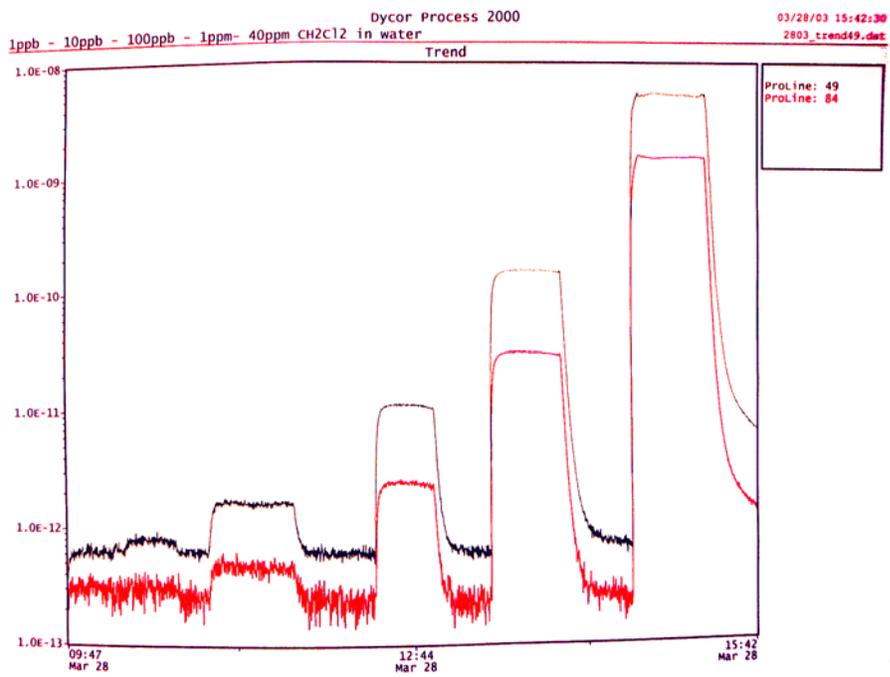
Specific Mass Spectrometry Advantages for the Application

Mass spectrometry has been used on-line for control and monitoring purposes for over 30 years. The advantages of mass spectrometry in the classic applications (EO production, fermentation of-gas analysis, high-speed ambient air sampling for fugitive emissions) are also applicable here.

- a. Speed of analysis. Mass spectrometry in general is a very fast analysis technique. Quadrupole-based instruments are the fastest mass spectrometers. Including delays for stream switching, the MIMS-equipped ProLine will be able to provide data as fast as 1 minute/stream a specification that, again, falls well within (and actually better by quite a bit) the published regulation guidelines for sampling frequency. As a comparison, mass spectrometry is generally 10 to 50 times faster than gas chromatographic analysis for similar applications.
- b. Specificity of analysis. Unlike instruments that provide a “total” reading of VOC levels, mass spectrometry offers direct identification of the species of interest. This level of specificity will allow the continuous speciation of the targeted VOC’s as a routine matter of course. This capability may reduce, or eliminate, off-site lab analysis for VOC speciation. Conversely, if a “totalized” VOC number is required, the mass spectrometer is able to survey all VOC’s and totalize them via the mathematics package.
- c. Direct analysis of the sample stream. Unlike sparging techniques which, of necessity, must take into account the flow rates into and out of the sparger to establish accurate volumes for correct concentration determinations, MIMS simply requires an appropriate liquid standard for calibration. These standards are readily available and are presented to the instrument in the same fashion as the sample stream itself. Thus, a very high correlation is developed between the calibration method and the actual sampling event – an absolute necessity for generating consistent, meaningful data.

Summary

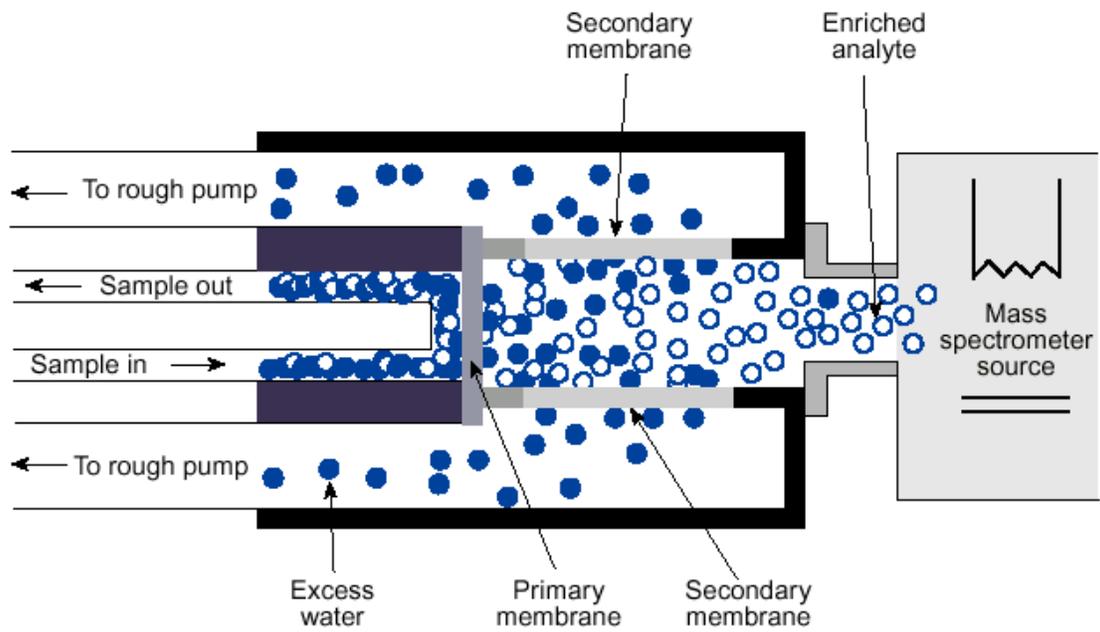
Based on the preliminary studies, it appears that MIMS is an attractive candidate for the continuous, on-line analysis of cooling tower wastewater. The advantages inherent in the use of on-line mass spectrometry are applicable to this task and bring a level of confidence, ease-of-use, and elegance that can be offered by no other technique.



Note: Image generated from a low quality digital photograph.



Compact Low-Cost Proline MS Package.



Schematic View of The Membrane Inlet MS

Questionnaire Response E

ANALYTICAL APPLIED SOLUTIONS L.L.C
DBA ANALYTICAL SYSTEMS INTERNATIONAL
1400 B Graham Drive Tomball, Texas 77375 U.S.A.
(281) 516-3950 FAX (281) 351-8925
Web Page: www.ASIWebPage.com
E Mail: sales@ASIWebPage.com
service@ASIWebPage.com

Re: Evaluation Of Continuous VOC Monitoring/Sampling Methods

1. What is the manufacturer's name and model number for the instrument being described?

Analytical Systems International (Keco R&D Inc) Model 204

2. Provide a brief description of how the instrument operates and the principles on which it is based (sampling system, sample media detector/analyzer, data collection/analysis/reporting, etc.).

<http://www.asiwebpage.com/product/prodpdf/VOC%20IN%20H2O%20EX-GP%20204.pdf>

Instrument operation consists of a self-cleaning filter to clean usually muddy cooling tower water. Valuing, Pressure regulation, and Flow meters are used to send sample water into a Membrane Stripper Transfer Unit (Ranger). See Ref. A attached. The water passes one side of a polymer membrane and volatile organic carbon (VOC) in the water permeates through the membrane. Clean dry carrier gas flowing past the other side of the membrane evaporates the permeated VOC and this clean relatively dry sample goes through GC injection valve and then into a tin oxide solid state sensor. The attached flow diagram, Ref. B shows the system. The solid-state sensor that responds to total VOC is very sensitive at low ppbw because of its exponential response. The GC is used to speciate the VOC's. The membrane transfer provides a so-called magnifying effect. A part per billion by weight sample in water provides a part per billion by volume sample many times longer in the carrier gas. The sensors can measure long term at below 5 ppbw Ref. C shows a recording of response of 5,15,30 and higher ppbw sample for 10 hours. If total VOC exceeds 50 ppbw then TCEQ regulation requires speciation of VOC's. GC readout when total VOC is much below 50 ppbw will separate components, lowering percentage of each, and may indicate none detectable. Reporting is by 40-20 mA output and RS 485 signaling. Ref. B (Copy mailed 7-1-03) shows an automatic permeation tube that can validate instrument response.

3. Does the instrument measure total volatile organic compounds (VOCs)? Speciated VOCs? What VOCs can be detected/quantified with this instrument and in what concentration range (ppm)? A list of compounds of special interest is provided below for reference.

The instrument responds to all VOCs, the sensor indicates total VOCs. Speciation is by GC column. Instruments in field service have been calibrated for most of the compounds listed as well as others.

4. What is the range of operation for the following parameters: flow rate (ml/min), temperature (°C), humidity (%), and pressure (kPa)? Identify any other critical parameters and their operating range.

Normally sample flow rate used is 20 ml/min although sweep flow in the sample flow line may be much higher for first response. The membrane sample transfer unit and permeation tube are in a thermostated oven. Special heating and insulations are used when in -40°C operation in Canada. See ref. A for other specifications.

<http://www.asiwebpage.com/product/prodpdf/VOC%20IN%20H2O%20EX-GP%20204.pdf>

5. Does the instrument provide continuous measurements? semi-continuous? For this purpose, continuous is defined as a minimum of one sample every 15 minutes. Identify the sampling interval. What is the response time associated with these measurements?

Measurement is continuous on line. When a GC readout is used sampling time may vary with type of column used. Response time including sample line absorption and instrument response varies with type of compound but averages 10 to 15 minutes.

6. How does the instrument achieve, determine, and assure equilibrium (steady state) during measurements?

A chart recording indicates equilibrium by a constant reading.

7. Identify the parameters at the most risk of affecting the accuracy of measurements obtained with this instrument (if possible, quantify the effect on accuracy).

Temperature can affect reading. An air-conditioned enclosure is recommended for low ppbw samples. See Ref. D for case study of a six-year-old installation in an air-conditioned instrument house. Readout is directly proportional to carrier flow rate. Readout is not sensitive to sample water flow rate. Attached VOC ISA Tech Paper 2001

8. How is the accuracy of the method affected by environmental changes in ambient temperature, humidity, and wind? What are the environmental limitations of this equipment?

Environmental conditions are provided for by final design for a job. Operating units are installed in environments from -40°C in Canada, the tropics in Venezuela and in desert environment. With custom modifications there are no Environmental Limits.

9. What are the quality assurance/quality control requirements for this instrument? What calibration frequency is needed and for what parameters (e.g., flow rate, temperature, pressure, detector, etc.)? Describe the calibration method (calibration phase: air, water)?

Quality assurance/quality controls are provided by a permeation tube reference standard built into the instrument for manual or automatic operation that validates instrument operation. The control room operator with a remote readout can verify status. Reference standard is mixed and immediately used eliminating determination of sample.

10. Identify a recommended preventative maintenance schedule for this instrument.

Primary spin clean filter regeneration is automatic and secondary filter is replaced monthly. IF permeation tube standard shows any change the operator checks pressure settings, flow rate and temperature control. We recommend at least once a week verification. Stability usually makes adjustments period 3 months or longer.

11. Is the instrument intrinsically safe? Describe any safety features of the equipment.

Air purge is provided for hazardous locations.

12. What is the cost of this instrument including any optional equipment that may be needed for this application?

See attached quotation Ref. E K-Model 204 Above

13. How many instruments are installed and currently operating (and for how long)? How many are in Texas?

See Ref. F (K-VOC in H₂S Reference) for partial customer list, we have over 20 years experience with about 100 installation world wide, many are in Texas.

14. If possible, provide samples of actual data obtained from the use of this equipment and describe actual conditions under which these data were collected (controlled laboratory experiments, field testing, etc.)

See Ref. D (VOC ISA Tech Paper 2001) for data, provided by Oxychem (now Equistar) from an operating ethylene plant and used to write an ISA paper case study on a Model 204 analyzer that has been in operation for 6 years. This shows a 72-hour run during which two benzene leaks were detected and corrective action taken at the two ppbw level. Figure 2 in that study is a calibration check at 20 ppb. Reference G is a field validation analysis by EPA method 301-5.3. This established precision of 0.196 ppmw and standard deviation of 0.98%.

15. If possible, provide two references of customers who currently use this equipment in the laboratory or in the field and whom we may contact regarding the use of this

equipment. Please provide name of contact, company, phone number, and email address for each reference.

References to contact are John Orendorff Equistar, 361-242-5035, 1501 McKenzie Road. Corpus Christy, TX 78410. Email: John.Orendorff@equistarchem.com and Pat Mullin Exxon Mobil 713-656-9088, 601 Jefferson St. Houston, TX 77002 Email: Patrick.B.Mullin@exxonmobil.com

16. Additional Relevant technical literature/information/comments are welcome.

The attached report Ref. G (K-VOC H2O Saturation Data) by TCEQ shows in detail problems with cooling towers leaks. The use of membrane transfer to strip VOC'S from water prevents fouling by mist and particulate. We recommend built in validation by permeation tube reference standards. See Ref. I (K-VOC TCEQ Letter 2000) and the letter from Bob Mann with TCEQ stating the Model 204 satisfies requirements for Best Available Control Technology (BACT) . Charles Kimbell letter addressing his questions & is included in a copy mailed 7-1-03.

If you would like additional information or clarification please contact Charles Kimbell cell phone 281-813-4877 or fax to 936-825-0600 or Tom Kimbell phone and E mail above.



Questionnaire Response F

Questionnaire for Continuous VOC Monitoring/Sampling Methods:

The University of Texas at Austin (UT) under contract to the Texas Commission on Environmental Quality (TCEQ) is performing an assessment of continuous VOC monitoring/sampling methods that can be used to analyze leaks of highly reactive VOCs from industrial cooling towers. Providing the information requested in this questionnaire will enable UT to include your system in our evaluation. It is important that we receive correct and detailed technical information about the operation and performance of this equipment so that an accurate evaluation can be made. If you have more than one instrument that can be used for this type of application, please submit a separate questionnaire for each one.

1. What is the manufacturer's name and model number for the instrument being described?

MANUFACTURER:
Siemens Applied Automation
500 West Highway 60
Bartlesville, OK 74003

Branch Office:
7101 Hollister Road
Houston, TX 77040

INSTRUMENT DESCRIBED:
MAXUM edition II on-line Process Gas Chromatograph

2. Provide a brief description of how the instrument operates and the principles on which it is based (sampling system, sample media, detector/analyzer, data collection/analysis/reporting, etc.).

In general, an analytical system consists of the sample extraction, sample transport, sample conditioning, analyzer, analyzer shelter and analyzer data communication. Independent whether the sample is a vapor or a liquid, a continuous sample stream is piped to the analyzer location in form of a "Fast Loop". Sample flow depends on distance, sample pipe diameter and permissible sample lag time. The sample preferably is returned to the process at a lower sample pressure location. From the fast loop a continuous "Analytical Loop" provides conditioned sample to the analyzer and preferably back into the fast loop. The sample is filtered, temperature stabilized if needed and flow and pressure stabilized if needed. Liquid samples can be vaporized continuously in order to provide a vapor sample. Although this procedure is typically done only for low boiling liquids such as LPG. The analyzer selects a fixed amount of sample from that analytical loop and injects it into the analyzer. If the sample is liquid it is vaporized inside the analyzer prior being flushed into the separation column. The separation system utilizes

typically micro-packed or capillary column selected according sample matrix and targeted measuring components. An at least 2 separation column with at least a backflush configuration is used. Detectors are typically Thermal Conductivity (TCD) or Flame Ionization (FID) detectors. The detector signal is amplified, integrated and compared with the calibration data from a known external standard. The results as well as status data are forwarded to a printer, a data collection system or a process control system. One or several Process Gas Chromatographs are accommodated in a weather protective enclosure, such as a cabinet or an air-conditioned fiberglass or metal shelter.

The attached brochures describe the analyzer and system possibilities in more detail.

3. Does the instrument measure total volatile organic compounds (VOCs)? Speciated VOCs? What VOCs can be detected/quantified with this instrument and in what concentration range (ppm)? A list of compounds of special interest is provided below for reference.

Each analyzer is customs configured.

For the specific applications discussed, the analyzer is setup to measure individual components to determine BTU and HR-VOC's for the Flares, and Total VOC (less Methane and less Ethane) as well as speciated individual VOC's up to C5 for Cooling Towers.

See attachment "2003 07 01 – Siemens – Analytical Configurations". The technical data there are pretty accurate. However, there maybe some minor corrections done over the next days.

High interest: benzene; ethylene; propylene; 1,3-butadiene; all butene (butylene) isomers

Medium interest: acetaldehyde; formaldehyde; all hexene isomers; isoprene; all pentene isomers; all trimethylbenzene isomers; m-,o-xylene

Moderate interest: n-,iso-butane; n-,iso-pentane, toluene

As you can see, the set-up at the moment is to comply with the chapter 115 required measurement with only one analyzer for the flares and only one analyzer for the cooling tower. Measuring Benzene as well as the "Medium Interest" components additionally, a second analyzer is required. Furthermore, it is doubtful that the measurement can be done within the 15 minutes required. However, in order to make a certain statement, a column development study has to be performed.

4. What is the range of operation for the following parameters: flow rate (ml/min), temperature (°C), humidity (%), and pressure (kPa)? Identify any other critical parameters and their operating range.

Sample flow rate: Flare Fast loop – depending on the pump capacity; flow rates of several liter/min are typical resulting in sample lag times below 60 seconds is typical
Flare Analytical loop – typical 50-100 cc/min resulting in sample lag time measured in seconds

Cooling Tower Fast loop – depending on water pressure (height of

cooling tower) and distance but flow rates of several liter/minute resulting in sample lag times of less than 60 seconds are typical.

Temperature: 0-120F (sample temperature has to be stabilized and independent of ambient temperature)
Humidity: 0-95% (non condensing)
Sample Pressure: Flare: 5-30 psi (at injection valve)
Cooling Tower – 5-30 psi (at injection valve)

5. Does the instrument provide continuous measurements? Semi-continuous? For this purpose, continuous is defined as a minimum of one sample every 15 minutes. Identify the sampling interval. What is the response time associated with these measurements?

Cycle Time: Flare – BTU & HR-VOC: < 450 seconds
Cooling Tower – Total VOC: <120 seconds
Cooling Tower – Speciated VOC: approximately 15 minutes

6. How does the instrument achieve, determine, and assure equilibrium (steady state) during measurements?

Flare: Sample-conditioning system ensures constant sample flow.
Heated sample conditioning enclosure provides constant sample temperature.
Just prior injecting the sample, the sample flow is momentarily stopped and the sample pressure is equilibrated to ambient pressure, Therefore ambient pressure is the sample pressure reference all the time.

Cooling Tower: Sparging system is temperature equilibrated or the water temperature is measured and is part of the calculation.
The sparging gas continuously flows through the injection valve. Just prior injecting the sample, the sample flow is momentarily stopped and the sample pressure is equilibrated to ambient pressure, Therefore ambient pressure is the sample pressure reference all the time.

7. Identify the parameters at most risk of affecting the accuracy of measurements obtained with this instrument (if possible, quantify the effect on accuracy).

Flare & Cooling Tower:
Sample pressure change due to injection volume change due to ambient pressure changes => +/- 2%
Reference standard change => depending on number of components, compatibility, and materials used.

Cooling Tower:
For the following statements, no specific quantitative data are available but are based on past experience. Calibrating the analyzer only assumes perfect efficiency of the sparging system. Any sparging efficiency degradation is not recognized. Especially the “Appendix

P” sparging system with the ‘beryl saddle” fillings is due to the very large exposed surface potentially subject to fast sparging efficiency degradation. Estimated in the low % range. Due to the high sparging gas flow, the influence on the sparging efficiency due to small sparging gas flow is estimated in the low percentage range.

8. How is the accuracy of the method affected by environmental changes in ambient temperature, humidity, and wind? What are the environmental limitations of this equipment?

See comments at 4.

Due to the ambient temperature changes it is recommended and common to install analyzers in climate controlled enclosures. That of course adds substantial costs that are in the neighborhood of the actual analyzer costs.

9. What are the quality assurance/quality control requirements for this instrument? What calibration frequency is needed and for what parameters (e.g., flow rate, temperature, pressure, detector, etc.)? Describe the calibration method (calibration phase: air, water)?

In order to improve on-line time, we have suggested monitoring additional parameters than normally done, such as carrier gas supply pressure and sample pressure. The analytical system itself has the capability to monitor essentially every analytical parameter. Among others, all together parameters such as analyzer oven temperature, carrier gas pressure, detector signal, sample pressure, sample flow, carrier gas supply pressure and retention times are monitored.

Flare validation and calibration:

Automatically performed by supplying a known standard and periodically analyzing that standard automatically. Results are compared to last calibration. Typically no operator intervention is necessary if results are within preset ranges. Due to the number of components involved several calibration cylinders are required and that complicates AutoCal. Therefore, because the response of an individual component does not change selectively compared to all other measuring components, it is suggested to use a single or few selected components to verify calibration. By demonstrating that these selected components have the same response it can be concluded with very high probability that all other components are accurate as well.

Cooling Tower:

Due to the nature of the volatile target components, it is rather difficult to calibrate the entire analytical system based on a liquid standard. Consequently, introduction of a vapor standard between the sample extraction system and the analyzer is suggested by TCEQ. However, as mentioned previously, that assumes that the sparging system functionality is constant. That assumption is not correct, especially because there is no verification whether changes occur or have occurred.

10. Identify a recommended preventative maintenance schedule for this instrument.

Flare:

Sample Conditioning System: Depending on flare and sample condition every 4-12 weeks

Analyzer: Every 6-12 month

Cooling Tower:

Sample Extraction System: Depending on the cooling water every 1-4 weeks

Analyzer: Every 6-12 month

11. Is the instrument intrinsically safe? Describe any safety features of the equipment.

System as build is suitable for hazardous area and certified according Class I, Div.2, Group C&D. System can be build for Class I, Div.I, Group B,C&D with significant increased costs.

12. What is the cost of this instrument including any optional equipment that may be needed for this application?

Budgetary Pricing:

Flare:	Analyzer: \$50K
	Sample Conditioning: \$20K
	Enclosure: \$70K
Cooling Tower:	Analyzer: \$55K
	Sample Conditioning: \$30K
	Enclosure: \$70K

13. How many instruments are installed and currently operating (and for how long)?

How many are in Texas?

Since about 1970:

There are about 15,000 Siemens on-line Process Gas Chromatographs installed

There are more than 3000 Siemens Chromatographs installed in Texas

There are more than a 1000 Siemens MAXUM II Process Gas Chromatographs installed.

14. If possible, provide samples of actual data obtained from the use of this equipment and describe actual conditions under which these data were collected (controlled laboratory experiments, field testing, etc.)

All actual field data are customer's data and have to be obtained from customers. We can't provide field data.

15. If possible, provide two references of customers who currently use this equipment in the laboratory or in the field and whom we may contact regarding the use of this equipment. Please provide name of contact, company, phone number, and email address for each reference.

Dan Podkulski
Senior Staff Group leader
ExxonMobil Baytown Chemical Plant
5000 Bayway Drive
Baytown, TX 77522-2002
281-834-2833
281-439-1271 (pager)
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Jerry W. Alley
Equistar Chemicals, LP
Central CSE Houston Region
Channelview, TX
281-862-5217 office
281-862-4440 fax
888-632-4407 pager
Jerry.Alley@equistarchem.com

16. Additional relevant technical literature/information/comments are welcome.

See attachments

I also have attached some of the slides we used on customer seminars especially for the sample preparation system and enclosure possibilities and requirements.

Questionnaire Response G

Questionnaire for Continuous VOC Monitoring/Sampling Methods:

The University of Texas at Austin (UT) under contract to the Texas Commission on Environmental Quality (TCEQ) is performing an assessment of continuous VOC monitoring/sampling methods that can be used to analyze leaks of highly reactive VOCs from industrial cooling towers. Providing the information requested in this questionnaire will enable UT to include your system in our evaluation. It is important that we receive correct and detailed technical information about the operation and performance of this equipment so that an accurate evaluation can be made. If you have more than one instrument that can be used for this type of application, please submit a separate questionnaire for each one.

1. What is the manufacturer's name and model number for the instrument being described?

MANUFACTURER:
Siemens Applied Automation
500 West Highway 60
Bartlesville, OK 74003

Branch Office:
7101 Hollister Road
Houston, TX 77040

INSTRUMENT DESCRIBED:
FIDAMAT Continuous Gas Analyzer

2. Provide a brief description of how the instrument operates and the principles on which it is based (sampling system, sample media, detector/analyzer, data collection/analysis/reporting, etc.).

Sample transport, conditioning and enclosures have been described in part 1. This analyzer is essentially an FID. A constant and continuous sample is flowing through the detector. The total amount of organic carbon is registered. The detector design and operation mode has to ensure that the CH-group is independent from the molecule it originates from. It either consists of a single detector measuring the Total VOC including Ethane and Methane. An alternative is using a dual detector version. The first detector is measuring Total VOC including Methane and Ethane. The second detector is utilizing a catalyst that converts Ethane and higher Hydrocarbons to CO₂ and consequently measures Methane selectively. By subtracting both detector signals from each other Total VOC less Methane can be determined continuously.

3. Does the instrument measure total volatile organic compounds (VOCs)? Speciated VOCs? What VOCs can be detected/quantified with this instrument and in what

concentration range (ppm)? A list of compounds of special interest is provided below for reference.

It measured Total VOC (Methane +) or as an alternative Total VOC (Ethane+).
Concentration range is 0.1 ppm to 10,000 ppm (with range switching)

High interest: benzene; ethylene; propylene; 1,3-butadiene; all butene (butylene) isomers

Medium interest: acetaldehyde; formaldehyde; all hexene isomers; isoprene; all pentene isomers; all trimethylbenzene isomers; m-,o-xylene

Moderate interest: n-,iso-butane; n-,iso-pentane, toluene

4. What is the range of operation for the following parameters: flow rate (ml/min), temperature (°C), humidity (%), and pressure (kPa)? Identify any other critical parameters and their operating range.

See parameters from attachment from part 1 “Siemens – Analytical Configurations”

5. Does the instrument provide continuous measurements? Semi-continuous? For this purpose, continuous is defined as a minimum of one sample every 15 minutes. Identify the sampling interval. What is the response time associated with these measurements?

Continuous measurement

6. How does the instrument achieve, determine, and assure equilibrium (steady state) during measurements?

Keeping all parameter constant, such as sample temperature and sample flow – very critical!

7. Identify the parameters at most risk of affecting the accuracy of measurements obtained with this instrument (if possible, quantify the effect on accuracy).

See attached brochure “FIDAMAT”

8. How is the accuracy of the method affected by environmental changes in ambient temperature, humidity, and wind? What are the environmental limitations of this equipment?

See answer part 1

9. What are the quality assurance/quality control requirements for this instrument? What calibration frequency is needed and for what parameters (e.g., flow rate, temperature, pressure, detector, etc.)? Describe the calibration method (calibration phase: air, water)?

See answer part 1

10. Identify a recommended preventative maintenance schedule for this instrument.

See answer part 1

11. Is the instrument intrinsically safe? Describe any safety features of the equipment.

No, analyzer is only available for General Purpose environment.

12. What is the cost of this instrument including any optional equipment that may be needed for this application?

Analyzer: Single Detector: \$18K

Dual detector: \$23 K

Sample Conditioning System: \$25K

Enclosure: \$ 20-60K depending on environment and configuration

13. How many instruments are installed and currently operating (and for how long)?

How many are in Texas?

Since 1992

There are more than 100 in the US

No information about installed base in Texas

14. If possible, provide samples of actual data obtained from the use of this equipment and describe actual conditions under which these data were collected (controlled laboratory experiments, field testing, etc.)

See answer part 1

15. If possible, provide two references of customers who currently use this equipment in the laboratory or in the field and whom we may contact regarding the use of this equipment. Please provide name of contact, company, phone number, and email address for each reference.

Have to be researched.

16. Additional relevant technical literature/information/comments are welcome.

See Attachment A

Questionnaire Response G, Attachment A

MAXUM[®] edition II Gas Sparger Specification

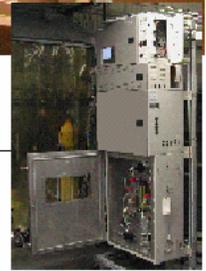
Function

Provides on-line sample preparation to allow the MAXUM edition II gas chromatographs to analyzer ppb levels of volatiles in water. The sparger system is coupled either with the MAXUM edition II isothermal or PTGC analyzer. All the standard features of the MAXUM edition II system are included in this analyzer system.



Mounting

Wall-mounted, attached below MAXUM edition II analyzer.



Installation Requirements

Should be protected from the weather. Ambient temperature from 33 to 122°F (1 to 50°C).

Sparger Configurations

Single Sparger system consisting of a single sample inlet, regulator, flow switch and water heater, with a backup sparger. Dual Sparger system consisting of two parallel sample inlets, regulators, water heaters, flow switches and spargers. The analyzer alternates between spargers.

Safety

Agency certified to the UL and Canadian standards for use in Class I, Division 1, Groups C, D hazardous locations.

Sparger Temperature Control

Air bath, electrically-heated to 135°F (57°C) ± 1°. A three mode temperature controller using an RTD sensor is used for control.

Analyzer and Sparger Air Requirements

25 psig (172 kPa) or higher, dry, clean, oil-free.

Isothermal GC	5 SCFM (140 liters/min)
PTGC	10 SCFM (280 liters/min)
Sparger System	3 SCFM (84 liters/min)
Optional Vortex Cooler	10 SCFM (280 liters/min) at 100 PSIG (688 kPa), -40° dewpoint.

Valve Air Requirements

50 PSIG (345 kPa) instrument air standard. Helium or nitrogen may be substituted for air.

Sparger Gas Requirements

30 cc/min of helium or nitrogen

Physical Properties of Sample at Entry to Sample System

2 to 5 GPM (7.6 to 18.9 l/min) of sample at a minimum pressure of 35 PSIG (2.4 bar), maximum pressure of 300 PSIG (20 bar). The sample temperature should be maintained between 33 and 122°F (1 and 50°C). The maximum particulate loading should not exceed 1% particulate. For sample outside of these conditions, Applied Automation will offer an alternate sample system.

Materials of Construction

Sample wetted parts are 300 series stainless, Teflon, Viton A, Borosilicate. The sparger cabinet has a stainless steel liner, and Swagelok fittings are used in the system.

Sample Streams

Maximum of 4 streams.

Detector

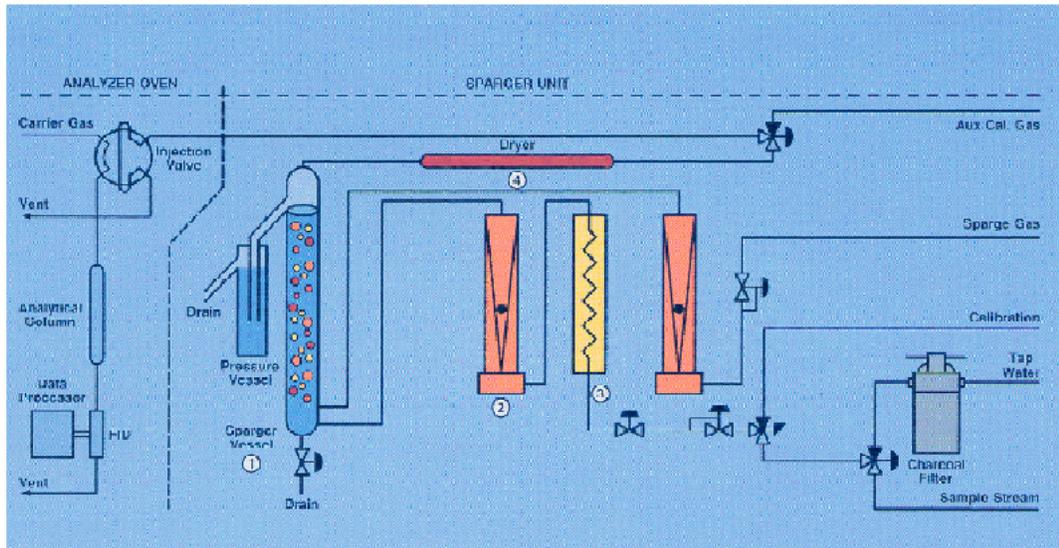
Flame ionization detector

Response Time

t_{90} = 12 minutes

Measurement Specifications

The reproducibility with benzene at 100 ppb is less than 3.4%. The linearity over a range of 1-600 ppb is +5%.



For more information contact:

Siemens Applied Automation
500 W. Highway 60
Bartlesville, OK 74003
Phone: 918-662-7000
Fax: 918-662-7052

7005192-001 08/02

Additional information obtained via email:

(from Ulrich K. Gokeler Ulrich.Gokeler@siemens.com)

ANALYZER MAINTENANCE:

Assuming the analyzer is an on-line process gas chromatograph, typical maintenance involves

1. Confirm retention time stability (during mandatory calibration)
2. Validate and calibrate analyzer response (during mandatory calibration)
3. Maintain injection valve: Depending on the actual valve design, diaphragm, rotary or slider valve, the entire valve or part of the valve has to be exchanged. Due to the clean sample injected, the recommended period is somewhere in the 12 month frequency. Depending on the valve, the technician and to stabilize the analyzer again, I would estimate a few hours off-line time.
4. Column Switching: The column switching valves essentially are affected almost as much as the injection valve, with about the same maintenance frequency and off-line time.
5. Analytics: Assuming that there is no excessive water carry over, the separation columns should be good for in excess of 2 years. Exchanging columns and setting up the system last about 1 day.
6. Detector & Electronics: No maintenance required

SAMPLE EXTRACTION MAINTENANCE:

Any extraction system is affected by the type of water and the environmental condition it is subject to. It can be expected that chlorinated cooling tower water generates less biological impurities such as algae. On the other hand chlorinated water has a more corrosive impact on all materials.

1. El-Paso Sparger: Due to the large exposed surface area inside the sparging vessel and because the very large surface of the beryl saddles, build-up of organic or inorganic material is expected. Initial tests in progress by users have confirmed that fear. At this point of time it is expected that the El-Paso sparger may have to be cleaned as often as 1x/week to 1x/month. Furthermore, experience has shown that the flowmeter used are especially subject to buildup for organic/inorganic material and consequently the floats will indicate incorrect reading after a few days already. Wrong flows have a direct impact on sparging efficiency. Cleaning and putting it back into service does not appear to be feasible because an estimated off-line time of several hours combined with the frequency really cuts quickly into the 95% availability. Therefore a redundant system is needed with one sparger in operation and one sparger clean sparger on standby. With the present El-Paso sparger design and as part of the maintenance activities also the tubing, flowmeters and overflow vessels have to be cleaned or exchanged. This design is a major maintainable item. Automatic rinsing with a solvent seems not be feasible because the large solvent quantities necessary.

2. Compact Sparger: A much more compact sparger design that has been used for such applications over the last 15 years seems a much better configuration. With only about 10" of water column and 1" diameter, the water volume flow is much less (50 cc/min) and the exposed surface are much smaller. Also the internal volume is not filled with material such as the beryl saddles. The sparging gas is introduced through a frit and therefore enters the water as tiny bubbles already. Furthermore, the sparging vessel has an automatic valve that permits the frequent emptying of the entire vessel in order to purge accumulated particulates, leafs..... from the vessel. Such a small sparger can be rinsed automatically and periodically using an appropriate solvent and an appropriate frequency. At best there is a loss of one analysis. Additional maintenance is typically only necessary every 2-3 month (water dependent).

CALIBRATION:

EXTRACTION SYSTEM:

Due to the volatility of the target components it is hardly possible to generate a representative and reproducible standard in water at the quantities required in the field. Consequently, as it is described, the analyzer is calibrated with a gas standard assuming that the extraction systems efficiency remains constant or that the preventative maintenance activities ensure that efficiency. As mentioned before that impacts the 95% on-line time, the costs of the operator and still does not guarantee correct functionality because there is no direct control.

By concentrating on the HRVOC's only, there is a good chance that a specific component can be used for continuous validation. Let's assume at a specific cooling tower i-Butane is never present. By continuously permeating a small amount of i-Butane into the sparging gas, i-Butane is present at a certain concentration all the time. Consequently, by measuring i-Butane and monitoring the quantity measured, it can be judged with certainty that the extraction systems functionality and efficiency is ensured. This technique has been used before and can be applied to any extraction system whether it is a sparger or membrane extraction design. By applying this technique, the true extraction efficiency is determined, can be taken into consideration and it improves validity of the measured data. Furthermore, even if the efficiency is changing, the change can be taken into consideration.

CHROMATOGRAPH:

On the other hand, for the chromatograph there is no need to calibrate daily and check linearity every 3 month. This does not give any credit to today's on-line process gas chromatographs and, to a lesser extent to the continuous FID analyzers at all. Even in critical process applications, the analyzer may be validated daily, but typically no more often than once or twice a week. Furthermore, even if multiple components are measured, often only a few of the components are validated and if they have not changed neither of them nor all the other components will be check or corrected. The reason is very simple. The linearity or sensitivity of specific components does not change individually. Almost all the time all components remain stable or change together in a specific separation system. Consequently in order to simplify the procedure and to increase on-line time without any significant loss of confidence, it is completely sufficient to validate selected components only instead validating or calibrating all components with the required high frequency. Keep in mind the huge quantity of calibration standards and time necessary. And because the large number of components for the flare for example, calibration takes between 6-8 man hours if nothing goes wrong, every 3 month and every time significant maintenance is done. If selected and representative components are validated, maybe only one per analyzer and certainly cheaper calibration gases are needed. Then the validation can be done even automatically and therefore increasing on-line time. If the validation fails, an alarm requests maintenance.

Questionnaire Response H

Questionnaire for Continuous VOC Monitoring/Sampling Methods:

The University of Texas at Austin (UT) under contract to the Texas Commission on Environmental Quality (TCEQ) is performing an assessment of continuous VOC monitoring/sampling methods that can be used to analyze leaks of highly reactive VOCs from industrial cooling towers. Providing the information requested in this questionnaire will enable UT to include your system in our evaluation. It is important that we receive correct and detailed technical information about the operation and performance of this equipment so that an accurate evaluation can be made. If you have more than one instrument that can be used for this type of application, please submit a separate questionnaire for each one.

1. What is the manufacturer's name and model number for the instrument being described?

Chemilux™-Alkene-1000

2. Provide a brief description of how the instrument operates and the principles on which it is based (sampling system, sample media, detector/analyzer, data collection/analysis/reporting, etc.).

The instrument uses laser-based photoacoustic spectroscopy to measure the concentration of various target species within gas-phase samples that are continuously drawn into a sample chamber from ambient conditions. This technique uses the photoacoustic effect to guarantee ultra-sensitivity, and wavelength-switching to subtract offsets and the contributions of interfering species. Measurements of concentration are available via a standard voltage (0-5 V) or current (4-20 mA) output, and are stored on an internal media device for downloading via a network.

3. Does the instrument measure total volatile organic compounds (VOCs)? Speciated VOCs? What VOCs can be detected/quantified with this instrument and in what concentration range (ppm)? A list of compounds of special interest is provided below for reference.

High interest: benzene; ethylene; propylene; 1,3-butadiene; all butene (butylene) isomers

Medium interest: acetaldehyde; formaldehyde; all hexene isomers; isoprene; all pentene isomers; all trimethylbenzene isomers; m-,o-xylene

Moderate interest: n-,iso-butane; n-,iso-pentane, toluene

Pranalytica's Photoacoustic sensors measure speciated VOC's. The lower detection limits are listed below and four orders of magnitude linear dynamic range is available in standard models, while five orders of magnitude can be achieved as an option.

Species	Lower Detection Limit [ppm]
1,3-Butadiene	0.003
1-Butene	0.008
1-Hexene	0.010
Acetaldehyde	0.028
Benzene	0.017
cis-2-Butene	0.038
Ethylene	0.001
Formaldehyde*	0.070
Isobutane	0.256
Isobutylene	0.002
Isoprene	0.002
n-butane	0.077
n-pentane	0.084
Propylene	0.004
Toluene	0.057
trans-2-Butene	0.009
Trimethylbenzene, 1,2,4-	0.034
Trimethylbenzene, 1,3,5-	0.051
Xylene, m-	0.057
Xylene, o-	0.035
Xylene, p-	0.068

*uses a different laser

5. Does the instrument provide continuous measurements? Semi-continuous? For this purpose, continuous is defined as a minimum of one sample every 15 minutes. Identify the sampling interval. What is the response time associated with these measurements?

Measurements are continuous, with updates every few minutes. Samples are drawn continuously at 400 SCCM, and the gas transit time is <10 seconds.

6. How does the instrument achieve, determine, and assure equilibrium (steady state) during measurements?

Because measurements are conducted over short time intervals and with a steady flowing system (i.e. there are no sudden starts or stops), equilibrium in temperature, pressure, flow rate and gas composition is achieved.

7. Identify the parameters at most risk of affecting the accuracy of measurements obtained with this instrument (if possible, quantify the effect on accuracy).

Unexpected interferences introduce the highest degree of risk.

8. How is the accuracy of the method affected by environmental changes in ambient temperature, humidity, and wind? What are the environmental limitations of this equipment?

Environmental changes in humidity and wind should have no impact on this instrument. The instrument is currently designed to analyze gas samples with a temperature of -40 to 40 °C, but can be designed to handle a wider temperature range. In its existing configuration, the instrument is designed for operating ambient temperatures of 15-35 °C (this range can be extended if necessary).

9. What are the quality assurance/quality control requirements for this instrument? What calibration frequency is needed and for what parameters (e.g., flow rate, temperature, pressure, detector, etc.)? Describe the calibration method (calibration phase: air, water)?

Calibration is recommended every 6 months with varying gas-phase concentrations of the target species in scrubbed, moist room air. Calibration does not depend on any factors other than the concentration of the target species.

10. Identify a recommended preventative maintenance schedule for this instrument.

Yearly preventative maintenance is recommended.

11. Is the instrument intrinsically safe? Describe any safety features of the equipment.

Yes, automatic safety interlocks, shutoffs and fuses prevent overheating, short-circuits, and exposure to laser radiation.

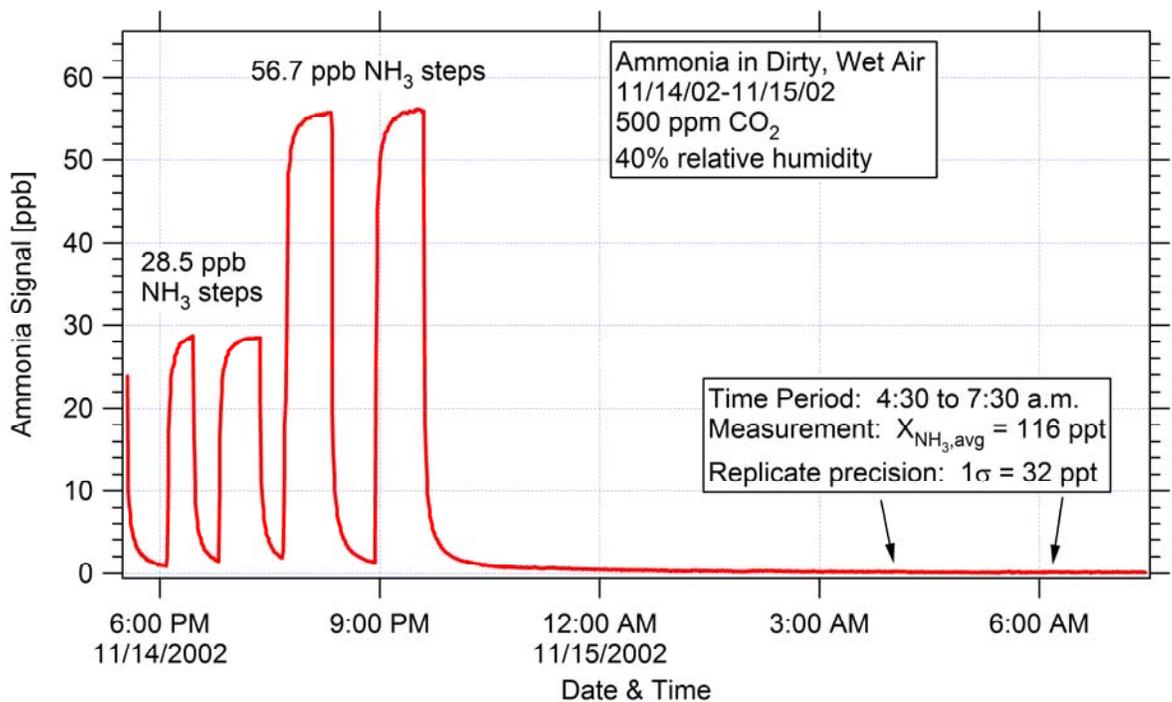
12. What is the cost of this instrument including any optional equipment that may be needed for this application?

Instrument cost for single-gas detection is \$20,000 (1 ppb sensitivity) to \$50,000 (100 ppt sensitivity) in quantity 1, with multi-gas detection available as an option. No optional equipment required. Instrument options include: graphical user interface with graphing capability and monitoring of the instrument's internal system diagnostics, and multiplexing for analyzing multiple gas streams simultaneously.

13. How many instruments are installed and currently operating (and for how long)? How many are in Texas?

Three instruments are installed and currently operating with 8 months of accumulated field time, none of which are in Texas.

14. If possible, provide samples of actual data obtained from the use of this equipment and describe actual conditions under which these data were collected (controlled laboratory experiments, field testing, etc.)



These data were obtained in laboratory conditions using controlled gas mixtures as a part of final quality control for a product shipment. Field data from the end-user will be available soon.

15. If possible, provide two references of customers who currently use this equipment in the laboratory or in the field and whom we may contact regarding the use of this equipment. Please provide name of contact, company, phone number, and email address for each reference.

These references will be available soon.

16. Additional relevant technical literature/information/comments are welcome.

A product brochure and four journal articles are attached (three are already published, one has been accepted for publication in *Applied Physics B*), which describe the methodology.

Pranalytica's Nitrolux™ Ammonia Sensor

Powered by O-Nose™ Technology

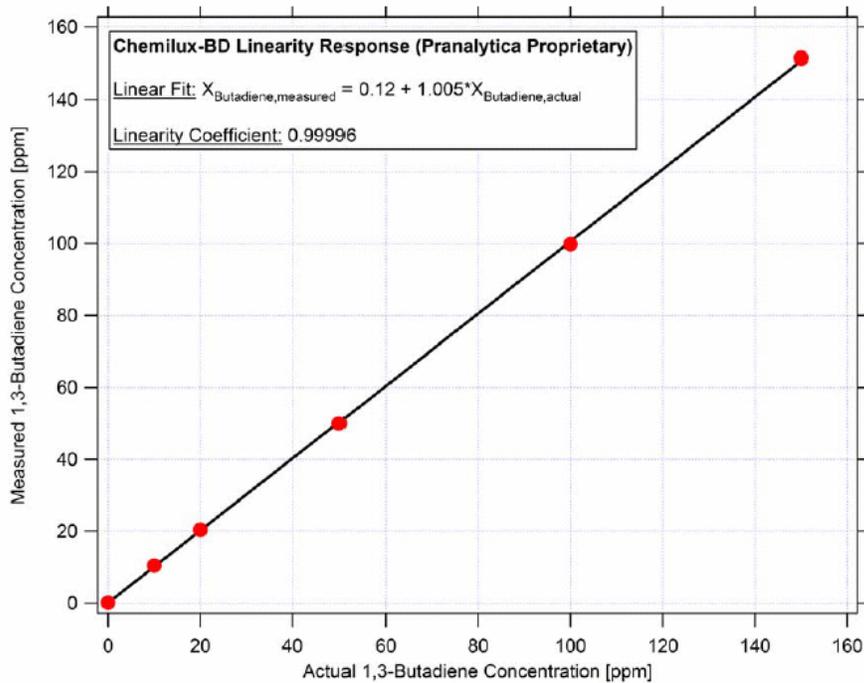


Additional information obtained via email:

(from Michael Webber webber@pranalytica.com)

Regarding long-term stability data of the calibration constant, we don't have a single encapsulated plot or dataset that I can send to you to maintain the point. However, we have several of our instruments installed in the field, the oldest of which has been in place 4+ months and has incurred no drift. Moreover, one of our instruments is nearly finished with its second month of independent testing by the EPA, and they have witnessed no drift during this time. Unfortunately, I will not be able to get data from the EPA or our customers to share with you so quickly. It will probably take me a few weeks, because these groups have their own protocols for vetting data before they are released. I'm sorry to have such an incomplete answer for you. However, I will further clarify that our product normalizes by the actual laser power with every single measurement, and therefore every single measurement is calibrated.

We are still very much interested in the application of VOC monitoring. I have also attached for your consideration measurements of VOC's (Dimethyl formamide and 1,3-butadiene) with our gas-sensing platform, to demonstrate that it has similar linearity and other positive attributes when measuring a species other than ammonia. I have also attached the pertinent spec sheets.





Pranalytica, Inc.
1101 Colorado Avenue
Santa Monica, CA 90401-3009
Tel: (310) 458-3345; Fax: (310) 458-0171

Specifications for Chemilux™ - BD (1,3-Butadiene) Analyzers

Sensitivity	Chemilux-BD: 100 ppb (parts per billion)
Measurement time	45 seconds
Sensitivity scales	Automatic and manual scale switching Chemilux-BD: 10 ppm FS to 200 ppm FS
Selectivity (freedom from interferences)	No interference from other hydrocarbons; no interference from nitrogen oxides, ammonia, hydrogen sulfide, sulfur dioxide, carbon monoxide and/or carbon dioxide
Response linearity	Better than 0.995% over the quoted operating range, stable for six months following factory calibration
Response time	Less than 1 measurement cycle (45 seconds)
Zero offset	Less than 1 ppm
Zero drift	Less than 1 ppm for six months following factory calibration
Operation	Continuous; needs no periodic maintenance
Output signals	Analog 0-5 V FS (optional at extra cost) Analog 4-20 mA FS (optional at extra cost)
Control system	Self-contained microprocessor
Data storage	On board (capacity to hold continuous data for 1 year)
Gas flow	400 scc/m
Gas handling	Direct measurement of 1,3-Butadiene in the gas sample; no preconcentration necessary
Gas inlet temperature	0 to 30 °C (wider range available; optional at extra cost)
Vacuum pump	Internal for continuous gas draw
Physical	Rack Mount: 19"W X 24" D X 10" H Weight: 75 lbs.
Power consumption	200W at 110 V, 60Hz AC
Networking	Internet ready; Can transfer data to a central site
Operating environment	10 to 30 °C; 0 – 95% RH (non-condensing); requires no special cooling.
Storage environment	-40 to 60 °C; 0 – 95% RH (non-condensing)
Special gas needs	None
Routine calibration	Not required at the quoted sensitivity; recommended recalibration every six months (recalibration service included in optional yearly service contract)
Warranty	90 days parts & labor; 1 year parts only

Appendix H

Statistical Analysis for TCEQ Work Order 55078-03-07

Section 1. The Data.

A total of 169 VOC observations were made, of which 25 were measurements of nominal “blank” water samples, and 144 were measurements of “spiked” samples. Of the 144 spiked observations, 24 were measurements of stripped residue. See the spreadsheet “Experimental Data” in **VOCspreadsheets.xls** for a complete list of the data produced for the analysis.

There were two measured variables:

- (1) **VOC** – the concentration of VOC expressed uniformly as ppbw. As anticipated, relatively few of the analyses use the VOC measurements in original scale on account of difficulty meeting the assumptions of the statistical models. The natural logarithm of VOC and the fourth root of VOC is used in some analyses. The most common form of VOC used in the analyses is Relative VOC, i.e., the ratio of VOC to the Reference level (see next point). Use of Relative VOC means that accuracy and precision are assessed in terms of percentage error, rather than absolute error.
- (2) **Reference** – a measurement of the concentration of VOC in the sample water prior to entering the experimental apparatus. This measurement is the same for all observations made at the same target level and has four distinct values in the data:

Target level	Reference
0	0
10	11
50	51.054
100	93.844
1000	983.94

For the purpose of estimating the accuracy of measurements, the Reference level is taken to represent “ground truth”, i.e., the concentration actually in the sample water – except in the case of blanks (target level = 0). Thus, accuracy is assessed relative to the reference level. However, relative accuracy (e.g., as a percentage deviation, or in logarithm scale) cannot be assessed with respect to a zero level that presumably represents the concentration in a blank sample or in a completely stripped sample. For blanks and stripped samples, accuracy is assessed in multiple ways, including a relative measure with respect to the median measured VOC (1.41 ppbw for the 25 blanks, 2.16366 ppbw for the 24 stripped samples).

The controlled variables included:

- (1) **Target level** – the intended VOC concentration level for spiked samples
- (2) **Blank** – a yes/no indicator for whether the observation was a blank sample
- (3) **Inlet** – a yes/no indicator for whether the VOC measurement was made at inlet to the apparatus
- (4) **Stripped** – a yes/no indicator for whether the VOC measurement was made of the stripped (residue) effluent from the apparatus
- (5) **Collection Method** – the method (Summa, Tedlar, VOA, FID) used to collect the sample for the observation. The singleton “FID”’s could not be used in the analysis because the lack of replicates for them precluded computation of an associated error variance.

(6) Analysis Method – the method used to analyze the concentration (Summa14, Summa18, FID). The relatively few FIDs were used in the analyses but were not combined with the Summa18s.

(7) Run – number of the run

(8) Replicate – number of the replicate

Section 2. Issues.

The TCEQ-identified issues that could be addressed with the experimental data were the following:

(1) Summary statistics

Means, standard deviations and counts are provided for VOC and RelativeVOC by collection method, blank or not, stripped or not, inlet or not, etc.

(2) Accuracy and precision

In this context, the concept of “accuracy” is distinguished from the concept of “precision.” *Accuracy* refers to how close the measurement is to the input *on average*, and *precision* refers to how much the individual measurements *spread* around their mean. The statistical model summarizes accuracy in terms of *bias*: the difference between the estimated concentration and the presumed true input concentration. Precision is summarized by the *standard deviation* of the individual measurements. In most cases, accuracy, bias, and precision, are assessed in *relative* terms, as percentage errors.

(3) Comparisons

Several comparisons of collection methods and analysis methods are possible, as summarized in the following table. Each comparison was restricted to an appropriate subset of the data.

Type of comparison	Data subset	Comparison
Collection methods	Spiked, not stripped	Summa – Tedlar
Collection methods	Stripped	VOA-Tedlar
Collection methods	Blanks	VOA-Summa
Collection methods	Inlet	VOA-Tedlar
Analysis methods	Stripped	Summa 14-Summa18

(4) Effect of VOC concentration level on results

This is assessed in terms of the contribution of VOC concentration to the model R-square in log scale and in relative scale.

(5) Stripping efficiency

The percentage of VOC remaining is assessed and compared to the theoretical ideal value of zero. In addition, the VOA and Tedlar measurements of stripped amounts are compared.

Section 3. The common statistical model.

The model reflects the design of the experiments as represented in the experimental matrix (Table B-2 of Attachment B, as ultimately amended) of the “Work Plan for TCEQ Work Order Number 55078-03-07”. There are potentially eight primary controlled factors and one uncontrolled factor. The eight controlled factors are listed in section 2 above. The uncontrolled factor is the true input concentration of VOC, taken to be the water reference value, as noted in section 2. Discussion with TCEQ personnel on August 18, 2003 identified the latter as a potential source of variation that it was desired to account for. The input concentration is to be measured for each run of the experiments, but those measurements are themselves subject to error, so the true input concentration cannot be known. To deal with this source of variation, the measured input concentration is introduced into the model as an explicit covariate. Statistical theory¹ indicates that the treatment proposed here for such models is appropriate if the error in the covariate is small in relation to the spread of the true covariate values. In fact, comparison of the reference values with the target values (see the table in section 1) suggests that the error in measuring the covariate is only a few percent. Thus the covariate error is small in relation to the spread in true covariate values, which cluster around the targeted input concentrations: 0, 10, 50, 100, and 1000 ppbw.

Not all of the possible combinations of factor levels were tested. This makes the experimental design a fractional factorial design. The addition of the uncontrolled input covariate makes the analysis of covariance an appropriate model.

Thus the fractional factorial analysis of covariance (ANACOVA) is a natural statistical model for this project. The mathematical form of this model, as adapted to the requirements of this project, is as follows:

$$Y_i = \mu + \boldsymbol{\beta}' \cdot \mathbf{1} + \delta x_i + \varepsilon_i$$

- Y_i is the VOC concentration value for observation i . For most analyses, this value was the *relative* VOC, i.e., the ratio of measured VOC to presumed ground truth (as measured by the VOC Reference value). An exactly accurate VOC measurement has a relative VOC of 1.000. Relative VOC measurements are of especial use because the difference between two relative VOC measurements expresses their difference as a percent of ground truth. Some analyses use Y_i as the natural logarithm of measured VOC or a power of measured VOC. Few analyses use Y_i as ordinary measured VOC because the modeling assumptions are not satisfied, in most cases, for this form.
- μ is the intercept for the model
- $\boldsymbol{\beta}$ is a vector of up to eight coefficients, corresponding to the eight control variables. $\mathbf{1}$ is a corresponding vector of ones.
- δ is the coefficient of the covariate (Reference).
- x_i is the value of the covariate (Reference) for observation i .
- ε_i the amount by which the observed VOC for observation i differs from the model prediction. ε_i is also called residual error.

For some of the analyses it was appropriate to omit certain of the predictor variables and/or to restrict the portion of the data used for the analyses. For example, in analyzing the blanks, it was inappropriate to use the spiked data and inappropriate to use the Spiked and Target variables,

¹ For example, Draper and Smith, Applied Regression Analysis (2nd Ed.), pp. 122-125.

neither of which varied within the blank data. In this example, the model modifications are motivated by both project and statistical considerations.

Section 4. Analyses.

Validation of the model.

The model is validated by testing its assumptions against the data measurements that are generated. The assumptions are:

1. The true model is linear in expectation: $E(Y_i) = \mu + \beta' \cdot \mathbf{1} + \delta x_i$.
2. The residual variance does not depend on any factor level.
3. The residuals are independent.
4. The residuals are normally distributed.

Standard statistical tests of misspecification are available to check each assumption. Techniques also exist to fix many problems that may arise.

Model validation is basically a check to see that the model has extracted all of the structure from the data. The signal is separated from the noise, and the noise is checked to be sure that no signal remains in it. This is accomplished by estimating all parameters (the signal), then calculating the difference (noise) between model estimates and the actual data. These differences are called residuals, or errors. Then the residuals are tested to see if they are a normal white noise process (assumptions 1-4 above).

I discuss these assumptions in reverse order:

The models do not pass the normal assumption (4). However, this is not a serious problem as long as inference is confined to groups of observations and is not extended to individual observations. That is the situation here. The ANACOVA procedure is rather robust to departures from normality for the inferences desired in this study. The Central Limit Theorem applies when data are as numerous as they are here.

Validation of independence (3) is difficult when the residuals lack a time dimension or some other variable to correlate with, in view of the fact that the residuals are by construction uncorrelated with all of the predictor variables. Generally, the validation of independence for essentially cross-sectional data such as these proceeds by qualitative considerations. Here, each observation was subjected to a measurement process that was applied independently (in operational terms) each time a measurement was made, even if some samples may have come from the same physical water and/or air supply. Great pains were taken to eliminate the possibility of physical cross-contamination of samples. Thus, we argue on qualitative grounds that the data may be regarded as independent.

As expected, the residual variability (2) was not the same at all target levels. When the VOC data were analyzed in original scale, the higher the spiking, the larger the residual variability in absolute terms. This heteroscedasticity problem was anticipated. A priori it was hoped that applying the logarithm transformation to the data could address the problem. However, analyzing the VOC measurements in natural log scale failed to fix the problem: In log scale, the residual variability was smaller at high concentrations than at lower. This suggested that the log transformation over-corrected the problem and pointed toward a power transformation as a solution. Indeed, analyzing the fourth root of VOC (i.e., VOC to the 0.25 power) provided a satisfactory solution to the statistical issue, although it made the results more difficult to interpret. The Relative VOC (i.e., VOC \div Reference) did not suffer this problem and the Relative VOC model passed the test for homoscedasticity.

Plots of the residuals against the predicted values showed no significant problem with the linearity assumption (1) for the models checked.

Thus, the model appears to meet the assumptions in a satisfactory manner, when Y is taken as the Relative VOC or as $Y^{0.25}$. Since the latter may seem a bit unnatural, I shall use it in conjunction with the more natural log VOC model – there is little difference between the two in terms of performance, apart from the heteroscedasticity issue.

Specific statistical analyses.

Issue 1: Summary Statistics.

Table 1 in the Appendix provides means and counts for VOC and Relative VOC by target level, collection method, stripped or not, blank or not, and inlet or not. Since the counts for the groups are rather small, standard deviations for the groups are not too meaningful and are omitted. Variability of the data is addressed in issue 2. The main impression conveyed by Table 1 is that the VOC measurements tend to be lower than presumed ground truth. Compare the Mean VOC column to the Target column to see that the former is usually lower. Also the mean Relative VOC column has values mostly less than 1.0 (not meaningful for the bottom four rows of stripped data).

As expected, the factors RUN and REPLICATE are statistically insignificant predictors. Table 3a (log scale), Table 3b (fourth root scale – which meets the model assumptions), and Table 3c (Relative VOC – which also meets the model assumptions) show that the potential factors RUN and REPLICATE do not contribute significantly to the explanatory power of the model. Therefore, these two variables are dropped from subsequent analyses discussed below. Their explanatory power and degrees of freedom are absorbed back into the error structure. The models that result from dropping the RUN and REPLICATE factors continue to meet the model assumptions, as discussed previously in this section (for the fourth root transformation and Relative VOC).

Models using logs and Relative (percentage) VOC for the spiked data do not work well with the parts of the data set for which VOC measurements “should” be approximately zero – namely, the blank data and the stripped data. Therefore, we distinguish three disjoint subsets of the data and analyze each separately: the blank data, the stripped data, and the spiked data that are not stripped.

Issue 2: Accuracy and Precision.

Accuracy and precision are assessed separately for spiked, blank, and stripped data. The difference between a measured value of VOC and the true value of VOC can be broken down into two parts: bias and variability, which are interpreted as accuracy and precision. Bias is defined as systematic over or under-estimation. To estimate bias and precision, we first run an appropriate model to get estimates of VOC (i.e., $E(Y_i)$). Ground truth is provided by Reference, in most cases. So bias of an individual measurement is estimated as the mean of the model prediction – ground truth. Precision is variability of the measurement around the estimated VOC. So $measured\ VOC - truth =$

$$(prediction - truth) + (measured\ VOC - prediction) = Bias + Precision.$$

Overall bias is estimated as the mean of $(prediction - truth)$; overall precision is estimated as the *standard deviation of measured VOC*.

Table 4 shows one of the ANOVA models used to get the predictions used in the calculations of bias and precision.

Table 5 shows the bias and precision estimates for spiked, blank and stripped data. For each method, the yellow highlighting shows estimated bias, the blue highlighting shows estimated precision. In Table 5a for the spiked data, we see that the summa collection method results in a systematic underestimate of “true” VOC by 3.86%, on average. Tedlar underestimates by 13.21%, on average. And VOA by 49.18%. Also, in Table 5a, the summa data are the most precise, varying by about 8.81% from their mean, on average. The Tedlar and VOA data are less precise.

In Table 5b for blanks, the units are in original scale (ppbw). The summa data have lower bias than the VOA data, whether ground truth is taken to be the median VOC (“EstBias”) or zero (“AltEstBias”). Summa is also more precise.

In Table 5c for stripped data, the units are also in original scale (ppbw). The Tedlar measurements have lower bias and are more precise than the VOA measurements.

Issue 3: Comparisons.

Table 6a shows the results for comparing summa and tedlar collection methods for spiked data that are not stripped and that come from the outlet rather than inlet. For this analysis, the data set was further restricted by omitting the inlet data. The reasons are that half of the inlet measurements are VOA, which the accuracy and precision analysis of issue 2, above, shows are subject to considerable bias and imprecision; whereas none of the outlet measurements are VOA. Moreover, measurement at outlet corresponds more closely to production use of the apparatus. If inlet measurements are included, then the magnitude of the summa-tedlar difference remains very similar (at -.1508) although the significance of the difference is considerably attenuated ($p = 0.1075$). Here, summa collection averages about 16.12% of ground truth below tedlar collection, and this difference is statistically significant ($p < 0.0001$).

Table 6b shows the results for comparing Method TO-14A and Method 18 for spiked data that are not stripped. Here, Method TO-14A analysis averages about 3.04% of ground truth above Method 18 collection, and this difference is not statistically significant ($p = 0.6967$). If the data are further restricted by excluding VOA-collected samples, as for Table 6a, then the difference between Method TO-14A and Method 18 narrows slightly and the significance remains about the same.

Table 6c shows the results for comparing VOA and Tedlar collection methods for spiked data that are not stripped, taken at inlet only. Here, VOA data average 31.69% of ground truth below Tedlar data, and this difference is statistically significant ($p = 0.0025$).

Table 6d shows the results for comparing VOA and Summa collection methods for blanks. Since all inlet measurements for blanks are VOA and all outlet measurements for blanks are Summa, then this is also a test of inlet – outlet differences. Original scale (ppbw) is used without transformation because of the difficulty of applying log and relative measures when the presumed ground truth is essentially zero. Here, VOA data average 2.2997 ppbw more than Summa data, and this difference is statistically significant ($p = 0.0386$) at the usual 0.05 significance level.

Issue 4: Effect of VOC concentration level on results.

The concentration level of VOC explains a substantial portion of the variation in VOC measurements. Table 7a shows the output of a model for spiked, non-stripped VOC in the fourth root form (which meets the modeling assumptions, as discussed above). The model has an extremely high R-square of 97.8642%. Concentration level (in the form of Reference level –

actually, the fourth root of Reference) is the controlling factor in the explanatory power and contributes $185.75474 / 194.3983413 = 95.554\%$ of explanatory power by itself. This is a common sense finding, as it says that the level of VOC that is measured depends primarily on how much VOC is in the medium to begin with. Substantially the same conclusion holds for the model with VOC in the more familiar logarithm form.

The model for Table 7a has concentration level as an explicit predictor on the right-hand-side of the model equation. When the form of VOC is changed to Relative VOC, then concentration level essentially moves to the left-hand-side of the model equation to become part of the response (VOC / Reference). If the concentration is then reinserted on the right-hand-side as a predictor, it would be desirable that it not have much effect on the relative response. It does not. Table 7b shows the result. The predictors explain 36.36% of the variation in Relative VOC measurements, with the Reference concentration explaining only $0.0146085 / 9.8730431 = 0.148\%$ by itself.

Issue 5: Stripping efficiency.

Only the 24 stripped observations were used to address the issue of stripping efficiency. Table 8a shows that stripping overall reduced VOC to 2.1834% of ground truth. That is, stripping successfully removed 97.8166% of the VOC present in the sample. But stripping did not reduce VOC to zero. The T-test of the hypothesis that stripping does reduce it to zero, on average, is rejected with a p-value < 0.0001 .

The stripping efficiency of the Tedlar and VOA collection methods was also compared. Table 8b shows the results. On average, VOA left about 1.070476 percent more of ground truth VOC than did the Tedlar collection method. This difference is statistically significant ($p = 0.0068$).

Note on Statistical Power and Confidence Intervals

Section 4 reports the results of five tests of statistical hypotheses that compare methods: Summa – Tedlar collection differences at outlet, Method 14 – Method 18 analysis differences, VOA – Tedlar collection differences at inlet, VOA-Summa collection differences for blanks (see Issue 3 above), and VOA – Tedlar stripping differences (see Issue 5 above). Tables for the approximate estimated statistical power of these tests are provided in the spreadsheet “Statistical Power” of **VOCspreadsheets.xls**. The null hypothesis for each test is $H_0: \text{mean difference} = 0$. The significance level of each test is set to the customary 0.05 to determine the rejection region for the test, which consists of both tails of the null hypothesis distribution of the mean difference estimator. That is, the rejection region consists of test values lying outside of the acceptance interval ($-1.96 * \text{standard error of mean difference estimator}$, $+1.96 * \text{standard error of mean difference estimator}$). The normal distribution is used as an approximation to the distribution of the mean difference estimator, rather than the slightly more accurate T distribution approximation (the T distribution acceptance interval would be at most a few percent wider). The sample standard error is used as an approximation to the unknown true standard error of the mean difference estimator. The “Statistical Power” spreadsheet is provided with the formulas so that the significance level could be changed by simply typing a new value into the appropriate yellow cell, and new power tables will dynamically regenerate. The tabled power values provide the approximate estimated probability of rejecting the null hypothesis of no difference when the true difference between methods is as given in the column “Posited True Separation” in the units

of the response variable (percent of ground truth for all comparisons except for VOA-Summa blanks).

Example: Suppose that we are testing whether the Summa and Tedlar collection methods are the same for non-stripped spiked outlet data (cf. Table 6a) with the significance level set at 0.05. Suppose that Summa and Tedlar actually differ by 0.099 (i.e., they actually differ by 9.9% of ground truth). Then cell C45 shows that the estimated power is 0.95. That is, the test has a 95% chance of (correctly) rejecting the null hypothesis of no difference.

Correspondingly, approximate estimated confidence intervals for these five differences are provided in the spreadsheet “Confidence Intervals” of **VOCspreadsheets.xls**. The computations show 95% intervals. However, the confidence percentage can be varied by typing a different number in the appropriate yellow cell. As for the power computations, the confidence intervals use the normal distribution rather than the slightly more accurate T distribution, and use the sample standard error as an approximation to the unknown true standard error of the mean difference estimator.

Example: An approximate 95 percent confidence interval for the difference between Summa and Tedlar collection methods for non-stripped spiked outlet data is (-0.1075, -0.2148). That is, one can be approximately 95% confident that the Summa collection method is between 10.75% and 21.48% of ground truth below the Tedlar collection method, on average.

Table 1: Means and Counts for VOC and Relative VOC Variables

Target	Mean VOC	Mean Relative VOC	Count	Collection Method	Stripped	Blank	Inlet
0	2.83	2.00658	16	VOA	No	Yes	Yes
0	0.53	0.37556	9	summa	No	Yes	No
10	9.02	0.82030	3	FID	No	No	No
10	2.40	0.21818	6	VOA	No	No	Yes
10	12.15	1.10455	6	summa	No	No	No
10	12.12	1.10152	6	tedlar	No	No	Yes
50	35.36	0.69253	3	FID	No	No	No
50	17.89	0.35048	6	VOA	No	No	Yes
50	41.91	0.82096	15	summa	No	No	No
50	50.14	0.98211	9	tedlar	No	No	No
50	37.48	0.73407	6	tedlar	No	No	Yes
100	40.55	0.43211	3	FID	No	No	No
100	89.86	0.95755	6	VOA	No	No	Yes
100	91.92	0.97954	15	summa	No	No	No
100	67.90	0.72352	6	tedlar	No	No	Yes
1000	293.06	0.29785	3	FID	No	No	No
1000	498.44	0.50657	6	VOA	No	No	Yes
1000	1010.04	1.02653	15	summa	No	No	No
1000	729.36	0.74127	6	tedlar	No	No	Yes
50	2.00	0.03919	6	tedlar	Yes	No	No
100	2.14	0.02279	6	tedlar	Yes	No	No
1000	17.74	0.01803	6	VOA	Yes	No	No
1000	7.21	0.00732	6	tedlar	Yes	No	No

Table 2: Differences among Runs for Spiked Data that are not Stripped

Run number	N Obs	Variable	Label	N	Mean	Std Dev	Minimum	Maximum
1	36	RelativeVOC	VOC / water reference	36	0.7715614	0.2723458	0.2181818	1.2272727
		LogVOC	Natural logarithm of VOC	36	4.2196380	1.7325241	0.8754687	6.8679810
2	36	RelativeVOC	VOC / water reference	36	0.8421288	0.2542352	0.2181818	1.1764401
		LogVOC	Natural logarithm of VOC	36	4.3293460	1.6907760	0.8754687	7.0540579
3	36	RelativeVOC	VOC / water reference	36	0.8827133	0.3698259	0.2181818	2.0636364
		LogVOC	Natural logarithm of VOC	36	4.3499472	1.6137078	0.8754687	6.8675828

Table 3a: Significance of RUN and REPLICATE for Spiked Data that are not Stripped (log scale)

Dependent Variable: LogVOC Natural logarithm of VOC					
Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	10	287.0725502	28.7072550	292.03	<.0001
Error	97	9.5353035	0.0983021		
Corrected Total	107	296.6078537			

R-Square 0.967852 Coeff Var 7.292038
 Root MSE 0.313532 LogVOC Mean 4.299644

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Target	3	276.3683690	92.1227897	937.14	<.0001
Inlet	1	6.4361440	6.4361440	65.47	<.0001
CollectionMethod	2	3.8942856	1.9471428	19.81	<.0001
Run	2	0.3532891	0.1766445	1.80	0.1713
Replicate	2	0.0204625	0.0102313	0.10	0.9013

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Target	3	262.2732821	87.4244274	889.34	<.0001
Inlet	1	0.8347264	0.8347264	8.49	0.0044
CollectionMethod	2	3.9072596	1.9536298	19.87	<.0001
Run	2	0.3532891	0.1766445	1.80	0.1713
Replicate	2	0.0204625	0.0102313	0.10	0.9013

Parameter		Estimate	Standard Error	t Value	Pr > t
Intercept		6.694994677	0.13754728	48.67	<.0001
Target	10	-4.703656361	0.09675797	-48.61	<.0001
Target	50	-3.162336589	0.08533251	-37.06	<.0001
Target	100	-2.238201355	0.08533251	-26.23	<.0001
Target	1000	0.000000000	.	.	.
Inlet	No	0.400813797	0.13754728	2.91	0.0044
Inlet	Yes	0.000000000	.	.	.
CollectionMethod	VOA	-0.554215495	0.09050879	-6.12	<.0001
CollectionMethod	summa	-0.187465040	0.12491400	-1.50	0.1367
CollectionMethod	tedlar	0.000000000	.	.	.
Run	1	-0.130309218	0.07390012	-1.76	0.0810
Run	2	-0.020601161	0.07390012	-0.28	0.7810
Run	3	0.000000000	.	.	.
Replicate	1	0.047500584	0.10750045	0.44	0.6596
Replicate	2	0.046026474	0.10750045	0.43	0.6695
Replicate	3	0.000000000	.	.	.

Table 3b: Significance of RUN and REPLICATE for Spiked Data that are not Stripped (Fourth root scale)

Dependent Variable: root25VOC		4th root of VOC			
Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	10	190.9106823	19.0910682	530.97	<.0001
Error	97	3.4876590	0.0359552		
Corrected Total	107	194.3983413			

R-Square Coeff Var Root MSE root25VOC Mean
 0.982059 5.942189 0.189619 3.191058

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Target	3	186.1329923	62.0443308	1725.60	<.0001
Inlet	1	3.4747930	3.4747930	96.64	<.0001
CollectionMethod	2	1.1662970	0.5831485	16.22	<.0001
Run	2	0.1362635	0.0681317	1.89	0.1559
Replicate	2	0.0003365	0.0001682	0.00	0.9953

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Target	3	177.2792024	59.0930675	1643.52	<.0001
Inlet	1	0.4373976	0.4373976	12.17	0.0007
CollectionMethod	2	1.1664033	0.5832017	16.22	<.0001
Run	2	0.1362635	0.0681317	1.89	0.1559
Replicate	2	0.0003365	0.0001682	0.00	0.9953

Parameter		Estimate	Standard Error	t Value	Pr > t
Intercept		5.297933117	B 0.08318629	63.69	<.0001
Target	10	-3.618360222	B 0.05851760	-61.83	<.0001
Target	50	-2.910716234	B 0.05160767	-56.40	<.0001
Target	100	-2.290705335	B 0.05160767	-44.39	<.0001
Target	1000	0.000000000	B .	.	.
Inlet	No	0.290140787	B 0.08318629	3.49	0.0007
Inlet	Yes	0.000000000	B .	.	.
CollectionMethod	VOA	-0.306108638	B 0.05473820	-5.59	<.0001
CollectionMethod	summa	-0.081623740	B 0.07554589	-1.08	0.2826
CollectionMethod	tedlar	0.000000000	B .	.	.
Run	1	-0.069656738	B 0.04469355	-1.56	0.1224
Run	2	0.010322478	B 0.04469355	0.23	0.8178
Run	3	0.000000000	B .	.	.
Replicate	1	0.005918590	B 0.06501447	0.09	0.9277
Replicate	2	0.003660216	B 0.06501447	0.06	0.9552
Replicate	3	0.000000000	B .	.	.

Table 3c: Significance of RUN and REPLICATE for Spiked Data that are not Stripped (Relative VOC scale)

Dependent Variable: RelativeVOC VOC / water reference					
Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	10	4.53460010	0.45346001	8.24	<.0001
Error	97	5.33844300	0.05503549		
Corrected Total	107	9.87304310			

R-Square Coeff Var Root MSE RelativeVOC Mean
 0.459291 28.19213 0.234596 0.832134

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Target	3	0.36126907	0.12042302	2.19	0.0943
Inlet	1	2.59145600	2.59145600	47.09	<.0001
CollectionMethod	2	1.35049291	0.67524646	12.27	<.0001
Run	2	0.22777941	0.11388971	2.07	0.1318
Replicate	2	0.00360270	0.00180135	0.03	0.9678

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Target	3	0.72604498	0.24201499	4.40	0.0060
Inlet	1	0.46922817	0.46922817	8.53	0.0044
CollectionMethod	2	1.35392231	0.67696115	12.30	<.0001
Run	2	0.22777941	0.11388971	2.07	0.1318
Replicate	2	0.00360270	0.00180135	0.03	0.9678

Parameter		Estimate	Standard Error	t Value	Pr > t
Intercept		0.8695694890 B	0.10291817	8.45	<.0001
Target	10	0.0261408698 B	0.07239804	0.36	0.7188
Target	50	-.1504916419 B	0.06384907	-2.36	0.0204
Target	100	0.0701673151 B	0.06384907	1.10	0.2745
Target	1000	0.0000000000 B	.	.	.
Inlet	No	0.3005125676 B	0.10291817	2.92	0.0044
Inlet	Yes	0.0000000000 B	.	.	.
CollectionMethod	VOA	-.3168958555 B	0.06772216	-4.68	<.0001
CollectionMethod	summa	-.1537089133 B	0.09346546	-1.64	0.1033
CollectionMethod	tedlar	0.0000000000 B	.	.	.
Run	1	-.1111519484 B	0.05529491	-2.01	0.0472
Run	2	-.0405845743 B	0.05529491	-0.73	0.4647
Run	3	0.0000000000 B	.	.	.
Replicate	1	0.0196801514 B	0.08043598	0.24	0.8072
Replicate	2	0.0196132299 B	0.08043598	0.24	0.8079
Replicate	3	0.0000000000 B	.	.	.

Table 4: ANOVA Model for Assessing Accuracy and Precision of Spiked Data that are not Stripped (Relative VOC scale)

Dependent Variable: RelativeVOC VOC / water reference					
Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	6	4.30321798	0.71720300	13.01	<.0001
Error	101	5.56982511	0.05514678		
Corrected Total	107	9.87304310			

R-Square	Coeff Var	Root MSE	RelativeVOC Mean
0.435855	28.22062	0.234834	0.832134

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Target	3	0.36126907	0.12042302	2.18	0.0946
Inlet	1	2.59145600	2.59145600	46.99	<.0001
CollectionMethod	2	1.35049291	0.67524646	12.24	<.0001

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Target	3	0.72861034	0.24287011	4.40	0.0059
Inlet	1	0.47639645	0.47639645	8.64	0.0041
CollectionMethod	2	1.35049291	0.67524646	12.24	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Summa-Tedlar	-0.15079829	0.09286429	-1.62	0.1075

Parameter		Estimate	Standard Error	t Value	Pr > t
Intercept		0.8382735111 B	0.06245444	13.42	<.0001
Target	10	0.0275961802 B	0.07224718	0.38	0.7033
Target	50	-.1504916419 B	0.06391359	-2.35	0.0205
Target	100	0.0701673151 B	0.06391359	1.10	0.2749
Target	1000	0.0000000000 B	.	.	.
Inlet	No	0.2943274983 B	0.10013979	2.94	0.0041
Inlet	Yes	0.0000000000 B	.	.	.
CollectionMethod	VOA	-.3168958555 B	0.06779060	-4.67	<.0001
CollectionMethod	summa	-.1507982925 B	0.09286429	-1.62	0.1075
CollectionMethod	tedlar	0.0000000000 B	.	.	.

Table 5a: Accuracy and Precision for Spiked Data that are not Stripped, by Method of Collection (Relative VOC scale)

Collection method	N Obs	Variable	N	Mean	Std Dev	USS
VOA	24	residVOC	24	-0.0000	0.2586	1.5386
		EstBias	24	-0.4918	0.0849	5.9707
summa	51	residVOC	51	0.0000	0.0881	0.3882
		EstBias	51	-0.0386	0.0891	0.4728
tedlar	33	residVOC	33	-0.0000	0.3374	3.6431
		EstBias	33	-0.1321	0.1011	0.9029

Estimated bias is in yellow (lower is better); estimated precision is in blue (lower is better).

Table 5b: Accuracy and Precision for Blank Data, by Method of Collection (Original scale for VOC: ppbw)

Collection method	N Obs	Variable	N	Mean	Std Dev	USS
VOA	16	residVOC	16	0.0000	3.0928	143.4800
		EstBias	16	1.4193	0.0000	32.2298
		AltEstBias	16	2.8293	0.0000	128.0775
summa	9	residVOC	9	-0.0000	0.5094	2.0757
		EstBias	9	-0.8805	0.0000	6.9768
		AltEstBias	9	0.5295	0.0000	2.5237

EstBias assumes ground truth is the median measured Blank VOC (1.41).

AltEstBias assumes ground truth is 0.000.

Estimated bias is in yellow (lower is better); estimated precision is in blue (lower is better).

Table 5c: Accuracy and Precision for Stripped Data, by Method of Collection (Original scale for VOC: ppbw)

Collection method	N Obs	Variable	N	Mean	Std Dev	USS
VOA	6	residVOC	6	0.0000	11.3049	639.0087
		EstBias	6	15.5750	0.0000	1455.4921
		AltEstBias	6	17.7387	0.0000	1887.9698
tedlar	18	residVOC	18	0.0000	2.1286	77.0268
		EstBias	18	1.6182	2.4920	152.7052
		AltEstBias	18	3.7819	2.4920	363.0158

EstBias assumes ground truth is the median measured Stripped VOC (2.16366).

AltEstBias assumes ground truth is 0.000.

Estimated bias is in yellow (lower is better); estimated precision is in blue (lower is better).

Table 6a: Comparison of Summa and Tedlar Collected Data for Nonstripped Spiked Outlet Observations (Relative VOC Scale)

Dependent Variable: RelativeVOC VOC / water reference

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	4	0.49063459	0.12265865	29.07	<.0001
Error	55	0.23206607	0.00421938		
Corrected Total	59	0.72270066			

R-Square	Coeff Var	Root MSE	RelativeVOC Mean
0.678890	6.734572	0.064957	0.964527

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Target	3	0.34455549	0.11485183	27.22	<.0001
CollectionMethod	1	0.14607910	0.14607910	34.62	<.0001

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Target	3	0.48736144	0.16245381	38.50	<.0001
CollectionMethod	1	0.14607910	0.14607910	34.62	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Summa-Tedlar	-0.16115092	0.02738818	-5.88	<.0001

Parameter		Estimate	Standard Error	t Value	Pr > t
Intercept		1.187679097 B	0.03211549	36.98	<.0001
Target	10	0.078017273 B	0.03137710	2.49	0.0160
Target	50	-0.205569730 B	0.02371886	-8.67	<.0001
Target	100	-0.046989613 B	0.02371886	-1.98	0.0526
Target	1000	0.000000000 B	.	.	.
CollectionMethod	summa	-0.161150916 B	0.02738818	-5.88	<.0001
CollectionMethod	tedlar	0.000000000 B	.	.	.

Table 6b: Comparison of Summa14 and Summa18 Analysis Methods for Nonstripped Spiked Observations (Relative VOC Scale)

Dependent Variable: RelativeVOC VOC / water reference

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	5	2.88841312	0.57768262	7.95	<.0001
Error	93	6.75527028	0.07263731		
Corrected Total	98	9.64368340			

R-Square	Coeff Var	Root MSE	RelativeVOC Mean
0.299513	32.92767	0.269513	0.818500

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Target	3	0.68874256	0.22958085	3.16	0.0283
Inlet	1	2.18856454	2.18856454	30.13	<.0001
AnalysisMethod	1	0.01110602	0.01110602	0.15	0.6967

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Target	3	0.71695531	0.23898510	3.29	0.0241
Inlet	1	1.60973331	1.60973331	22.16	<.0001
AnalysisMethod	1	0.01110602	0.01110602	0.15	0.6967

Parameter	Estimate	Standard Error	t Value	Pr > t
Summa14-Summa18	0.03042206	0.07780173	0.39	0.6967

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	0.6510936363 B	0.09499272	6.85	<.0001
Target 10	0.0208357221 B	0.08469980	0.25	0.8062
Target 50	-.1504916419 B	0.07335218	-2.05	0.0430
Target 100	0.0701673151 B	0.07335218	0.96	0.3413
Target 1000	0.0000000000 B	.	.	.
Inlet No	0.3171881643 B	0.06737828	4.71	<.0001
Inlet Yes	0.0000000000 B	.	.	.
AnalysisMethod summa14	0.0304220616 B	0.07780173	0.39	0.6967
AnalysisMethod summa18	0.0000000000 B	.	.	.

Table 6c: Comparison of VOA and Tedlar Collection Methods at Inlet for Nonstripped Spiked Observations (Relative VOC Scale)

Dependent Variable: RelativeVOC VOC / water reference

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	4	1.77599331	0.44399833	3.81	0.0097
Error	43	5.00809043	0.11646722		
Corrected Total	47	6.78408374			

R-Square	Coeff Var	Root MSE	RelativeVOC Mean
0.261788	51.19272	0.341273	0.666644

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Target	3	0.57091751	0.19030584	1.63	0.1955
CollectionMethod	1	1.20507580	1.20507580	10.35	0.0025

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Target	3	0.57091751	0.19030584	1.63	0.1955
CollectionMethod	1	1.20507580	1.20507580	10.35	0.0025

Parameter	Estimate	Standard Error	t Value	Pr > t
VOA-Tedlar	-0.31689586	0.09851701	-3.22	0.0025

Parameter		Estimate	Standard Error	t Value	Pr > t
Intercept		0.7823666805	0.11014537	7.10	<.0001
Target	10	0.0359297321	0.13932409	0.26	0.7977
Target	50	-.0816440318	0.13932409	-0.59	0.5609
Target	100	0.2166134755	0.13932409	1.55	0.1273
Target	1000	0.0000000000	.	.	.
CollectionMethod	VOA	-.3168958555	0.09851701	-3.22	0.0025
CollectionMethod	tedlar	0.0000000000	.	.	.

Table 6d: Comparison of VOA and Summa Collection Methods for Blanks (Original VOC Scale --ppbw)
(Equivalent to comparing Inlet (VOA) to Outlet (Summa) measurements for blanks)

Dependent Variable: VOC Measured VOC value (ppbw)

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	1	30.4634991	30.4634991	4.81	0.0386
Error	23	145.5557481	6.3285108		
Corrected Total	24	176.0192472			

R-Square	Coeff Var	Root MSE	VOC Mean
0.173069	125.6961	2.515653	2.001377

Source	DF	Type I SS	Mean Square	F Value	Pr > F
CollectionMethod	1	30.46349910	30.46349910	4.81	0.0386

Source	DF	Type III SS	Mean Square	F Value	Pr > F
CollectionMethod	1	30.46349910	30.46349910	4.81	0.0386

Parameter	Estimate	Standard Error	t Value	Pr > t
VOA-Summa	2.29973953	1.04818881	2.19	0.0386

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	0.529543333 B	0.83855105	0.63	0.5339
CollectionMethod VOA	2.299739535 B	1.04818881	2.19	0.0386
CollectionMethod summa	0.000000000 B	.	.	.

Table 7a: Effect of VOC Concentration Level on Results: Contribution to R-square When Included in Model (Log Scale for VOC)

Dependent Variable: root25VOC 4th root of VOC

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	4	190.2464335	47.5616084	1179.90	<.0001
Error	103	4.1519078	0.0403098		
Corrected Total	107	194.3983413			

R-Square	Coeff Var	Root MSE	root25VOC Mean
0.978642	6.291737	0.200773	3.191058

Source	DF	Type I SS	Mean Square	F Value	Pr > F
root25Reference	1	185.7547400	185.7547400	4608.18	<.0001
Inlet	1	3.3654682	3.3654682	83.49	<.0001
CollectionMethod	2	1.1262253	0.5631126	13.97	<.0001

Source	DF	Type III SS	Mean Square	F Value	Pr > F
root25Reference	1	177.1554928	177.1554928	4394.85	<.0001
Inlet	1	0.2317358	0.2317358	5.75	0.0183
CollectionMethod	2	1.1262253	0.5631126	13.97	<.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	-.1076574688 B	0.06315641	-1.70	0.0913
root25Reference	0.9648125867	0.01455362	66.29	<.0001
Inlet No	0.1894347117 B	0.07900748	2.40	0.0183
Inlet Yes	0.0000000000 B	.	.	.
CollectionMethod VOA	-.3061086378 B	0.05795816	-5.28	<.0001
CollectionMethod summa	0.0155612675 B	0.07373640	0.21	0.8333
CollectionMethod tedlar	0.0000000000 B	.	.	.

Table 7b: Effect of VOC Concentration Level on Results: Remaining Contribution to R-square after Inclusion in Response (Relative Scale for VOC)

Dependent Variable: RelativeVOC VOC / water reference

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	4	3.58956137	0.89739034	14.71	<.0001
Error	103	6.28348172	0.06100468		
Corrected Total	107	9.87304310			

R-Square	Coeff Var	Root MSE	RelativeVOC Mean
0.363572	29.68165	0.246991	0.832134

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Reference	1	0.01460850	0.01460850	0.24	0.6256
Inlet	1	2.36363148	2.36363148	38.75	<.0001
CollectionMethod	2	1.21132140	0.60566070	9.93	0.0001

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Reference	1	0.01495373	0.01495373	0.25	0.6216
Inlet	1	0.17234535	0.17234535	2.83	0.0958
CollectionMethod	2	1.21132140	0.60566070	9.93	0.0001

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	0.8166116610 B	0.05324671	15.34	<.0001
Reference	0.0000297580	0.00006010	0.50	0.6216
Inlet No	0.1639784421 B	0.09755927	1.68	0.0958
Inlet Yes	0.0000000000 B	.	.	.
CollectionMethod VOA	-.3168958555 B	0.07130023	-4.44	<.0001
CollectionMethod summa	-.0290840644 B	0.09089702	-0.32	0.7496
CollectionMethod tedlar	0.0000000000 B	.	.	.

Table 8a: Efficiency of Stripping for all Stripped Data

Analysis Variable : RelativeVOC VOC / water reference

N	Mean	Std Dev	t Value	Pr > t
24	0.0218340	0.0130522	8.20	<.0001

Table 8b: Comparison of Stripping Efficiency of VOA and Tedlar Collection Methods, for all Stripped Data

Dependent Variable: RelativeVOC VOC / water reference

Source	DF	Sum of Squares	Mean Square	F Value	Pr > F
Model	3	0.00316401	0.00105467	27.96	<.0001
Error	20	0.00075429	0.00003771		
Corrected Total	23	0.00391830			

R-Square 0.807496
 Coeff Var 28.12676
 Root MSE 0.006141
 RelativeVOC Mean 0.021834

Source	DF	Type I SS	Mean Square	F Value	Pr > F
Target	2	0.00282023	0.00141012	37.39	<.0001
CollectionMethod	1	0.00034378	0.00034378	9.12	0.0068

Source	DF	Type III SS	Mean Square	F Value	Pr > F
Target	2	0.00304814	0.00152407	40.41	<.0001
CollectionMethod	1	0.00034378	0.00034378	9.12	0.0068

Parameter	Estimate	Standard Error	t Value	Pr > t
VOA-Tedlar	0.01070476	0.00354562	3.02	0.0068

Parameter	Estimate	Standard Error	t Value	Pr > t
Intercept	0.0073234767 B	0.00250713	2.92	0.0084
Target 50	0.0318708843 B	0.00354562	8.99	<.0001
Target 100	0.0154664492 B	0.00354562	4.36	0.0003
Target 1000	0.0000000000 B	.	.	.
CollectionMethod VOA	0.0107047619 B	0.00354562	3.02	0.0068
CollectionMethod tedlar	0.0000000000 B	.	.	.

Approximate Estimated Confidence Intervals for Selected Differences

Table 6a: Summa-Tedlar Collection Comparison

Estimated difference =	-0.16115
Standard error =	0.027388
Confidence percentage =	95
Upper limit =	-0.1075
Lower limit =	-0.2148

Table 6b: Summa14-Summa18 Analysis Comparison

Estimated difference =	0.030422
Standard error =	0.027388
Confidence percentage =	95
Upper limit =	0.0841
Lower limit =	-0.0233

Table 6c: VOA-Tedlar Inlet Comparison

Estimated difference =	-0.31690
Standard error =	0.098517
Confidence percentage =	95
Upper limit =	-0.1238
Lower limit =	-0.5100

Table 6d: VOA-Summa Blank Comparison

Estimated difference =	2.29974
Standard error =	1.048189
Confidence percentage =	95
Upper limit =	4.3542
Lower limit =	0.2453

Table 8b: VOA-Tedlar Stripping Comparison

Estimated difference =	0.01070
Standard error =	0.003546
Confidence percentage =	95
Upper limit =	0.0177
Lower limit =	0.0038

Appendix H - SAS Code of Statistical Analysis

```

*****;
** Data analysis for TCEQ project (Vince Torres) **;
*****;
options ls=120 ps=100 nocenter nodate nonumber;
title;

data tceq;
  input Obs Target ExperimentLevel Run $ Replicate $ Reference Blank $ Inlet $ Outlet $ Stripped $ CollectionMethod $ A
  label target = 'Target level for VOC';
  label run = 'Run number';
  label replicate = 'Replicate number';
  label reference = 'Water reference';
  label blank = 'Is the data spiked? (Y/N)';
  label inlet = 'Is the data collected at inlet? (Y/N)';
  label outlet = 'Is the data collected at outlet? (Y/N)';
  label stripped = 'Is the data stripped? (Y/N)';
  label CollectionMethod = 'Collection method';
  label AnalysisMethod = 'Analysis method';
  label VOC = 'Measured VOC value (ppbw)';
  label LogVOC = 'Natural logarithm of VOC';
  label root25VOC = '4th root of VOC';
  label RelativeVOC = 'VOC / water reference';
  label LogReference = 'Natural logarithm of reference';
  * Set water reference for all blanks = median of the 25 measured blank values *;
  if blank = 'Yes' then reference = 1.41;
  LogVOC = log(VOC);
  root25VOC = VOC**.25;
  RelativeVOC = VOC / reference;
  root25Reference = Reference**.25;
  LogReference = log(reference);
  ** Note: Inlet and Outlet are collinear;
  cards;
1 0 10 1 1 0 Yes Yes No No VOA summa14 10.7
2 0 10 1 2 0 Yes Yes No No VOA summa14 10.7
3 0 10 3 1 0 Yes Yes No No VOA summa14 2.4
4 0 10 3 2 0 Yes Yes No No VOA summa14 2.4
5 0 50 1 1 0 Yes Yes No No VOA summa14 1.94641043
6 0 50 1 2 0 Yes Yes No No VOA summa14 1.94641043
7 0 50 1 1 0 Yes No Yes No summa summa18 0.19811
8 0 50 1 2 0 Yes No Yes No summa summa18 0.19811
9 0 50 1 3 0 Yes No Yes No summa summa18 0.19811
10 0 50 3 1 0 Yes Yes No No VOA summa14 1.941956276
11 0 50 3 2 0 Yes Yes No No VOA summa14 1.941956276
12 0 100 1 1 0 Yes Yes No No VOA summa14 1.41384932
13 0 100 1 2 0 Yes Yes No No VOA summa14 1.41384932
14 0 100 1 1 0 Yes No Yes No summa summa18 0.18202
15 0 100 1 2 0 Yes No Yes No summa summa18 0.18202
16 0 100 1 3 0 Yes No Yes No summa summa18 0.18202
17 0 100 3 1 0 Yes Yes No No VOA summa14 1.411947067

```

Appendix H - SAS Code of Statistical Analysis

18	0	100	3	2	0	Yes	Yes	No	No	VOA	summa14	1.411947067
19	0	1000	1	1	0	Yes	Yes	No	No	VOA	summa14	1.410049926
20	0	1000	1	2	0	Yes	Yes	No	No	VOA	summa14	1.410049926
21	0	1000	1	1	0	Yes	No	Yes	No	summa	summa18	1.23235
22	0	1000	1	2	0	Yes	No	Yes	No	summa	summa18	1.19188
23	0	1000	1	3	0	Yes	No	Yes	No	summa	summa18	1.20127
24	0	1000	3	1	0	Yes	Yes	No	No	VOA	summa14	1.410049926
25	0	1000	3	2	0	Yes	Yes	No	No	VOA	summa14	1.410049926
26	10	10	1	1	11	No	Yes	No	No	VOA	summa14	2.4
27	10	10	1	2	11	No	Yes	No	No	VOA	summa14	2.4
28	10	10	1	1	11	No	Yes	No	No	tedlar	summa14	3.7
29	10	10	1	2	11	No	Yes	No	No	tedlar	summa14	3.7
30	10	10	1	1	11	No	No	Yes	No	summa	summa14	13.3
31	10	10	1	2	11	No	No	Yes	No	summa	summa14	13.5
32	10	10	1	1	11	No	No	Yes	No	FID	FID	8.45
33	10	10	2	1	11	No	Yes	No	No	VOA	summa14	2.4
34	10	10	2	2	11	No	Yes	No	No	VOA	summa14	2.4
35	10	10	2	1	11	No	Yes	No	No	tedlar	summa14	10.6
36	10	10	2	2	11	No	Yes	No	No	tedlar	summa14	10.4
37	10	10	2	1	11	No	No	Yes	No	summa	summa14	11.3
38	10	10	2	2	11	No	No	Yes	No	summa	summa14	11.4
39	10	10	2	1	11	No	No	Yes	No	FID	FID	9.64
40	10	10	3	1	11	No	Yes	No	No	VOA	summa14	2.4
41	10	10	3	2	11	No	Yes	No	No	VOA	summa14	2.4
42	10	10	3	1	11	No	Yes	No	No	tedlar	summa14	21.6
43	10	10	3	2	11	No	Yes	No	No	tedlar	summa14	22.7
44	10	10	3	1	11	No	No	Yes	No	summa	summa14	11.6
45	10	10	3	2	11	No	No	Yes	No	summa	summa14	11.8
46	10	10	3	1	11	No	No	Yes	No	FID	FID	8.98
47	50	50	1	1	51.05406703	No	Yes	No	No	VOA	summa14	14.96682966
48	50	50	1	2	51.05406703	No	Yes	No	No	VOA	summa14	14.85076098
49	50	50	1	1	51.05406703	No	Yes	No	No	tedlar	summa14	35.69921271
50	50	50	1	2	51.05406703	No	Yes	No	No	tedlar	summa14	35.76477763
51	50	50	1	1	51.05406703	No	No	Yes	Yes	tedlar	summa14	2.095158693
52	50	50	1	2	51.05406703	No	No	Yes	Yes	tedlar	summa14	2.095158693
53	50	50	1	1	51.05406703	No	No	Yes	No	summa	summa18	41.08207009
54	50	50	1	2	51.05406703	No	No	Yes	No	summa	summa18	40.4676276
55	50	50	1	3	51.05406703	No	No	Yes	No	summa	summa18	40.51790908
56	50	50	1	1	51.05406703	No	No	Yes	No	summa	summa14	41.08207009
57	50	50	1	2	51.05406703	No	No	Yes	No	summa	summa14	40.4676276
58	50	50	1	1	51.05406703	No	No	Yes	No	tedlar	FID	49.22107287
59	50	50	1	2	51.05406703	No	No	Yes	No	tedlar	FID	47.96497558
60	50	50	1	3	51.05406703	No	No	Yes	No	tedlar	FID	48.65365473
61	50	50	1	1	51.05406703	No	No	Yes	No	FID	FID	35.86588629
62	50	50	2	1	51.05406703	No	Yes	No	No	VOA	summa14	20.14969237
63	50	50	2	2	51.05406703	No	Yes	No	No	VOA	summa14	20.29383654
64	50	50	2	1	51.05406703	No	Yes	No	No	tedlar	summa14	36.34291933
65	50	50	2	2	51.05406703	No	Yes	No	No	tedlar	summa14	36.54471839
66	50	50	2	1	51.05406703	No	No	Yes	Yes	tedlar	summa14	1.903432524

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67	50	50	2	2	51.05406703	No	No	Yes	Yes	tedlar	summa14	1.903432524
68	50	50	2	1	51.05406703	No	No	Yes	No	summa	summa18	41.93370658
69	50	50	2	2	51.05406703	No	No	Yes	No	summa	summa18	42.09018501
70	50	50	2	3	51.05406703	No	No	Yes	No	summa	summa18	41.38045356
71	50	50	2	1	51.05406703	No	No	Yes	No	summa	summa14	41.93370658
72	50	50	2	2	51.05406703	No	No	Yes	No	summa	summa14	42.09018501
73	50	50	2	1	51.05406703	No	No	Yes	No	tedlar	FID	50.35882775
74	50	50	2	2	51.05406703	No	No	Yes	No	tedlar	FID	49.76297673
75	50	50	2	3	51.05406703	No	No	Yes	No	tedlar	FID	48.83158305
76	50	50	2	1	51.05406703	No	No	Yes	No	FID	FID	37.21856981
77	50	50	3	1	51.05406703	No	Yes	No	No	VOA	summa14	18.49011257
78	50	50	3	2	51.05406703	No	Yes	No	No	VOA	summa14	18.61040389
79	50	50	3	1	51.05406703	No	Yes	No	No	tedlar	summa14	41.52706961
80	50	50	3	2	51.05406703	No	Yes	No	No	tedlar	summa14	38.98362574
81	50	50	3	1	51.05406703	No	No	Yes	Yes	tedlar	summa14	2.004503383
82	50	50	3	1	51.05406703	No	No	Yes	Yes	tedlar	summa14	2.004503383
83	50	50	3	1	51.05406703	No	No	Yes	No	summa	summa18	43.47796983
84	50	50	3	2	51.05406703	No	No	Yes	No	summa	summa18	43.25263751
85	50	50	3	3	51.05406703	No	No	Yes	No	summa	summa18	42.19225858
86	50	50	3	1	51.05406703	No	No	Yes	No	summa	summa14	43.47797
87	50	50	3	2	51.05406703	No	No	Yes	No	summa	summa14	43.25264
88	50	50	3	1	51.05406703	No	No	Yes	No	tedlar	FID	52.3018955
89	50	50	3	2	51.05406703	No	No	Yes	No	tedlar	FID	52.46569111
90	50	50	3	3	51.05406703	No	No	Yes	No	tedlar	FID	51.70542
91	50	50	3	1	51.05406703	No	No	Yes	No	FID	FID	32.98465269
92	100	100	1	1	93.84432521	No	Yes	No	No	VOA	summa14	93.82864439
93	100	100	1	2	93.84432521	No	Yes	No	No	VOA	summa14	94.27301332
94	100	100	1	1	93.84432521	No	Yes	No	No	tedlar	summa14	76.9600743
95	100	100	1	2	93.84432521	No	Yes	No	No	tedlar	summa14	75.91139654
96	100	100	1	1	93.84432521	No	No	Yes	Yes	tedlar	summa14	2.159378863
97	100	100	1	2	93.84432521	No	No	Yes	Yes	tedlar	summa14	2.159378863
98	100	100	1	1	93.84432521	No	No	Yes	No	summa	summa18	84.05081216
99	100	100	1	2	93.84432521	No	No	Yes	No	summa	summa18	87.79935494
100	100	100	1	3	93.84432521	No	No	Yes	No	summa	summa18	85.33350657
101	100	100	1	1	93.84432521	No	No	Yes	No	summa	summa14	84.05081216
102	100	100	1	2	93.84432521	No	No	Yes	No	summa	summa14	87.79935494
103	100	100	1	1	93.84432521	No	No	Yes	No	FID	FID	45.9270862
104	100	100	2	1	93.84432521	No	Yes	No	No	VOA	summa14	84.1003687
105	100	100	2	2	93.84432521	No	Yes	No	No	VOA	summa14	83.87539203
106	100	100	2	1	93.84432521	No	Yes	No	No	tedlar	summa14	77.96171993
107	100	100	2	2	93.84432521	No	Yes	No	No	tedlar	summa14	75.67442303
108	100	100	2	1	93.84432521	No	No	Yes	Yes	tedlar	summa14	2.096311294
109	100	100	2	2	93.84432521	No	No	Yes	Yes	tedlar	summa14	2.096311294
110	100	100	2	1	93.84432521	No	No	Yes	No	summa	summa18	91.96631008
111	100	100	2	2	93.84432521	No	No	Yes	No	summa	summa18	93.16696844
112	100	100	2	3	93.84432521	No	No	Yes	No	summa	summa18	92.05222794
113	100	100	2	1	93.84432521	No	No	Yes	No	summa	summa14	91.96631008
114	100	100	2	2	93.84432521	No	No	Yes	No	summa	summa14	93.16696844
115	100	100	2	1	93.84432521	No	No	Yes	No	FID	FID	37.67077876

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116	100	100	3	1	93.84432521	No	Yes	No	No	VOA	summa14	91.28986748
117	100	100	3	2	93.84432521	No	Yes	No	No	VOA	summa14	91.79442364
118	100	100	3	1	93.84432521	No	Yes	No	No	tedlar	summa14	50.39584069
119	100	100	3	2	93.84432521	No	Yes	No	No	tedlar	summa14	50.48499334
120	100	100	3	1	93.84432521	No	No	Yes	Yes	tedlar	summa14	2.160425516
121	100	100	3	2	93.84432521	No	No	Yes	Yes	tedlar	summa14	2.160425516
122	100	100	3	1	93.84432521	No	No	Yes	No	summa	summa18	98.13800942
123	100	100	3	2	93.84432521	No	No	Yes	No	summa	summa18	97.05040942
124	100	100	3	3	93.84432521	No	No	Yes	No	summa	summa18	97.13257578
125	100	100	3	1	93.84432521	No	No	Yes	No	summa	summa14	98.13800942
126	100	100	3	2	93.84432521	No	No	Yes	No	summa	summa14	97.05040942
127	100	100	3	1	93.84432521	No	No	Yes	No	FID	FID	38.0560731
128	1000	1000	1	1	983.9399668	No	Yes	No	No	VOA	summa14	415.1871843
129	1000	1000	1	2	983.9399668	No	Yes	No	No	VOA	summa14	411.2634681
130	1000	1000	1	1	983.9399668	No	Yes	No	No	tedlar	summa14	773.1369684
131	1000	1000	1	2	983.9399668	No	Yes	No	No	tedlar	summa14	776.6606793
132	1000	1000	1	1	983.9399668	No	No	Yes	Yes	VOA	summa14	3.341220226
133	1000	1000	1	2	983.9399668	No	No	Yes	Yes	VOA	summa14	3.162434375
134	1000	1000	1	1	983.9399668	No	No	Yes	Yes	tedlar	summa14	2.16689781
135	1000	1000	1	2	983.9399668	No	No	Yes	Yes	tedlar	summa14	2.16689781
136	1000	1000	1	1	983.9399668	No	No	Yes	No	summa	summa18	930.9824267
137	1000	1000	1	2	983.9399668	No	No	Yes	No	summa	summa18	961.0062943
138	1000	1000	1	3	983.9399668	No	No	Yes	No	summa	summa18	921.1421999
139	1000	1000	1	1	983.9399668	No	No	Yes	No	summa	summa14	930.9824267
140	1000	1000	1	2	983.9399668	No	No	Yes	No	summa	summa14	961.0062943
141	1000	1000	1	1	983.9399668	No	No	Yes	No	FID	FID	274.8097891
142	1000	1000	2	1	983.9399668	No	Yes	No	No	VOA	summa14	457.3902724
143	1000	1000	2	2	983.9399668	No	Yes	No	No	VOA	summa14	459.6678587
144	1000	1000	2	1	983.9399668	No	Yes	No	No	tedlar	summa14	782.9236948
145	1000	1000	2	2	983.9399668	No	Yes	No	No	tedlar	summa14	778.468112
146	1000	1000	2	1	983.9399668	No	No	Yes	Yes	VOA	summa14	23.6211484
147	1000	1000	2	2	983.9399668	No	No	Yes	Yes	VOA	summa14	23.31157004
148	1000	1000	2	1	983.9399668	No	No	Yes	Yes	tedlar	summa14	10.22285716
149	1000	1000	2	2	983.9399668	No	No	Yes	Yes	tedlar	summa14	10.12387611
150	1000	1000	2	1	983.9399668	No	No	Yes	No	summa	summa18	1157.546449
151	1000	1000	2	2	983.9399668	No	No	Yes	No	summa	summa18	1119.264489
152	1000	1000	2	3	983.9399668	No	No	Yes	No	summa	summa18	1148.942883
153	1000	1000	2	1	983.9399668	No	No	Yes	No	summa	summa14	1157.546449
154	1000	1000	2	2	983.9399668	No	No	Yes	No	summa	summa14	1119.264489
155	1000	1000	2	1	983.9399668	No	No	Yes	No	FID	FID	298.8124287
156	1000	1000	3	1	983.9399668	No	Yes	No	No	VOA	summa14	628.1628599
157	1000	1000	3	2	983.9399668	No	Yes	No	No	VOA	summa14	618.9405683
158	1000	1000	3	1	983.9399668	No	Yes	No	No	tedlar	summa14	631.6448378
159	1000	1000	3	2	983.9399668	No	Yes	No	No	tedlar	summa14	633.3366589
160	1000	1000	3	1	983.9399668	No	No	Yes	Yes	VOA	summa14	26.22818384
161	1000	1000	3	2	983.9399668	No	No	Yes	Yes	VOA	summa14	26.76767026
162	1000	1000	3	1	983.9399668	No	No	Yes	Yes	tedlar	summa14	9.236186454
163	1000	1000	3	2	983.9399668	No	No	Yes	Yes	tedlar	summa14	9.318453414
164	1000	1000	3	1	983.9399668	No	No	Yes	No	summa	summa18	959.6834093

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165	1000	1000	3	2	983.9399668	No	No	Yes	No	summa	summa18	931.4782918
166	1000	1000	3	3	983.9399668	No	No	Yes	No	summa	summa18	960.6237667
167	1000	1000	3	1	983.9399668	No	No	Yes	No	summa	summa14	959.6834093
168	1000	1000	3	2	983.9399668	No	No	Yes	No	summa	summa14	931.4782918
169	1000	1000	3	1	983.9399668	No	No	Yes	No	FID	FID	305.5724911

;;;

```
*****;
** SUMMARY STATISTICS -- Cell means and counts **;
*****;
```

```
proc sort data=tceq;
  by stripped target CollectionMethod blank inlet;
proc means data=tceq noprint;
  var VOC RelativeVOC;
  by stripped target CollectionMethod blank inlet;
  output out=outstat mean=MeanVOC MeanRelativeVOC n=nVOC nRelativeVOC;
  title 'Means and Counts';
proc print data=outstat;
  var target meanVOC meanRelativeVOC nVOC CollectionMethod stripped blank inlet ;
RUN;
```

```
*****;
** RUN and REPLICATE are not significant for non-stripped spiked measurements **;
*****;
proc means data=tceq(where=(CollectionMethod ne 'FID' and blank='No' and stripped='No'));
  var RelativeVOC logVOC;
  class run;
  title 'Run and Replicate are not significant for non-stripped spiked measurements';
RUN;
```

```
proc glm data=TCEQ(where=(CollectionMethod ne 'FID' and blank='No' and stripped='No'));
  class Target Run Replicate Blank Inlet Outlet Stripped CollectionMethod AnalysisMethod;
  model logVOC = target inlet CollectionMethod run replicate / solution;
  output out=anova1a p=predVOC r=residVOC;
  title1 'Analysis of Variance 1a: RUN and REPLICATE are not significant for non-stripped spiked measurements';
RUN;
```

```
proc plot data=anova1a;
  plot residVOC * predVOC /vpos=40 hpos=80;
RUN;
```

```
proc glm data=TCEQ(where=(CollectionMethod ne 'FID' and blank='No' and stripped='No'));
  class Target Run Replicate Blank Inlet Outlet Stripped CollectionMethod AnalysisMethod;
  model RelativeVOC = target inlet CollectionMethod run replicate / solution;
  output out=anova1b p=predVOC r=residVOC;
  title1 'Analysis of Variance 1b: RUN and REPLICATE are not significant for non-stripped spiked measurements';
RUN;
```

```
proc plot data=anova1b;
  plot residVOC * predVOC /vpos=40 hpos=80;
RUN;
```

```
** Redo Anova1a with less compressing transformation than log;* (Tedlar, inlet, level 10);
proc glm data=TCEQ(where=(CollectionMethod ne 'FID' and blank='No' and stripped='No'));
```

Appendix H - SAS Code of Statistical Analysis

```

class Target Run Replicate Blank Inlet Outlet Stripped CollectionMethod AnalysisMethod;
model root25VOC = target      inlet      CollectionMethod run replicate / solution;
output out=anova1a1 p=predVOC r=residVOC;
title1 'Analysis of Variance 1a(1): RUN and REPLICATE are not significant for non-stripped spiked measurements (root2
RUN;
proc plot data=anova1a1;
plot residVOC * predVOC /vpos=40 hpos=80;
RUN;

*****;
** ACCURACY AND PRECISION **;
*****;

** ACCURACY AND PRECISION for non-stripped spiked measurements **;
proc glm data=TCEQ(where=(CollectionMethod ne 'FID' and stripped = 'No' and blank = 'No'));
class Target Run Replicate Blank Inlet Outlet Stripped CollectionMethod AnalysisMethod;
model logVOC = target inlet      CollectionMethod / solution;
estimate 'Summa-Tedlar' CollectionMethod 0 1 -1 / E;
output out=anova2a p=predVOC r=residVOC;
title1 'Analysis of Variance 2a: ACCURACY AND PRECISION for non-stripped spiked measurements (log scale for VOC)';
RUN;
data anova2a;
set anova2a;
EstBias = predVOC - logReference;
proc means data=anova2a maxdec=4 n mean std uss;
var residVOC EstBias;
class CollectionMethod;
title1 'Anova2a: Accuracy and precision statistics for methods (log scale)';
RUN;
** Redo Anova2a with less compressing transformation than log;
proc glm data=TCEQ(where=(CollectionMethod ne 'FID' and stripped = 'No' and blank = 'No'));
class Target Run Replicate Blank Inlet Outlet Stripped CollectionMethod AnalysisMethod;
model root25VOC = target inlet      CollectionMethod / solution;
estimate 'Summa-Tedlar' CollectionMethod 0 1 -1 / E;
output out=anova2a1 p=predVOC r=residVOC;
title1 'Analysis of Variance 2a(1): ACCURACY AND PRECISION for non-stripped spiked measurements (root25 scale for VOC
RUN;
data anova2a1;
set anova2a1;
EstBias = predVOC - root25VOC;
proc means data=anova2a1 maxdec=4 n mean std uss;
var residVOC EstBias;
class CollectionMethod;
title1 'Anova2a(1): Accuracy and precision statistics for methods (root25 scale)';
RUN;

proc glm data=TCEQ(where=(CollectionMethod ne 'FID' and stripped = 'No' and blank = 'No'));
class Target Run Replicate Blank Inlet Outlet Stripped CollectionMethod AnalysisMethod;

```

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```

model RelativeVOC = target inlet          CollectionMethod / solution;
estimate 'Summa-Tedlar'  CollectionMethod    0  1  -1 / E;
output out=anova2b p=predVOC r=residVOC;
title1 'Analysis of Variance 2b: ACCURACY AND PRECISION for non-stripped spiked measurements (relative scale for VOC)
RUN;
data anova2b;
  set anova2b;
  * Note: The expected value for relative reference is reference / reference = 1 *;
  EstBias = predVOC - 1;
proc means data=anova2b maxdec=4 n mean std uss;
  var  residVOC EstBias;
  class CollectionMethod;
  title1 'Anova2b: Accuracy and precision statistics for methods (relative scale)';
RUN;

** ACCURACY AND PRECISION for Blank measurements (original scale for VOC) **;
proc glm data=TCEQ(where=(CollectionMethod ne 'FID' and stripped = 'No' and blank = 'Yes'));
  class Target Run Replicate Blank Inlet Outlet Stripped CollectionMethod AnalysisMethod;
  * Inlet and CollectionMethod are collinear, there is only one target (0) for Blanks *;
  model VOC =
  estimate 'Summa-VOA'      CollectionMethod  -1  1  / E;
  output out=anova2c p=predVOC r=residVOC;
  title1 'Analysis of Variance 2c: ACCURACY AND PRECISION for Blank measurements (original scale for VOC)';
RUN;
data anova2c;
  set anova2c;
  * Note: The expected value for relative reference is reference / reference = 1 *;
  EstBias = predVOC - Reference; * Note: Blanks use median blank as Reference;
  AltEstBias = predVOC;
proc means data=anova2c maxdec=4 n mean std uss;
  var  residVOC EstBias AltEstBias;
  class CollectionMethod;
  title1 'Anova2c: Accuracy and precision statistics for Blanks (original scale)';
RUN;

** ACCURACY AND PRECISION for Stripped (residue) measurements (original scale for VOC) **;
proc glm data=TCEQ(where=(CollectionMethod ne 'FID' and stripped = 'Yes' and blank = 'No'));
  class Target Run Replicate Blank Inlet Outlet Stripped CollectionMethod AnalysisMethod;
  * Inlet does not vary (all are No);
  model VOC = target
  estimate 'Tedlar-VOA'  CollectionMethod    -1  1  / E;
  output out=anova2d p=predVOC r=residVOC;
  title1 'Analysis of Variance 2d: ACCURACY AND PRECISION for Stripped (residue) measurements (original scale for VOC)';
RUN;
data anova2d;
  set anova2d;
  * Note: The expected value for relative reference is reference / reference = 1 *;
  EstBias = predVOC - 2.16366; * Note: Stripped measurements use median of 24 strippeds as Reference;
  AltEstBias = predVOC;

```

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```

proc means data=anova2d maxdec=4 n mean std uss;
  var residVOC EstBias AltEstBias;
  class CollectionMethod;
  title1 'Anova2d: Accuracy and precision statistics for Stripped (residue) measurements (original scale)';
RUN;

*****;
** COMPARISONS **;
*****;
** SUMMA vs TEDLAR for non-stripped spiked measurements (relative scale) - Inlet and outlet**;
proc glm data=TCEQ(where=(CollectionMethod ne 'FID' and stripped = 'No' and blank = 'No'));
  class Target Run Replicate Blank Inlet Outlet Stripped CollectionMethod AnalysisMethod;
  model RelativeVOC = target inlet      CollectionMethod / solution;
  estimate 'Summa-Tedlar'  CollectionMethod      0 1 -1 / E;
  title '3a1: SUMMA vs TEDLAR for non-stripped spiked measurements (relative scale) - Inlet and outlet';
** SUMMA vs TEDLAR for non-stripped spiked measurements (relative scale) - Outlet only **;
proc glm data=TCEQ(where=(CollectionMethod ne 'FID' and stripped = 'No' and blank = 'No' and inlet='No'));
  class Target Run Replicate Blank Inlet Outlet Stripped CollectionMethod AnalysisMethod;
  model RelativeVOC = target      CollectionMethod / solution;
  estimate 'Summa-Tedlar'  CollectionMethod      1 -1 / E;
  title '3a2: SUMMA vs TEDLAR for non-stripped spiked measurements (relative scale) - Outlet only';
** SUMMA14 vs SUMMA18 Analysis Method - including blanks**;
proc glm data=TCEQ(where=((AnalysisMethod='summa14' or AnalysisMethod='summa18') and stripped='No'));
  class Target Run Replicate Blank Inlet Outlet Stripped CollectionMethod AnalysisMethod;
  model RelativeVOC = target      inlet      AnalysisMethod / solution;
  estimate 'Summa14-Summa18'  AnalysisMethod      1 -1 / E;
  title '3b1: SUMMA14 vs SUMMA18 Analysis Method - including blanks, excluding stripped';
** SUMMA14 vs SUMMA18 Analysis Method - excluding blanks and stripped **;
proc glm data=TCEQ(where=((AnalysisMethod='summa14' or AnalysisMethod='summa18') and blank='No' and stripped='No'));
  class Target Run Replicate Blank Inlet Outlet Stripped CollectionMethod AnalysisMethod;
  model RelativeVOC = target      inlet      AnalysisMethod / solution;
  estimate 'Summa14-Summa18'  AnalysisMethod      1 -1 / E;
  title '3b2: SUMMA14 vs SUMMA18 Analysis Method - excluding blanks and stripped';
** VOA vs Tedlar at inlet - excluding blanks from error variance **;
proc glm data=TCEQ(where=(inlet='Yes' and blank='No' and stripped='No'));
  class Target Run Replicate Blank Inlet Outlet Stripped CollectionMethod AnalysisMethod;
  model RelativeVOC = target      CollectionMethod / solution;
  estimate 'VOA-Tedlar'  CollectionMethod      1 -1 / E;
  title '3c: VOA vs TEDLAR at inlet - excluding blanks from error variance';
RUN;
** VOA vs Tedlar for blanks **;
proc glm data=TCEQ(where=(blank='Yes'));
  class Target Run Replicate Blank Inlet Outlet Stripped CollectionMethod AnalysisMethod;
  * CollectionMethod and Inlet are collinear -- they test the same thing*;
  model VOC =      CollectionMethod / solution;
  estimate 'VOA-Summa'  CollectionMethod      1 -1 / E;
  title '3d: VOA vs TEDLAR for blanks (equivalent to Inlet=Yes vs Inlet=No)';
RUN;

```

Appendix H - SAS Code of Statistical Analysis

```
*****;
** Effect of VOC concentration on measured VOC result **;
*****;
proc glm data=TCEQ(where=(CollectionMethod ne 'FID' and blank='No' and stripped='No'));
  class Target Run Replicate Blank Inlet Outlet Stripped CollectionMethod AnalysisMethod;
  model logVOC = logReference      inlet      CollectionMethod / solution;
  output out=anova4a p=predVOC r=residVOC;
  title1 'Anova 4a: Effect of VOC concentration for non-stripped spiked measurements';
RUN;
proc plot data=anova4a;
  plot residVOC * predVOC /vpos=40 hpos=80;
RUN;
proc glm data=TCEQ(where=(CollectionMethod ne 'FID' and blank='No' and stripped='No'));
  class Target Run Replicate Blank Inlet Outlet Stripped CollectionMethod AnalysisMethod;
  model root25VOC = root25Reference      inlet      CollectionMethod / solution;
  output out=anova4b p=predVOC r=residVOC;
  title1 'Anova 4b: Effect of VOC concentration for non-stripped spiked measurements';
RUN;
proc plot data=anova4b;
  plot residVOC * predVOC /vpos=40 hpos=80;
RUN;
proc glm data=TCEQ(where=(CollectionMethod ne 'FID' and blank='No' and stripped='No'));
  class Target Run Replicate Blank Inlet Outlet Stripped CollectionMethod AnalysisMethod;
  model RelativeVOC = reference      inlet      CollectionMethod / solution;
  output out=anova4c p=predVOC r=residVOC;
  title1 'Anova 4c: Effect of VOC concentration for non-stripped spiked measurements';
RUN;
proc plot data=anova4c;
  plot residVOC * predVOC /vpos=40 hpos=80;
RUN;

*****;
** Stripping Efficiency **;
*****;
proc glm data=TCEQ(where=(stripped='Yes'));
  class Target Run Replicate Blank Inlet Outlet Stripped CollectionMethod AnalysisMethod;
  model RelativeVOC = target      CollectionMethod / solution;
  estimate 'VOA-Tedlar'      CollectionMethod      1      -1 / E;
  output out=anova5a p=predVOC r=residVOC;
  title1 'Anova 5a: Efficiency of stripping: Estimate VOA-Tedlar difference';
RUN;
proc plot data=anova5a;
  plot residVOC * predVOC /vpos=40 hpos=80;
RUN;
proc means data=TCEQ(where=(stripped='Yes')) n mean std t probt ;
  var RelativeVOC;
  title1 'Anova 5b: Efficiency of stripping';
RUN;
```

Appendix I

Cooling Tower Emissions Calculator (CTEC)

User Documentation

Background

The CTEC calculator is intended as a screening tool for estimating emissions of individual VOCs across a cooling tower. Estimates of emissions should be taken as approximate and the user should be aware of model limitations and assumptions before using the calculator.

This documentation provides the user with a concise summary of CTEC input requirements, CTEC output, and the major assumptions used in deriving the CTEC model. Requirements for input units are embedded directly in the Main CTEC worksheet of the CTEC calculator.

Software

The CTEC calculator was developed using Microsoft[®] EXCEL 2002. It is a spreadsheet program with cell protection so that the original equations used in the model cannot be edited.

User Input

The user must input specific information regarding the cooling tower of interest into the cells highlighted as light blue on the spreadsheet page denoted as Main CTEC. These cells correspond to rows 19-40 in column k of sheet Main CTEC. The model comes with example entries for a hypothetical cooling tower and benzene as the chemical of interest. New input is required for each specific cooling tower and target chemical application.

The “Required User Input” section contains a description of the specific entry and units that are required for proper model usage. These will be self explanatory to many, but a brief description of each entry is provided below.

Name of VOC of interest: This entry provides a means for the user to document the specific chemical used in the calculation.

Inlet concentration of VOC of interest: This entry is the concentration of the VOC of interest in water at the top of the cooling tower. It can be measured by any of a number of means, e.g., the El Paso Method. It is incumbent upon the user to determine a representative inlet concentration.

Inlet water flow rate to cooling tower: This entry corresponds to the volumetric flow rate of water at the top of the cooling tower. This value is adjusted by the CTEC calculator in each stage as evaporation occurs during water transport through the tower. Water flow rate is an important parameter affecting mass transfer phenomena in the cooling tower and is used in Onda correlations for mass transfer coefficients.

Make-up water flow rate: This entry is taken as a volumetric flow rate of make-up water used to replenish the cooling tower water stream as evaporation occurs. It is assumed for model simplification that make-up water is added on a continuous basis. The specified make-up water flow rate is used as an estimate of the continuous evaporation rate of water, which is apportioned to each stage of the cooling tower in accordance with water temperatures and corresponding water vapor pressures in each stage.

Total air to total water inlet flow ratio: The CTEC calculator is based on an assumption of cross-flow air stream, i.e., air flows at right angles to downward water flow with no air flow between cooling tower stages. This leads to a higher concentration driving force between water and air, and hence emissions, in each stage if an air-to-water flow ratio similar to that in a counter-current flow system is employed. Gas flow rate is also an important parameter that affects predictions of gas-phase mass transfer coefficients. CTEC predictions are sensitive to this entry and the user should attempt to obtain best available data for this entry.

Total height of tower (from water entry to sump): This entry is the total height of the packed section of the cooling tower, from points of water entry to exit (above the underlying sump).

Void fraction of cooling tower: This entry corresponds to the fraction of the volume of the packed section of the cooling tower that contains physical (solid) packing media. Typical values for void fraction in packed systems are greater than 0.90. The void fraction is necessary for calculations related to overall area of contact between water and adjacent air.

Cross-sectional area of cooling tower: This entry corresponds to the cross sectional area of the cooling tower perpendicular to water flow. It is a required parameter in Onda correlations for liquid and gas-phase mass transfer coefficients.

Specific surface area of packing media: This entry should be information that is available through the distributor or manufacturer of the packing media. It corresponds to the total surface area per unit volume of packing and is important in terms of prediction of the total wetted surface area within the cooling tower.

Effective diameter of packing: This entry should be information that is available through the distributor or manufacturer of the packing media. It is an important parameter for estimating both liquid and gas-phase mass transfer coefficients.

Surface area of sump: This entry corresponds to the horizontally projected area of the sump at the bottom of the cooling tower and is needed to estimate emissions from the sump.

Temperature of inlet cooling water: This entry corresponds to water that enters at the top of the cooling tower. All entries related to temperature are important, as many of the properties of air and water (e.g., density, viscosity, vapor pressure of water, liquid and gas-phase mass molecular diffusion coefficients) needed to determine mass transfer coefficients or to attribute water evaporation rates across the cooling tower are a strong function of water temperature and temperature of adjacent air.

Temperature of water at tower bottom (above sump): This entry corresponds to water that is discharged from the bottom of the packing media, immediately upstream of the underlying sump.

Temperature of water in sump: This entry corresponds to the water in the sump below the cooling tower.

Temperature of ambient air: This entry corresponds to the temperature of ambient air prior to entering the cooling tower, and is assumed to be the same for each stage of the cooling tower.

Relative humidity of ambient air: This entry corresponds to the relative humidity of ambient air prior to entering the cooling tower, and is assumed to be the same for each stage of the cooling tower. It is used in calculations to apportion evaporative emissions from the tower. However, its impact on CTEC results is relatively small.

Molecular weight of VOC of interest: This entry is required for estimating gas and liquid-phase mass transfer coefficients associated with the sump at the bottom of the cooling tower.

Henry's law constant of VOC of interest (@ 25 °C): This entry is required to calculate mass transfer between water in each stage of the cooling tower and adjacent air in the tower. It is a critical entry that has a significant impact on CTEC predictions. The user must enter a value of Henry's law constant at 25 °C; the CTEC calculator adjusts the Henry's law constant to temperatures specific to each stage of the cooling tower in accordance with an assumption that solubility changes with temperature are small relative to changes in VOC vapor pressure with temperature. The user should note that the Henry's law constant is "unitless" and corresponds to the equilibrium concentration of the chemical of interest in the GAS PHASE divided by the concentration in the AQUEOUS PHASE, where both concentrations are expressed in the same units.

Boiling point of chemical of interest: This entry is used to estimate vapor pressure changes with temperature for the VOC of interest.

Diffusion coefficient of VOC in water (@ 25 °C): The user must provide a molecular diffusion coefficient for the chemical of interest in water. This can be calculated or obtained through measurements as reported in the literature. The input value of the diffusion coefficient in water must be at 25 °C. The CTEC calculator automatically adjusts to water temperatures associated with each cooling tower stage. Values of molecular diffusion coefficients in water and air are required for estimation of liquid and gas-phase mass transfer coefficients in accordance with Onda correlations.

Diffusion coefficient of VOC in air (@ 25 °C): The user must provide a molecular diffusion coefficient for the chemical of interest in water. This can be calculated or obtained through measurements as reported in the literature. The input value of the diffusion coefficient in water must be at 25 °C. The CTEC calculator automatically adjusts to water temperatures associated with each cooling tower stage. Values of molecular diffusion coefficients in water and air are required for estimation of liquid and gas-phase mass transfer coefficients in accordance with Onda correlations.

CTEC Output

Results associated with CTEC predictions are located on Main CTEC worksheet and reside in rows 1 – 13 and columns K-N. They are highlighted in a light green color, with dark green descriptive column and row edges. The first column (denoted “Stage”) corresponds to the stage of cooling tower relative to the inlet boundary condition (stage 0). Stage 11 corresponds to the sump below the cooling tower. Thus, every calculation involves a division of the cooling tower into 10 stages (1-10). The height of each stage is the total cooling tower height divided by 10. The second column of results corresponds to the concentration (C_1) of the VOC of interest in mg/L at each stage of the cooling tower. The third column lists the predicted emission rate (E) in kg/hr at each stage of the cooling tower and the underlying sump. The fourth column corresponds to the overall percent contribution of each stage to total emissions of the VOC of interest from the cooling tower.

Total emissions in kg/hr of the VOC of interest from the entire cooling tower system (tower + underlying sump) is provided below the main results table in a single cell highlighted in yellow. Immediately below the total emissions cell is another yellow-highlighted cell that contains the overall stripping efficiency for the VOC of interest for a single pass through the cooling tower.

The user can also observe plots of the liquid concentrations and emission rates across the cooling tower by clicking on the worksheets denoted as “Plot_C_Profile” and “Plot_E_Profile”, respectively.

Model Assumptions and Limitations

The CTEC calculator is based on a large number of assumptions. The most significant assumptions are listed below:

1. The system operates under steady-state conditions.
2. The cooling tower can be treated as a series of 10 stages. With respect to both the liquid and gas phases, each stage can be treated as a well-mixed reactor. This is also true for the liquid phase of the underlying sump, allowing appropriate mass balances to be developed for each stage/sump, and each phase (water and air).
3. The cooling tower consists of packing media through which the cooling water flows.
4. The cooling water is relatively clean; matrix effects associated with dissolved organic or ionic species are negligible.
5. Onda correlations are relevant for predicting liquid and gas-phase mass transfer coefficients for each stage of the cooling tower.
6. Air flow is perpendicular to water flow (cross-flow ventilation design) with no connectivity of air between the cooling tower stages.
7. The headspace above the underlying sump is well ventilated so that the concentration of the VOC of interest is negligible above the water surface.
8. Mass transfer across the surface of the sump is estimated based on experimental studies related to mass transfer across ocean surfaces (there is no published model for accurately estimating mass transfer across the air-water interface of a sump below a cooling tower).
9. The ambient concentration of the VOC of interest is negligible relative to the concentration in the gas-phase inside the cooling tower, and can therefore be neglected.
10. The rate of evaporation of water within the cooling tower is equal to the rate of make-up water flow rate, which is assumed to be continuous.
11. The rate of evaporation of cooling water within each stage of the cooling tower is attributed in accordance with the relative water vapor driving force in each stage, and is therefore a strong function of the vapor pressure of water (and hence water temperature) in each stage.
12. The density of water is constant across the cooling tower.
13. The gas-phase within the cooling tower acts as an ideal gas, allowing for calculations of air density within each stage of the tower.

14. The surface tension of water drops linearly with temperature within the range of water temperatures within the cooling tower.
15. Aqueous solubility changes with temperature for the VOC of interest are small relative to changes in vapor pressure with temperature, so that changes in Henry's law constant are related solely to change in vapor pressure.
16. Detailed energy calculations are not employed in the CTEC model. As a screening estimate the temperature of the gas-phase within each stage of the cooling tower is taken to be the average of the ambient air temperature and temperature of cooling water within each stage.

CTEC: Cooling Tower Emissions Calculator

This "emissions calculator" was developed by researchers at The University of Texas at Austin. It is intended for estimation of VOC emissions during leaks in industrial heat exchange units. The model is of a "screening" nature. Where assumptions have been made they err on the side of conservatism, i.e., over-estimation of emissions. The model can also be used with site-specific measurements of mass transfer coefficients, etc., if additional accuracy is desired. CTEC assumes cross-flow fluid contact and cooling towers with quantifiable packing (fill) media.

RESULTS ----->

Stage	Cl (mg/L)	E (kg/hr)	% contrib
0	10	-	-
1	7.94	7.64	25.9
2	6.38	5.72	19.4
3	5.20	4.33	14.7
4	4.28	3.32	11.3
5	3.56	2.57	8.7
6	3.00	2.01	6.8
7	2.55	1.59	5.4
8	2.19	1.27	4.3
9	1.90	1.03	3.5
10	1.67	0.81	2.7
Sump	11	1.58	0.03

Total Emissions (kg/hr)

29.5

Stripping Efficiency (%)

82

Required User Input

	Units	Value(s)
Name of VOC of interest (for future reference)	-	Benzene
Inlet concentration of VOC of interest	mg/L	10
Inlet water flow rate to cooling tower	cubic meters per second	1
Make-up water flow rate	cubic meters per second	0.05
Total air to total inlet water flow ratio	unitless	0.5
Total height of tower (from water entry to sump)	meters	10
Void fraction of cooling tower	-	0.93
Cross-sectional area of cooling tower	square meters	120
Specific surface area of packing media	square meters/cubic meter	100
Effective diameter of packing	meters	0.025
Critical surface tension of packing media	N/m	0.033
Surface area of sump	square meters	150
Temperature of inlet cooling water	degrees kelvin	323
Temperature of water at tower bottom (above sump)	degrees kelvin	306
Temperature of water in sump	degrees kelvin	303
Temperature of ambient air	degrees kelvin	296
Relative humidity of ambient air	%	50
Molecular weight of VOC of interest	g-mol/mol	78
Henry's law constant for VOC of interest (@ 25 oC)	dimensionless (Cg/Cl _{iq})	0.23
Boiling point of the chemical of interest	degrees kelvin	353.5
Diffusion coefficient of VOC in water (@ 25 oC)	square meters / second	1.30E-09
Diffusion coefficient of VOC in air (@ 25 oC)	square meters / second	1.20E-05