SOUTH COAST AIR QUALITY MANAGEMENT DISTRICT

METHOD 25.3

DETERMINATION OF LOW CONCENTRATION NON-METHANE NON-ETHANE ORGANIC COMPOUND EMISSIONS FROM CLEAN FUELED COMBUSTION SOURCES

MONITORING AND ENGINEERING BRANCH
MONITORING AND ANALYSIS
March 2000

TABLE OF CONTENTS

LIST OF FIGURES

METHOD 25.3

DETERMINATION OF LOW CONCENTRATION NON-METHANE NON-ETHANE ORGANIC COMPOUND EMISSIONS FROM CLEAN FUELED COMBUSTION SOURCES

Section 1 of 5

1. Overview and Applicability

1.1 Principle

The procedures used in this Volatile Organic Compound (VOC) source test method are similar to the approach of Method 25.1, but have been modified for the purposes of improving accuracy at low concentrations. The method eliminates positive interferences for low concentration VOC due to high levels of stack carbon dioxide and moisture. As with Method 25.1, duplicate gas samples are withdrawn from a source at a constant rate through condensate traps (traps) followed by evacuated canisters. The method differs from Method 25.1 in that stack condensate is collected at ice water (~32 ^{o}F) temperature in the traps as opposed to the lower dry ice temperature. For low concentrations, the ~32 ^{o}F traps have proven to be sufficient for trapping condensate and preventing unrecoverable VOC from being collected in the canisters. With clean sources, since the condensate consists largely of water, the traps consist of small impingers initially charged with ultra-pure water as a heat transfer medium. Interfering carbon dioxide in the traps is purged into the canisters using a ultra-pure grade inert gas. Particulate matter is prevented from interfering with the method by using an in-stack filter. Since the water does, however, have limitations on the amount of insoluble material that can be homogeneously retained, the method is limited to VOC concentrations of less than 50 ppm as carbon (ppmC) or 25 ppmC in the trap section.

VOC concentration as Non-Methane Non-Ethane Organic Compounds (NMNEOC) is determined by combining the results from the independent analyses of the condensate in

each trap and the gas in its associated canister. The traps are analyzed for total organic carbon by liquid injection into an infra-red total organic carbon analyzer. The canisters are analyzed for NMNEOC using the Method 25.1 approach. The analysis consists of foreflush and backflush of a gas chromatography (GC) column followed by an oxidizer, methanizer, and a flame ionization detector (FID). The GC separates the VOC component from the sample; the oxidizer converts the VOC to carbon dioxide; the methanizer converts the resulting carbon dioxide to methane. The results are determined by the FID in units of parts per million by volume as carbon (ppmC). Carbon monoxide and fixed gases (carbon dioxide and oxygen) can be determined by analysis of the canister portion of the sample by SCAQMD Method 10.1.

The method is written to represent the configuration used during validation testing. Mention of trade names in this source test method does not constitute endorsement by SCAQMD; the model names and numbers are given as those used during the validation phase of the method. Other manufacturers of equipment may be used subject to demonstration of equivalency as approved by the SCAQMD.

A bias correction factor of 1.086 must be applied to the final results of this method. The use of this bias correction factor is required by the USEPA as determined during the validation phase of the method (refer to Section 5.3).

1.2 Applicability

This method replaces the method that was formerly known as SCAQMD Draft Method 25.2. Former Draft Method 25.2 has been removed from consideration due to inherent shortcomings in its approach which have been proven to cause both a low bias and poor precision. **Source test results achieved by former Draft Method 25.2 are, therefore, not considered as valid for SCAQMD purposes.**

Method 25.3 measures low concentration VOC emissions as NMNEOC expressed as ppmC. Since it is not adversely affected by the unpredictability of VOC composition in combustion products, the method is particularly applicable to combustion processes. In its total carbon approach, the method is not affected by compound specific instrument response factor variables often encountered in other detection methods. This method is applicable when the following conditions are met:

1. Combustion sources must use clean fuels. Clean fuels are defined as natural gas, refinery fuel gas, butane, LPG, landfill gas, digester gas, methanol and ethanol.

2. The resulting concentration as measured by this method must be less than 50 ppmC or alternatively 25 ppmC in the trap portion with a higher limit on the canister portion evaluated case by case depending on the compounds present.

Supporting data has shown that for concentrations above 50 ppmC (or 25 ppm in the trap) or for non-clean fueled combustion sources, a bias will occur due to limitations in the condensate trap design (see *Interferences*). For these situations, refer to Method 25.1.

The method may be applied to sources of higher concentrations where exclusively water soluble VOC is encountered. The applicability of the method to these situations must be evaluated by the SCAQMD on a case by case basis.

The method may be used without the condensate trap and its associated procedures only for ambient temperature sources where no combustion products or other sources of moisture other than ambient are present. Additionally, the resulting concentration as measured by this method must be less than 50 ppmC. The applicability of the method to these situations must be evaluated by SCAQMD on a case by case basis.

The lower detection limit of the method is 1 ppm NMNEOC as carbon.

For determining mass emissions, a molecular weight per carbon ratio must be established to account for bonded oxygen, hydrogen, chlorine, or other elements. Similarly for converting ppmC to actual ppm, the average carbon number must be estimated. Section five of this method provides guidelines for determining molecular weight per carbon.

This method assumes that methane and ethane are the only significant VOC exempt compounds commonly found in combustion exhausts. The NMNEOC results can be corrected for other exempt compounds when present, using an appropriate method approved by SCAQMD, CARB, and EPA for determining exempt content.

1.4 Limitations and Interferences

In cases where combustion type control devices are used to control streams containing exempt compounds as specified in SCAQMD Rule 102, a positive bias towards VOC will occur if a correction is not made for the presence of exempt compounds.

Supporting data has shown a potential negative bias when sampling streams of over 50 ppmC due to design limitation of the condensate traps which were designed for lower concentrations. This is believed to be caused by non-homogeneity in the water traps with insoluble species present.

Sampling combustion sources burning non-clean fuels can cause a negative bias. This is also due to limitations in the low-concentration trap design combined with the presence of high molecular weight, semi-volatile, condensable, insoluble material which tends to separate from the water in the trap.

Ammonia present in concentrations above 15 ppm can reduce the level of precision of this method but does not cause a specific low or high bias.

Because of the low concentration of VOC encountered, contamination, if present can cause a significant bias. The procedures of this method have been designed to eliminate potential contamination. It is, however, imperative that the equipment cleaning and sample handling procedures are carefully followed.

If samples are extracted from a stratified stream, a positive or negative bias may occur. Samples must be extracted from well mixed locations or employ multi-point sampling (see *Field Procedures*).

Procedures for minimizing the effects of any of the above interferences where applicable are not all addressed in this method. Alternative procedures must be evaluated on a case by case basis and are subject to SCAQMD approval.

METHOD 25.3

DETERMINATION OF LOW CONCENTRATION NON-METHANE NON-ETHANE ORGANIC COMPOUND EMISSIONS FROM CLEAN FUELED COMBUSTION SOURCES

Section 2 of 5

2. Sampling Apparatus and Field Equipment Preparation

2.1 Sampling Apparatus

The sampling system consists of an in-stack filter, a probe, a Teflon line, a condensate trap, a flow controller, a vacuum gauge, a valve, and a canister (see Figure 25.3-1). The sampling equipment can be constructed from commercially available components. The internal volume of the entire sampling apparatus excluding the canister must not exceed one percent of the canister volume in order to avoid dilution by the sample system dead space. The following is a detailed description of the sampling system component requirements.

a. In-Stack Filter

A ≤2 micron, 316 type stainless steel or other high temperature non-corrosive material filter located at the stack end of the probe tip. The filter can be the small frit type inserted into a 0.25 in. tube fitting connected to the probe tip.

b. Probe

Seamless stainless steel tubing, 0.25 in. outside diameter and cut to a length of half the stack diameter or sufficient length to extend near the stack or duct center to avoid dilution effects from the sampling port. When sampling, the probe is fixed with the connector line end flush with the port entrance so that the stack gases heat the entire probe length.

c. Condensate Trap

The condensate trap is designed as a small 4 ml glass bodied impinger. The body is a commonly available 4 ml narrow screw top glass vial which is used not only as the trap body but also for sample storage with its supplied Teflon lined screw cap. The approximate dimensions of the vials are 1.8 in. total height, 0.6 in. o.d., and 0.3 in. i.d. at the upper threaded opening. A 0.25 in. hole must be made in a spare screw cap for affixing the condensate trap to the sampling assembly. Size 009 and a size 006 Viton "O" rings are used to seal and retain the glass vial to the sampling assembly. See Figure 25.3-2 for specifications on condensate trap design. For sampling, the condensate trap is charged with approximately 2 ml of hydrocarbon free water. The 4 ml trap size is sufficient for stack moistures of up to 25% by volume. For higher stack moistures, the trap design must be scaled up accordingly.

d. Connector Line

Seamless Perfluoroalkoxy (also known as PFA, a type of Teflon) tubing, 0.125 in. outside diameter x 0.026 in. wall thickness and cut to length of no more than 18 in. The connector line is connected to the probe with a stainless steel tube reducer. The other end of the connector line must extend into the condensate trap with a tapered end having an opening of less than 0.020 in. so that small bubbles are formed in the condensate trap. This tapered end can be formed by applying a point source of heat to approximately one inch of a continuous section of tubing so that the temperature of the section is heated to near the melting point. The opposite sides of the heated section can be pulled apart while twisting torsionally to form a split at the heated section. The narrow tips created at the ends of the tubing split can then be trimmed appropriately to create the small opening. When assembled, the tubing extends from the probe reducer to within 0.125 in. from the bottom of the condensate trap as shown in Figure 25.3-2.

e. Ice water bath

A container is affixed to the sampling apparatus to hold ice and water used to cool the condensate trap. The ice bath must be of sufficient cross section to surround the condensate trap with an appropriate amount of ice to maintain the ice water temperature (minimum 2.5 in. diameter). The ice bath must be approximately one inch in height (for 4 ml trap size) so that the condensate trap vial connection remains above the top of the ice bath container and the overflowing cold water will be below the connector level. This is done to eliminate the risk of contamination. The ice bath must also be positioned sufficiently high so that the water level of the bath is higher than the water level inside the condensate trap.

f. Flow Rate Controller

A vacuum flow regulator, rotameter, fine orifice, or other flow regulator capable of maintaining a constant flow rate (± 10%) at the probe tip over the sampling period. The flow controller is located downstream of the condensate trap so that its function is unaffected by the condensate. For flows regulated by rotameters or orifices with a control valve, the control valve will require constant adjustment during sampling due to the declining pressure differential. The control valve must be located between the canister and the rotameter or orifice. For a critical orifice, where a control valve is not used, sampling must be terminated if the vacuum in the canister drops below the level where a constant flow cannot be achieved. This type of orifice can be prepared using a GC syringe needle fixed concentrically into 1/4 in. stainless steel tubing. Epoxy or silicone adhesive has been successfully used for this purpose. The desired flow rate for one hour sampling time for a 6-liter canister is ~70 ml/min and can be achieved using a short (appropriate) length of 0.0045” syringe needle. The flow rates can be fine tuned by adjusting the length of the inner needle tube.

g. Vacuum Gauge

A stainless steel gauge cleaned for electronic use is specified for monitoring vacuum in the tank and sampling system between the flow controller and sample flow valve both during sampling and leak checks (0 to 30 in. Hg Vacuum).

h. Sample Flow Valve

Stainless steel bellows valve is used for starting, stopping, or regulating sample flow and is located between the vacuum gauge and sample canister.

i. Sample Canister

The electro-polished stainless steel canister has a volume of 6 ± 0.5 liters. The canister volume is determined to the nearest 10 ml as described in section 3.8.

i. Sampling Assembly

The assembled sampling apparatus in its "ready for transport" configuration is shown in Figure 25.3-1. An exploded view of the sample line and condensate trap assembly is shown in Figure 25.3-2. A stainless steel quick connector is useful for connecting and disconnecting the canister from the remainder of the sampling assembly.

2.2 Sampling Reagents

The condensate trap is initially charged with approximately 2 ml hydrocarbon free water such as deionized or distilled water. This water must have a TOC content of less than one ppmC.

2.3 Sampling Equipment Preparation

2.3.1 Sampling Equipment Cleaning

The sampling equipment preparation must be performed in a clean indoor laboratory type environment and not in the field. All equipment that contacts the sample excluding the canister, but including the remaining equipment listed in section 2.1 and other equipment that contacts the sample such as connectors and end caps, must be thoroughly cleaned as follows: Soak the equipment in non-residue, rinsable type laboratory glassware detergent and water. Scrub all accessible surfaces and remove all visible surface residues. Rinse the equipment thoroughly first with tap water then with deionized water. At this point onward, be certain not to touch any part of the internal sample path or open connection ends with any object that has not been cleaned using the above procedure and particularly not at anytime with hands or fingers. Use powder-free latex gloves while handling cleaned equipment. Blow the equipment pieces dry with ultra-pure grade air (< 0.5 ppm hydrocarbon) while holding the pieces by the outside surface which does not contact the sample. Under no circumstances should uncleaned compressed air be used for drying parts due to the possibility of entrained compressor lube oil or other droplets causing contamination. After drying, the equipment excluding the canister can be assembled as in Figure 25.3-1 using a clean empty glass vial on the condensate trap assembly during transportation to the field. Clean the probe and filter assembly by exposing to elevated temperatures using an open flame while passing air through the assembly. Gradually move the flame along the entire length of the probe at a rate so that the probe is heated to a glowing orange in each section contacted by the flame, then allow to cool. Seal the open ends of the probe and sampling assembly using a clean cap or foil.

2.3.2 Canister Preparation

The following equipment are needed for canister preparation:

a. Manometer

Must be capable of measuring pressure to within 1 mm Hg in the 0-900 mm range. Manometer must be NIST traceable.

b. Vacuum Pump

Capable of producing a full 30 in. Hg of gauge vacuum (<10 mm Hg. absolute pressure). This is to evacuate the sample tanks and intermediate collection vessels (see Sections 3.3 and 3.4).

Do not use canisters previously used for other types of sampling where concentrations of >50 ppmC were encountered. Clean the Summa polished canisters by sequential filling with pure nitrogen gas and evacuating to approximately 3 mm Hg. It has been determined that ten cycles are sufficient to result in a <1 ppmC for a pure nitrogen blank check. After the last cleaning cycle, fill the canister with pure nitrogen gas to ~900 in. Hg then allow it to set overnight. Perform a tank blank analysis on the nitrogen gas in the canister as in Section 4. The backflush concentration should be 0.5 ppmC or less, otherwise repeat the cleaning-blanking process. Finish the cleaning process by filling the canister with pressurized gas, and then evacuating the canister to ~ zero mm Hg. The laboratory can establish a cleaning procedure without the blank test on the basis of the history of the canisters used and previous data on the cleaning-blanking process. Save the data for future QA/QC SCAQMD audits.

The sample tank is leak checked by isolating it from the vacuum pump and allowing the tank to sit for at least 10 minutes. The tank is acceptable if no change in tank vacuum is noted.

2.3.3 Condensate Trap Vial Preparation

Store 200 to 300 ml of the hydrocarbon free water in a clean glass jar with a glass stopper at normal refrigerator temperature (approximately 5 ^{o}C). Analyze the water for TOC content at ice water temperature as in Section 4. If the TOC content is less than 1 ppmC, keep the water for future use. If the TOC content is more than 1 ppmC, replace the water, and repeat the process. Label both a clean threaded 4 ml glass vial and a threaded cap as a set. Tare and record the vial and cap set. Fill the vial with ~2 ml of the hydrocarbon free water (approximately half full) and tightly replace the corresponding cap. Prepare an adequate number of vials for the deployment of the duplicate samples that will be collected. Extra vials must be prepared for reagent blanks and connector line rinses. It is important that plenty of water from the same batch is left in the stoppered glass jar for use during analysis. The vials and the remaining water in the stoppered glass jar are then stored at refrigerator temperature in the laboratory until transport to the field.

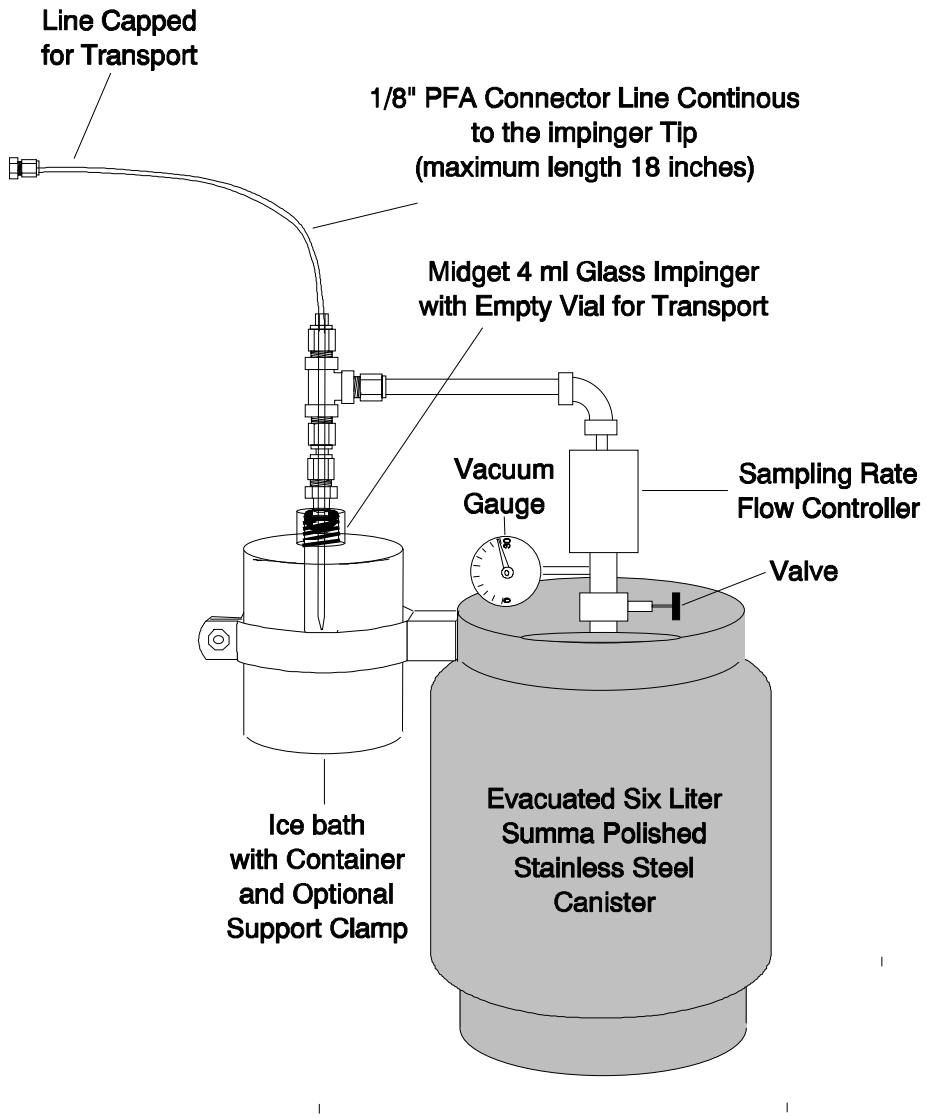

Figure 25.3-1 Preparation of Sampling Apparatus

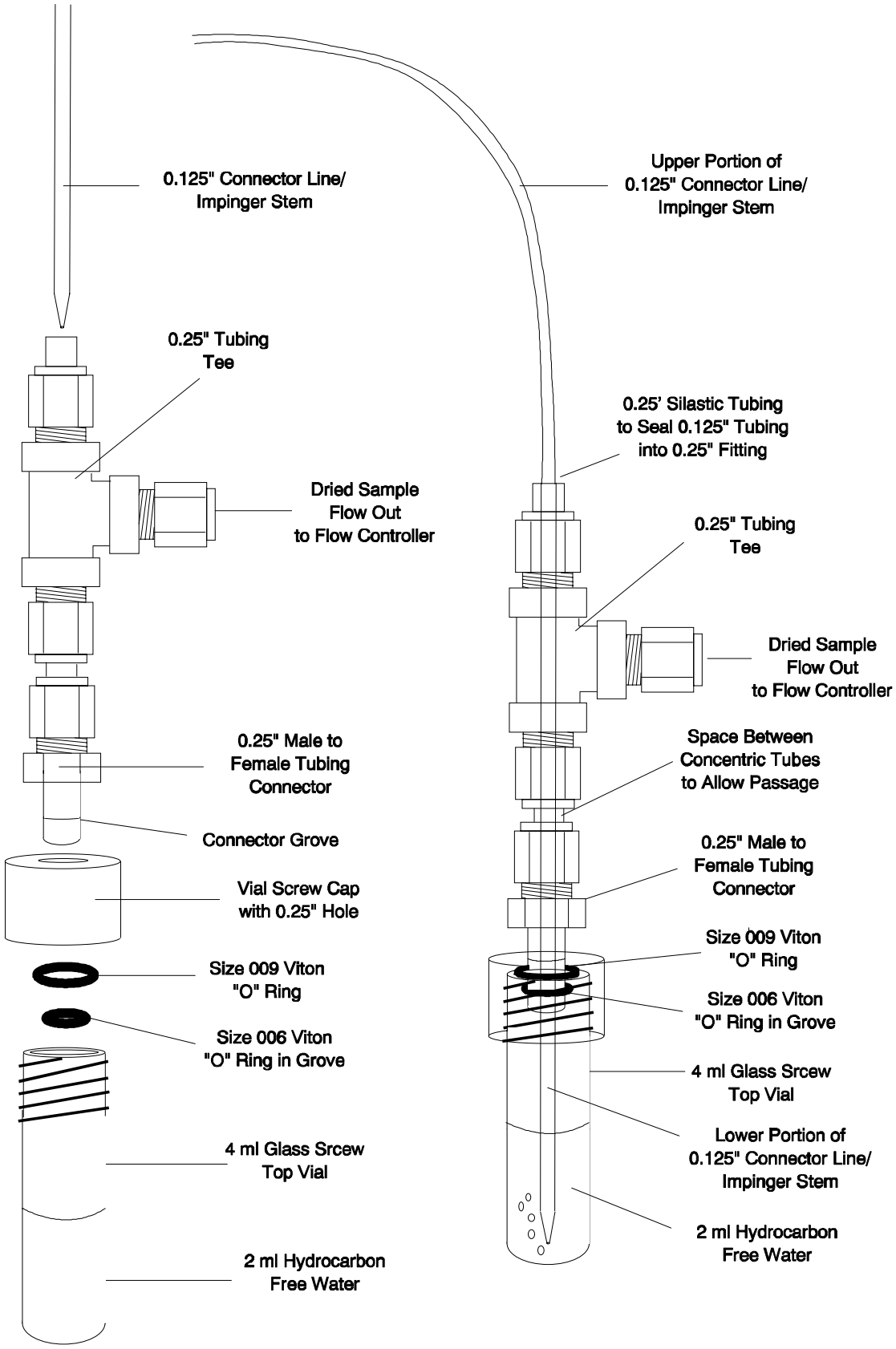

Figure 25.3-2 Condensate Trap Detail

METHOD 25.3

DETERMINATION OF LOW CONCENTRATION NON-METHANE NON-ETHANE ORGANIC COMPOUND EMISSIONS FROM CLEAN FUELED COMBUSTION SOURCES

Section 3 of 5

3. Field Procedures

Individual sampling runs shall consist of duplicate simultaneous samples as described in this section. The descriptions are provided for individual samples in the duplicate set for purposes of simplicity. Condensate trap blanks are required for use during analysis. By following the equipment cleaning and canister preparation procedures, full field blanks are not required but may be employed if deemed necessary. Field blanks would consist of a full sampling assembly handled and analyzed identically to the actual samples with the exception that samples are not drawn into the containers. Results from sampling must not be corrected using either field blanks or any type of ambient sampling for reporting purposes. The results from either field blanks or ambient samples may be reported along with the sampling results.

3.1 Pre-test Determinations

Samples must be taken at well mixed and uniform locations, i.e. far from situations causing stratification such as duct junctions, addition of dilution air, combustion zones, or other flow disturbances that may alter the concentration profile. Alternatively, an approved stratification check (refer to SCAQMD Source Test Manual Chapter X) using a portable hydrocarbon analyzer may be used to check for stratification of less than 10% or for a representative sampling point within a stratified duct. Multi-point sampling can alternatively be employed but will require multiple concurrent samples with associated probe lengths due to in-stack probe heating requirements.

The required sampling time interval is dependent on the applicable rule or permit condition that is to be evaluated. In most cases when not specified, a full one hour sampling period will be required since results will be used to determine emissions in lb/hr.

Sampling should begin and end only when the process has been operating for a sufficient length of time and steady state operation can be assured. A steady state is defined as operating at constant operating temperature, feed rate, fuel rate, product application or throughput rate, etc., and that the production rate is steady throughout the process. For batch or cyclic processes, the sampling period must encompass at least one complete cycle or batch. The sampling period must also begin and end at the same point in the cycle so that portions of the cycle are not over or under-represented.

3.2 On-site Equipment Assembly

Once in place at the sampling location, the equipment can be assembled as shown in Figure 25.3-3 with the probe connected but not inserted into the stack. Care must be taken during this step to avoid contamination of the internal surfaces of the condensate trap parts by any contact with objects or dust in the area. The condensate trap water vials must be chilled for a minimum of 5 minutes before sampling. The chilled condensate trap vial is attached by removing the empty vial placed on the assembly during transport and replacing with the water filled sample vial. The empty vial is then capped with the water vial lid so that the combination is kept clean while not in use during sampling. Once the vial is attached to the condensate trap assembly, the equipment must remain in the upright position so that the condensate trap water does not drain out of the condensate trap assembly into the flow controller.

The condensate trap can then be positioned with ice in the ice bath The position of the ice bath relative to the condensate trap is such that the vial connection will be above the top of the ice bath container so that the overflowing ice and cold water will be below the connector level. The ice bath must also be positioned sufficiently high so that the water

level of the bath is higher than the water level inside the condensate trap. After completing the assembly, record the vial and canister identification numbers on the field data sheet as in Figure 25.3-4.

3.3 Pretest Leak Check

A pretest leak check is required. After assembling the sampling system as shown in Figure 25.3-3, make certain that the fitting at the probe that holds the in-stack filter is tightly capped. The leak check is performed by opening and closing of the sample flow valve so that the valve is partially open for a sufficient amount of time to introduce the canister vacuum to the remainder of the system. Immediately after the sample flow valve is closed, the vacuum gauge may initially drop numerically in vacuum if a restricting orifice is used as a flow controller. The vacuum drop should cease at numerically above 10 in. Hg. At this point a cease in movement of the vacuum gauge for a period of ten minutes indicates an acceptable leak check on the sampling system. Additionally, when sampling is initiated, the vacuum gauge must indicate a canister vacuum of numerically greater than 28 in. Hg. If this initial vacuum is numerically less than 28 in. Hg, a leak in the canister subsequent to its evacuation is indicated.

3.4 Sampling Operation

Uncap the filter fitting at the probe tip and place the probe in the stack with the opening of the probe tip tangent to the stack flow. Clamp or fasten the probe in place so that the entire stainless steel probe is within the heat of the stack and as far into the stack as possible while avoiding melting the PFA connector line. The purpose of this probe placement is to ensure that no condensation occurs in the probe. Condensation in the PFA connector line is, however, acceptable. If present, the condensation should begin to form after the junction of the probe to the PFA connector line. This can be verified by visual observation of the condensation through the semitransparent PFA material. Clean the port

as much as possible before inserting the probe. When inserting the probe into the stack, care must be taken so that the probe opening does not contact the stack port internal surface residues or residues on the internal stack wall. Seal the port around the probe so that ambient air does not dilute the stack gases.

If the process that is being sampled is operating under normal representative operating conditions or the conditions specified by the permit conditions, sampling may begin. To begin sampling, open the sample flow control valve and maintain a steady flow that varies by no more than 10% so that the canister is filled from its full 30 in. Hg vacuum to a numerical vacuum of 2 - 15 in. Hg over the specified sampling period as determined in section 2.3.

Immediately after sampling has commenced, record the initial canister vacuum and clock time. If this initial vacuum is numerically less than 28 in. Hg, then the sample is invalidated. Provide ice in the ice bath during sampling to maintain a constant ice bath temperature of ~32 ^{o}F. Record the canister vacuums at regular intervals (15 minute recommended) during sampling as an indicator of constant flow into the canisters. Fill in the remaining information as prompted by the field data sheet in Figure 25.3-4. At the end of the sampling period, record the final vacuum and clock time, then close the sample flow valve. Remove the probe from the stack, note the condition of the in-stack filter, and recap the probe at the filter fitting.

If the sampling is interrupted due to a shutdown in the process being sampled or for an upset of normal or specified operation, close the sample flow valve to interrupt sampling. Record vacuum gauge readings and clock time. When the source resumes the normal or specified operating conditions, sampling may resume by reopening the sample flow control valve.

3.5 Reference Point Velocity

If a flow rate is to be measured for determining mass emissions, monitor velocity at a reference point during sampling. Take velocity readings at five minute intervals during the sampling period, or more often when the velocity or temperature fluctuates by more than 20 percent. Use the ratio of average reference point readings during sampling to average reference point readings during the traverse to correct the average stack velocity during the traverse. This is done so that average concentration measured during sampling corresponds to the average flow rate experienced during sampling.

3.6 Post Test Procedures

Immediately after sampling, perform a post test leak check as in section 2.6 with the maximum vacuum that can be achieved with the vacuum remaining in the canister.

After the post-test leak check, disconnect the PFA line from the probe. Rinse the condensate present in the line into the condensate trap with 0.5 to 1.0 ml of hydrocarbon free water. This is accomplished by introducing a small amount of the remaining tank vacuum to the line while dipping the open end of the line briefly into a spare vial of the hydrocarbon-free water. During this step, observe the water level in the trap and avoid over-filling the trap to avoid the water being drawn into the flow controller. After the connector line has been flushed, the condensate trap body is disconnected, capped, sealed, and stored at approximately 32 ^{o}F. Alternatively the connector line can be capped and the condensate trap left connected to the sampling assembly. If the condensate trap is left connected, it does not need to be stored at 32 ^{o}F but must not be allowed to exceed 85 ^{o}F.

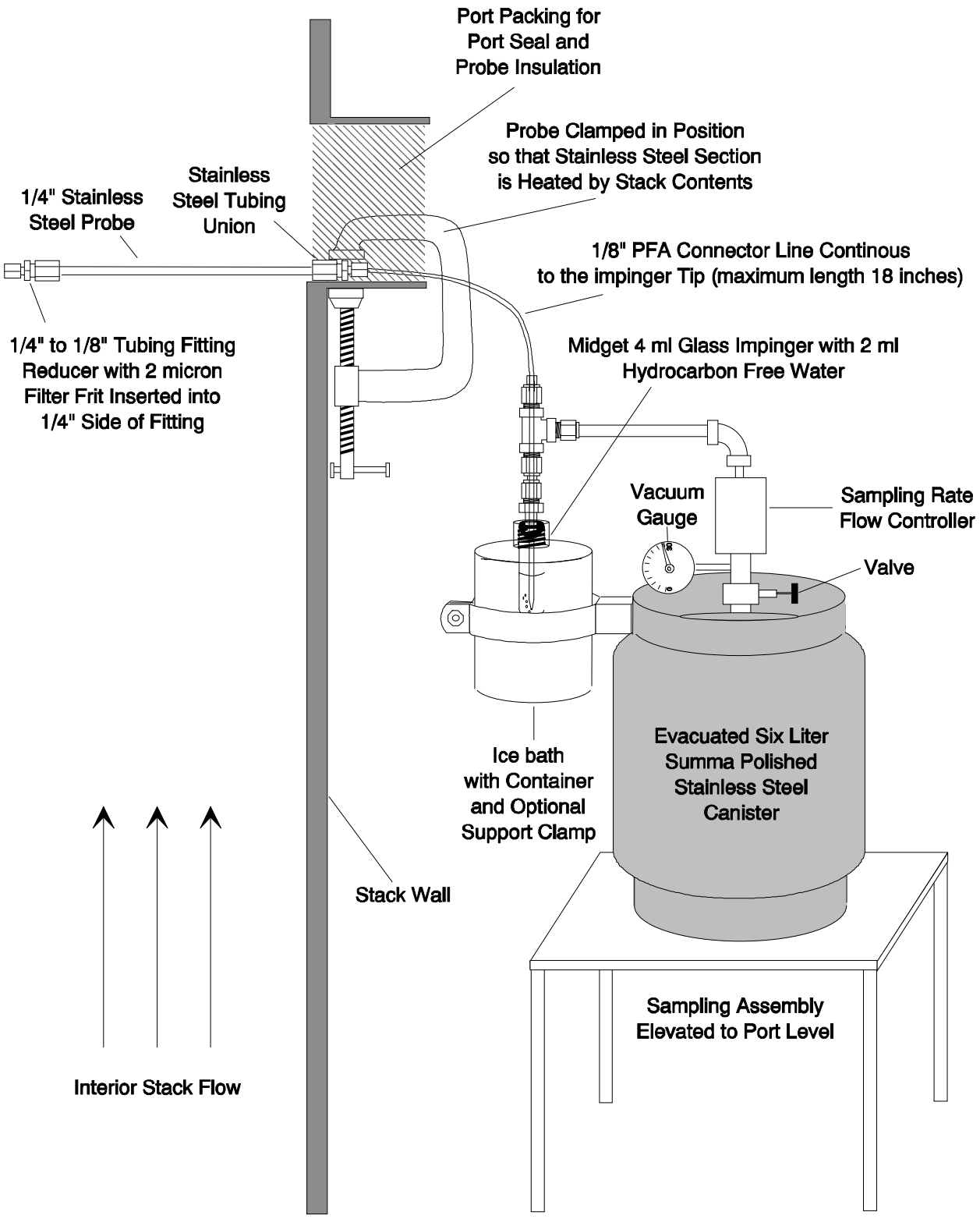

Figure 25.3-3 Sampling Apparatus During Sampling

Test No._____ Date_____

Company Name_____ Recorded by_____

Sampling Location_____

METHOD 25.3 FIELD DATA SHEET

Pre-Test Leak Check:
Gauge Vacuum_____/_____in. Hg
Loss in 60 seconds____/_____in. Hg

Post-Test leak Check
Gauge Vacuum:_____/_____in. Hg
Loss in 60 seconds:___/_____in. Hg

Reference Point #_____

Sample Data

	Sample #1	Sample #2
Canister No.		
Trap No.		
Controller No.		
Location within Stack		
Initial Time		
Initial Vacuum (in. Hg)		
Intermediate Time		
Intermediate Vacuum (in. Hg)		
Intermediate Time		
Intermediate Vacuum (in. Hg)		
Intermediate Time		
Intermediate Vacuum (in. Hg)		
Final Time		
Final Vacuum (in. Hg)		

Reference Point Data

Time	Velocity Head ($in.H_20$)	Temperature (^oF)

Observations_____

Figure 25.3-4 Field Data Sheet

METHOD 25.3

DETERMINATION OF LOW CONCENTRATION NON-METHANE NON-ETHANE ORGANIC COMPOUND EMISSIONS FROM CLEAN FUELED COMBUSTION SOURCES

Section 4 of 5

4. Laboratory Procedures

The analyst must demonstrate prior to initial use that each of the analyzers used in this method is capable of measuring low concentration NMNEOC. For the canister analysis this includes a demonstration of proper separation, oxidation, reduction, and measurement. This demonstration must also prove that the equipment can resolve lower concentration standards at just above the lower detection limit (1 ppm) of this method. Achieving low concentration analysis for NMNEOC by this method requires contaminant free equipment, an appropriate baseline subtraction, and an appropriate range of calibration. This demonstration of the analyzers' performance must be approved by the SCAQMD laboratory for use in this method.

4.1 Sample Receipt

a) Check the correctness of labels, number of samples vials, number of canisters, and "Chain of Custody" forms for completeness of information.

a) Inspect the water sample vials for leakage. The canister gauge reading (if equipped) should be 2 -15 in. .Hg, otherwise make a note.

a) Sample delivery personnel sign and date to relinquish the samples.

a) Laboratory personnel sign and date to receive the sample.

a) Store the sample vials in a clean refrigerator, and the canisters in a secured area. The vials must be purged within 24 hours from sampling. The analysis must be performed within ten days from sampling.

4.2 Sample Purge

a) Allow the sampling canisters to equilibrate to room temperature; then, using the calibrated high precision manometer specified in Section 2.3.2(a), measure the pressure of each canister to the nearest 1 mm Hg. The pressure should be similar to the final sampling pressure as indicated by the sampling gauge. If a significant pressure loss is observed indicating a leak, invalidate the sample. Invalidate the sample when the absolute return pressure is less than 200 mm Hg. Record this pressure as return pressure (Pr) before proceeding to the purge step.

b) Reassemble the sample vial to the remainder of the sampling assembly. If the condensate trap vial was left connected to the sampling apparatus, it must be quickly capped when disconnected to check canister vacuum, and kept upright until reconnection after the received pressure has been taken. When the sampling apparatus is reassembled, a leak check must be performed as in Section 3.3.

c) Connect the probe tip to a source of ultra pure grade nitrogen or argon and introduce a flow of slightly greater than that of the sampling rate at the ultra pure gas source. The gas source must contain a tee that is open to the atmosphere such that excess pressure is bled to the atmosphere. Refer to Figure 25.3-5 for a schematic of this configuration.

d) Open the sampling canister valve and allow the pure gas to purge through the assembly and into the canister. The minimum purging gas flow rate is 25 to 30 ml/minute. The bubbling characteristics should be similar to that encountered during sampling. Allow the gas to purge for 10 minutes or until the vacuum drops to 2 in. Hg numerically lower than the received vacuum.

e) After the purge period, close the purge gas valve first and allow any residual pressure to vent through the purge gas line tee before closing the canister valve to avoid back flushing the condensate trap assembly.

f) Remove the sample vial and cap securely. The glass vial is then analyzed for TOC or stored at refrigerator temperature until analysis.

g) Remove the sampling assembly then pressurize the canister with pure argon or nitrogen gas to a pressure between 860-910 mm Hg. Shut off pressure from pure gas source, wait until reading is stable, record the reading as final pressure (Pf).

h) Disconnect the canister from the purge gas line and seal. The sample canister is analyzed by TCA or stored until analysis.

4.3 Apparatus and Reagents for TOC Analysis on the Traps

4.3.1 Shimadzu TOC-5000 Analyzer

The TOC-5000 analyzer is automated. Total organic carbon (TOC) is measured by the difference between total carbon (TC) and inorganic carbon (IC). TC, containing both organic and inorganic carbon, is measured by oxidizing an aliquot of sample with a Platinum catalyst at 650 ± 5 ^{o}C using an air carrier/ oxidizer. The CO2 gas is quantified against the stored calibration curve by a non-dispersive infra-red (NDIR) detector. IC is measured by injecting an aliquot of sample into a phosphoric acid (H_3PO_4) vessel. The CO_2 released from acidification of inorganic carbonaceous compounds with the acid is sparged with air and then quantified the same way as CO_2 from TC. The difference of the two results is TOC.

\

4.3.2 Other Apparatus and Reagents for TOC Analysis

250 ul glass syringe

Glass vials, 4 and 15 ml size with Teflon lined screw caps

Refrigerator set to a temperature of approximately 5 ^{o}C

Ice water bath

Analytical balance capable of weighing to 0.1 mg

Laboratory glassware as need

Deionized (DI) water containing <1 ppmC TOC

Potassium hydrogen phthalate (KHP), AR grade or equivalent

Sodium carbonate, A.C.S. grade or equivalent

Sodium hydrogen carbonate, A.C.S. grade or equivalent

Three to six volatile organic compounds, with known purity, representing the expected organic class of compounds in the sample

Ultra zero air containing <0.1 ppmC

4.4 Preparation of Standards and Reagents for TOC Analysis

The following Equation (1) can be used for preparing a known carbon stock standard with any pure carbonaceous compound:

$$\text{mgC/Kg (ppmC)} = (W_t \times n \times A_c \times 1000 \text{ mg/g}) \times 1000 \text{ g/kg}/(MW \times W_s) \quad (1)$$

W_t = weight of compound in grams

n = number of carbon atoms per molecule

A_c = atomic weight of carbon

MW = molecular weight of the compound

W_s = weight of solution (100 g)

Note: in the TOC analysis section only, ppm is on a weight basis

For a 1000 ppmC TOC stock standard, mix 0.2125 g KHP with a balance of DI water and make 100g of solution. Cap tightly, and store in a refrigerator. Discard after two months.

For a 1000 ppmC TC stock standard, mix 0.3497 g $NaHCO_3$ and 04412 g of Na_2CO_3, with a balance of DI water to make 100 g of solution. Cap tightly, and store in a refrigerator. Discard the solution if a fibrous or flaky material appears.

Prepare working standards for TOC from the stock standard solutions; accurately weigh aliquots of stock standard in a tarred 15 ml size, screw cap vial. Add DI water to about 80% capacity, reweigh the total solution. Calculate the concentration of working standard using Equation 2:

$$\text{ppmC of working standard} = \text{ppmC stock standard} \times W_s/W_{ts} \quad (2)$$

where W_s = weight in grams of stock standard

W_{ts} = weight in grams of total solution

The recommended concentrations for TOC working standards are 10 ppmC, 40 ppmC and 100 ppmC. TC standards are prepared in the same manner.

A TOC mixture for QC (QC standard) is prepared in the same manner as the standards choosing organic compounds in the same class that represent the expected compounds in the sample. The content of the stock solution may not be given in units of ppmC for an individual component. For example, formaldehyde in water contains 37% formaldehyde. Add concentrations of individual components to get the total concentration as carbon.

4.5 TOC Analysis of Traps

a) Take the sample vials including field blank from the refrigerator one at a time, wipe off any water on the vial prior to opening.

b) If less than 4 ml of water is present in the vials, open each vial add DI water (which had been used for pre-field sampling preparation) to ~4 ml, cap the vial, and allow it to equilibrate to room temperature.

c) Dry each sample vial, and weigh. Return all vials to the refrigerator.

d) The TOC analyzer is calibrated, prepared for sample analysis, and run according to Manufacturer's Instruction Manual. The following steps are applied generically the TOC analysis.

e) Prepare an adequate ice-water bath and replenish ice as required during the entire analysis.

f) Each analytical run for all DI water blanks, standards, field blanks, samples, and controls consists of three injections/run with three wash cycles. These are all performed at ice-water bath conditions. Perform the first run using the laboratory DI water as a cleanup and a lab blank. Run the DI water until the average TOC of three injections is less than 1 ppmC by using the previously stored calibration files.

g) Run TOC and TC standards and store in the calibration files according to the calibration instruction in the manual. Multiple calibration files can be stored for the various levels anticipated. Experience has shown that it is not required to run new standards and new calibration on every batch of samples.

h) For each batch, initially check the validity of stored calibrations by running a TOC and a TC standard at expected concentrations. Rerun the standard solutions if the average area count of a standard is greater than ±2% of the calibration.

i) The analysis for each batch of samples is run in the following order:

Run a QC standard in the range of expected concentration.
Run the field blank.
Run the samples.
Run QC standards that bracket the sample concentrations.

4.6 TOC Analysis Quality Assurance (QA) Criteria

a) The precision of the TOC analysis must be 10% or less as determined using the percent coefficient of variation (COV) from the three injections calculated as follows:

COV = 100 x (standard deviation / mean)

Where: The standard deviation of TOC is determined from the square root of the sum of the squares of the standard deviations for TC and IC.

b) Accuracy of the QC sample as % difference from the prepared concentration must be within ±10%.

c) TOC of the field blank concentration can be reported along with the results but not used to correct the results. The field blank is typically equal or higher than lab DI water blank (typically ~ 1 ppmC).

d) IC concentration of sample should be less than 10 ppmC (typically ~2 to 5 ppmC), otherwise, make a note on the report.

4.7 TOC Calculations

Subtract the laboratory DI water blank TOC (not field blank) from the average of the three sample analyses to yield a result for TOC in ug/ml of condensate trap water (C_i). Calculate the amount of organic carbon as part per million by volume (ppmv) as gaseous carbon in the sample using the following equation:

$C_w = (C_i \times V_i \times P_a \times V_{id})/(V_c \times P_r \times A_c)$

where:

A_c = Atomic weight of carbon (12.01 g/mol)

C_w = gaseous concentration of TOC as ppmv in condensate trap water

C_i = TOC concentration in ug/ml of condensate trap water

(Assume TOC concentration ug/g = ug/ml at 4^oC)

V_i = volume of condensate trap water in ml

V_{id} = volume of ideal gas per mole at 25^oC (24.4652 liters/mole)

V_c = volume of the SUMMA canister in liters

P_a = atmospheric pressure in mm Hg (760 mm Hg)

P_r = return pressure in mm Hg

4.8 Apparatus and Reagents for TCA Analysis by GC/FID on Canisters

4.8.1 TCA System

The Total Combustion Analysis (TCA) system consists of gas chromatography (GC) modified with a backflush valve with reversed flow capability for back-flushing the trapped NMNEOC. It is also equipped with a catalytic oxidizer, a catalytic reducer, a flame ionization detector (FID), and a data handling system. A gas sample is injected, using a 1 ml fixed loop 6-port gas injection valve, onto a dual packed column. The NMNEOC analyzer is a semi-continuous GC/FID analyzer capable of: (1) separating carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), ethane (C_2H_6), ethylene (C_2H_4), and NMNEOC, (2) oxidizing the NMNEOC to CO_2, and CO to CO_2, (3) reducing the resulting CO_2 to CH_4, (4) quantifying the CH_4, and (5) after ethane elutes from the GC column, the column is heated and backflushed to release remaining organic compounds. The resulting CH_4 is quantified against a stored standard curve by the FID detector. See Figure 25.3-6 for a flow chart of the instrument. The instrumentation system flow diagram is shown in Figure 25.3-7.

The analytical equipment are available commercially or can be constructed from available components by a qualified instrument laboratory. The analyzer consists of the following major components:

a. Sample Injection System

A heated six-port valve injector fitted with a 1 ml sample loop is recommended. The sample loop consists of a sufficient length of 1/16 in. stainless steel tubing so that the desired internal volume is achieved. The installation of the valve is depicted in Figure 25.3-7. The sample injection port and sample loop must be equipped with a heating

mechanism that maintains the specified temperature of 150 ± 5 °C. The six port valve is located in the column oven.

b. Separation Column(s)

The gas chromatographic system consists of a two part column capable of separating carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4), ethane (C_2H_6), ethylene (C_2H_4), and NMNEOC. The two part column consists of Tenax GC 80/100 mesh in a 1 ft. length of 1/8 in. stainless steel tubing, in series with Chromosorb 106 80/100 mesh in a 6 ft length of 1/8 in. stainless steel tubing. The NMNEOC is trapped in the Tenax section of the column while the remaining compounds are eluted through the Chromosorb section. The backflush procedure is also performed through both sections of the column. The column is contained in an oven capable of performing the temperature ramping as specified in Section 4.9. A heated four port valve is used to control flow direction through the column as shown in Figure 25.3-7.

c. Oxidation Catalyst

A catalyst system capable of oxidizing CH_4 to CO_2 with at least 95 percent efficiency is acceptable. The oxidation catalyst system consists of 15% chromium III oxide on 4 mm alumina pellets packed in the center 4 in. section of a 12 in. length of 1/4 in. diameter Inconnel tubing. The remaining space on both ends of the tubing is packed with quartz wool for retention of the catalyst. The oxidation catalyst is contained within a heating device capable of maintaining a temperature of 650 ± 5 °C. A four port valve is used to control flow during either oxidation or

regeneration modes of the oxidation catalyst. The installation of the valve is depicted in Figure 25.3-7.

d. Reduction Catalyst (Methanizer)

A catalyst system capable of reducing CO_2 to CH_4 with at least 95 percent efficiency is acceptable. The reducing catalyst consists of nickel on Gas Chrom R 80/100 mesh. To prepare the material, first dry the Gas Chrom R 80/100 at 120 ^{o}C overnight. Allow to cool to room temperature in a dessicator. Dissolve 1 g of nickelous nitrate in 30 ml deionized water. Slowly add 10 g of the dried Gas Chrom R 80/100 mesh with constant stirring. Heat to dryness on a hot plate, then dry overnight at 230 ± 5 ^{o}C. Allow again to cool to room temperature in a dessicator. The catalyst is then packed in the center 4 in. section of a 12 in. length of 3/16 in. diameter Inconnel tubing. Each of the remaining space at either end of the tubing is packed with quartz wool. The reduction catalyst is contained within a heating device capable of maintaining a temperature of 380 ± 5 ^{o}C. Reduction gas (hydrogen) is supplied to the nickel catalyst tube by a tee fitting between the oxidation and nickel catalyst tubes at a flow rate of approximately 45% of the total final flow.

e. Flame-Out Buffer

The flame out buffer consists of Haysep Q 80/100 mesh packed in a 6 ft. length of 1/8 in. diameter stainless steel tubing. The flame out buffer is maintained at the FID detector temperature of 220 ± 5 ^{o}C.

f. FID

An FID with a linear response (± 5 percent) over the operating range of 0.5 to 50 ppm CH_4 is acceptable.

g. Data Recording System

Digital integration system compatible with the FID is used for permanently recording the analytical results. The system must have a software program capable of point to point baseline subtraction from the standard and sample runs.

h. Sample flow valves

Three multi-port valves are needed to accomplish the sample, carrier, and purge gas flow paths in this method. As specified in sections 4.8.1a, 4.8.1b, and 4.8.1c, a six port valve is used in the sample injection system, a four port valve is used to control flow through the separation columns, and a four port valve is needed for regeneration of the oxidation catalyst. Figure 25.3-7 depicts the configuration of these four valves and the position during each of two modes for each valve.

i. Syringes

Gas tight syringes, 30 ml and 100 ml capacities.

j. Reagents

1. Chromatographic grade helium as carrier gas.
2. Reagent grade hydrogen for reduction of CO_2 and FID fuel.
3. USP breathing grade hydrogen-free air for FID combustion.
4. Three point NIST traceable CO calibration standards

5. Three point NIST traceable CO_2 calibration standards
6. NIST traceable 1 ppm, 3 ppm, 10 ppm, and 100 ppm CH_4 standards in pure nitrogen
7. NIST traceable 1 ppm, 3 ppm, 10 ppm, and 100 ppm C_2H_4 standards in pure nitrogen
8. NIST traceable 1 ppm, 3 ppm, 10 ppm, and 100 ppm iso-butane standards for backflush in pure nitrogen
9. A high purity CO_2 (approximately 12% to 15% in pure hydrogen free nitrogen) is required as a background determination for high CO_2 sample.
10. Other standards as required

Note: Alternatively multi-component gases can be used for each concentration.

4.8.2 Other Apparatus and Reagents for TCA Analysis

Optionally the entire TCA system may be automated to control the temperatures, valving, and detector attenuation using a computer and control software. This system may feature analog/digital interface and a computer or an integrator for the data handling system.

4.9 TCA Analysis on the Canisters

4.9.1 Instrument Parameters and Gas Flow Rates

Set instrument parameters as follows:

Sample Injection Port/Loop : $150 \pm 5\ ^{o}C$

Detector : $220 \pm 5\ ^{o}C$

Oxidation catalyst : $650 \pm 5\ ^{o}C$

Reduction catalyst : 380 ± 5 ^{o}C

Heated transfer lines : 105 ± 5 ^{o}C

Sample flow valves : inside separation column oven

Separation Column Oven

Initial : 50 ± 2 ^{o}C for 8 minutes starting at injection

Ramp : Increase at a rate of 50 ^{o}C/min for 2 minutes

Final : 150 ± 5 ^{o}C for 5 minutes

Column Bake-Out : 190 ± 5 ^{o}C for 2 minutes

Gas flow rates:

Helium Carrier	: 30 ml/min
Oxidation Catalyst Regeneration Air	: 100 ml/min
Oxidation Catalyst Air	: 180 ml/min
Methanizer Hydrogen	: 12.3 ml/min
FID Hydrogen	: 30 ml/min
FID Air	: 300 ml/min

4.9.2 Equipment Conditioning

a) Establish all initial temperatures and gas flow rates as specified above.

b) Switch the valving so that the GC carrier stream is routed through the oxidation catalyst system (Valves 1 and 2 of Figure 25.5-7 in Position 1) for 5 minutes.

c) Switch the valving so that the GC carrier stream is routed through both the oxidation catalyst and the reduction catalyst system (Valve 3 of Figure 25.5-7 in Position 1).

d) Turn on the detector air and hydrogen gases, then ignite the detector. The detector attenuation is set at 8 and the range at 12.

e) Flush the 30 ml size sample syringe five times with ultra pure nitrogen.

f) Flush ultra pure nitrogen gas through the sampling connector fitting for 30 seconds for cleaning purposes.

g) Clean the injection system by flushing at least three syringe volumes of ultra pure nitrogen gas.

4.9.3 TCA Procedure

Reproduce exactly the timing of valve switching and column temperature changes for each blank, sample, and standard runs in a series. The following is the sequence of events that occur during a single injection of standard, baseline, or sample; the required sequence in which standards blanks and samples are injected is given in Section 4.9.4. Refer to Figure 25.3-7 for references to the valve and position numbers as indicated in parentheses and to Figure 25.3-8 for a summary of the equipment operation.

a) Verify that the column temperature is 50 ± 2 ^{o}C and that the sample loop valve is switched so that the carrier gas is routed through the column (valve 1 in position 1). Also verify that the column valve is switched so that the carrier flows in the forward direction (valve 2 on position 1) and that the oxidizer valve is switched so that the carrier is routed through the oxidizer (valve 3 in position 1)

b) Inject at least 25 ml of sample with the 30 ml size syringe.

c) Immediately after completing the sample injection, switch the sample loop valve so that the carrier flows in the forward direction so that the sample loop is swept through the column (valve 1 in position 2)

d) Observe the chromatogram and allow the CO_2, CH_4, ethylene (if present), and ethane to be eluted from the column. An example chromatogram is shown in Figure 25.3-9. The period of time during which this takes place should be approximately eight minutes.

e) After ethane elutes, switch the column valve to backflush mode so that the carrier flow reverses direction through the column and elutes organics as a back-flush peak (valve 2 in position 2).

f) Immediately upon switching to backflush mode heat the column oven using a pre-set temperature profile so that the backflush elutes at a rate so that the detector responds in its analytical detection range. The temperature profile should be approximately a follows: Ramp: Increase at a rate of 50 ^{o}C/min for 2 minutes, Final: 150 ± 5 ^{o}C for 5 minutes.

In all of the steps, the valving is such that the effluent from the column is directed to the oxidation reduction and FID detector system. Detector output for the back-flush peak is sent to the integrator where a response vs. time curve is plotted and the area under the back-flush peak is integrated. The switching can be accomplished by manual or automated valving.

Since NMNEOC is a mixture, this back-flush peak may not be symmetrical; however, the area under a response vs. time curve is proportional to the amount of carbon present in the sample.

For high CO_2 (3% to 15%) and low back-flush (backflush from <1 to 10 ppm) samples, adjust run time to allow the detector signal to return to the baseline

before the back-flush peak elutes. Measure the CO_2 content separately by an instrument capable of measuring % levels CO_2 such as SCAQMD Method 10.1.

4.9.4 Order of Standard, Background, and Sample Injections

Several standards and backgrounds are run with a batch of samples because of the difficulty in measuring low level concentrations. The following is the order in which the standards and backgrounds must be run in relation to the samples. Each step is run through the full fore-flush and backflush of the procedure as previously described in Section 4.9.3.

a) Inject laboratory air to condition the system and serve as system check by comparing to historical injections. The system should be able to detect the background level of 2 - 10 ppm and be consistent with historical levels, otherwise repeat the laboratory air injection.

b) Inject CO_2 free N_2 gas to determine "background nitrogen" for NMNEOC peak (back-flush). The area counts of the back-flush should be within a historical acceptable area, otherwise repeat the background nitrogen injection. Save the background nitrogen chromatogram for background subtraction on the subsequent runs.

c) Inject three level concentrations of TCA standards (recommended: 3, 10 and 100 ppmv) to create a 3-point calibration curve. Accept the calibration curve if the measured concentrations are within 10% of the check standards. Otherwise repeat.

d) After calibration, again inject the background nitrogen.

e) Inject a 1 ppmv back flush standard. The measured back-flush concentration must be within ± 20% of the standard, otherwise repeat the background nitrogen and the 1 ppm backflush standard.

f) Inject the samples in duplicate (each sample is analyzed two times as in Section 4.9.3). Analyze low concentration samples before high concentration samples. No more than eight injections (four duplicates) may be performed in a single batch. Inject the nitrogen background between batches and at the end of the sample injections.

g) Run two QC standards, choose concentration levels that bracket the sample concentrations if possible. If the sample has back-flush concentration close to 1 ppmv, use 1 ppmv as the lower of the QC standards. The measured back-flush concentration should be within ± 20% of the standard, otherwise select a new background nitrogen for baseline subtraction as follows: Select the new background nitrogen chromatogram by injecting nitrogen followed by the 1 ppmv back flush standard. When the results of the 1 ppm back-flush standard are within the ± 20% criteria, the chromatogram for the nitrogen can be used for baseline subtraction. If necessary, divide a large batch of samples runs in the same day into small batches, and use different background nitrogen for baseline subtraction as long as the 1 ppmv back flush standard before and after that particular batch meet the ± 20% criteria.

In standby mode, the column temperature is set to 190 ± 5 ^{o}C. The valving is set so that air is allowed to flow through the oxidation catalyst in the backflush mode overnight (valve 1 position 2, valve 2 position 2, valve 3 position 2). This step is essential for the oxidation catalyst to be at full capacity for the next use.

The instrument must not be used unless the oxidation catalyst has been regenerated in this manner.

4.10 TCA Analysis Quality Assurance (QA) Criteria

Pre and post run QC concentrations must be within 10% the standard concentrations.

The following are the required agreement between duplicate analyses of a sample:

Back-flush concentration (ppmv)	% difference from mean
1-3	20
4-6	15
7-12	12
13-30	10
31-50	5

If the duplicate analyses do not fall within the required limit, run a third analysis. If after the third analysis, the mean does not meet the above requirements, review the instrument calibration and the baseline nitrogen for errors, make necessary changes, then restart from the background nitrogen step (Step d).

4.11 TCA Calculations

Calculate the concentration of component in the canister using the following equation :

$$C_c = C_m \times DF \times (P_f/P_r)$$

where

C_c = end of sampling canister concentration, ppmv

C_m = average of duplicate measured concentrations from TCA analysis, ppmv

DF = syringe dilution factor if applicable

P_f = canister pressure after pressurization, mm Hg

P_r = before purging canister pressure, mm Hg

Calculate the total VOC as equivalent to gaseous carbon using the following equation:

$$\text{Total VOC (ppmC)} = C_w + C_c$$

where

C_w = VOC from condensate trap water (ppmC)

C_c = VOC from canister(ppmv)

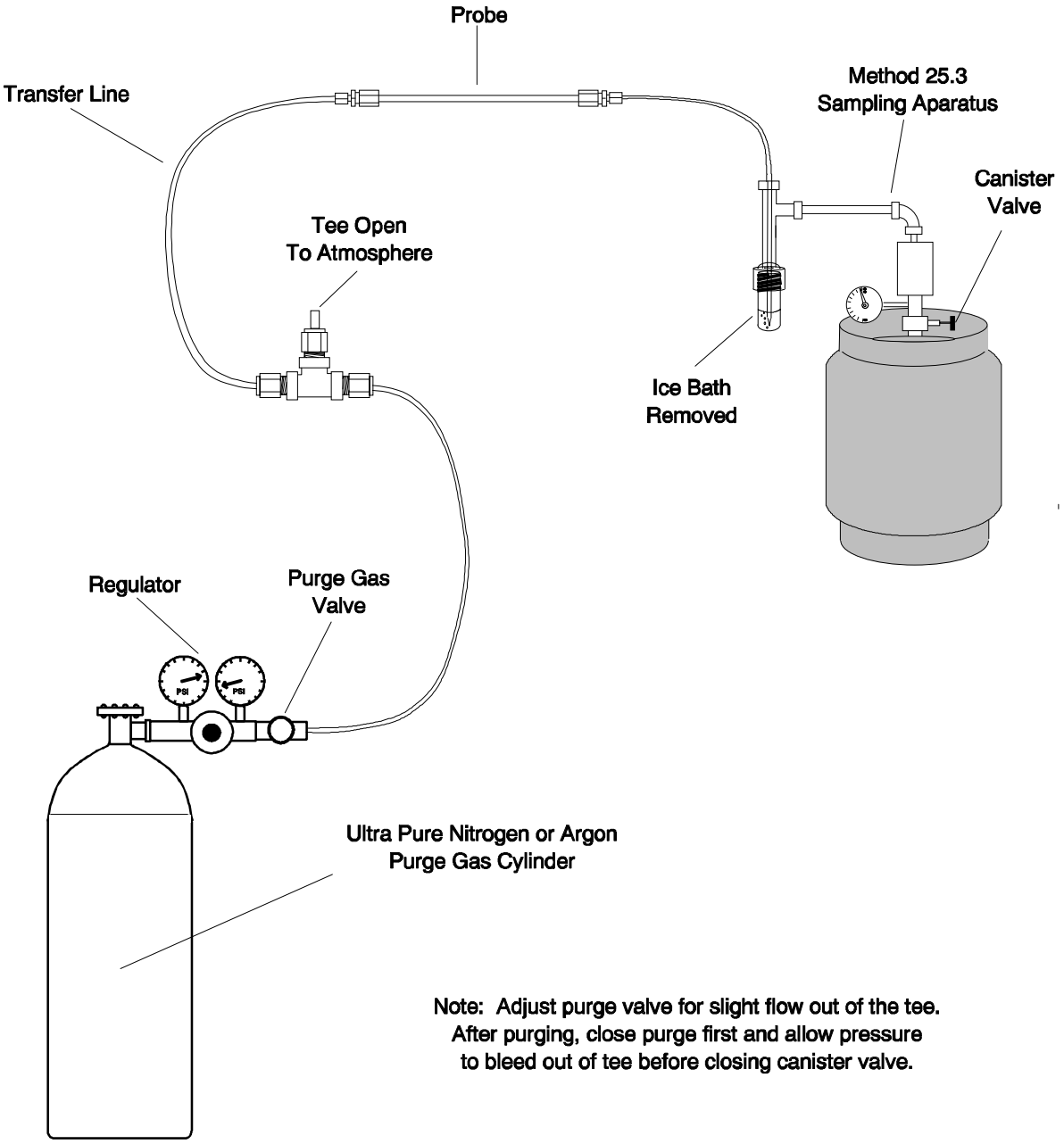

Figure 25.3-5 Inert Gas Purging

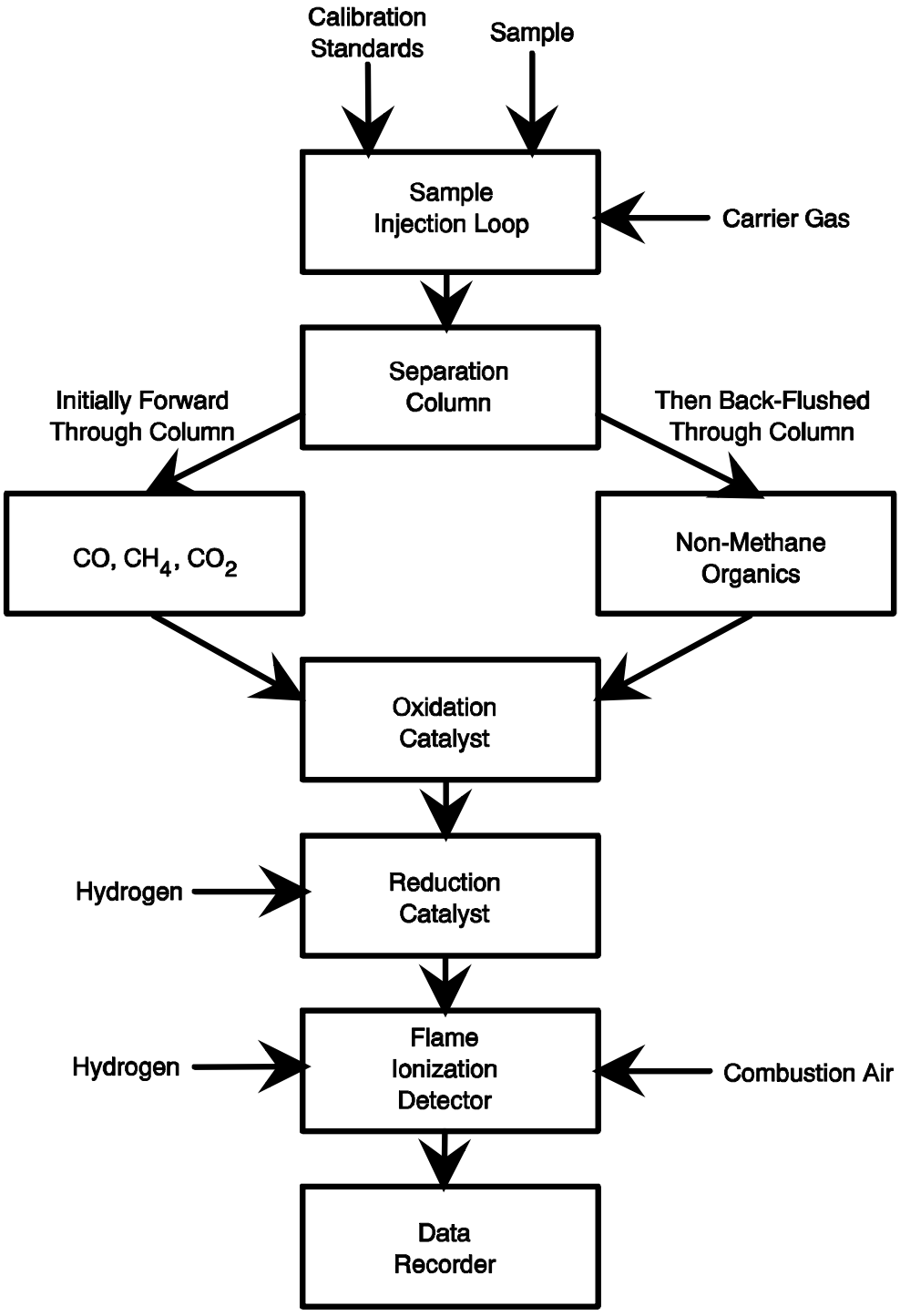

Figure 25.3-6 Flow Diagram for TCA Analysis on Canisters

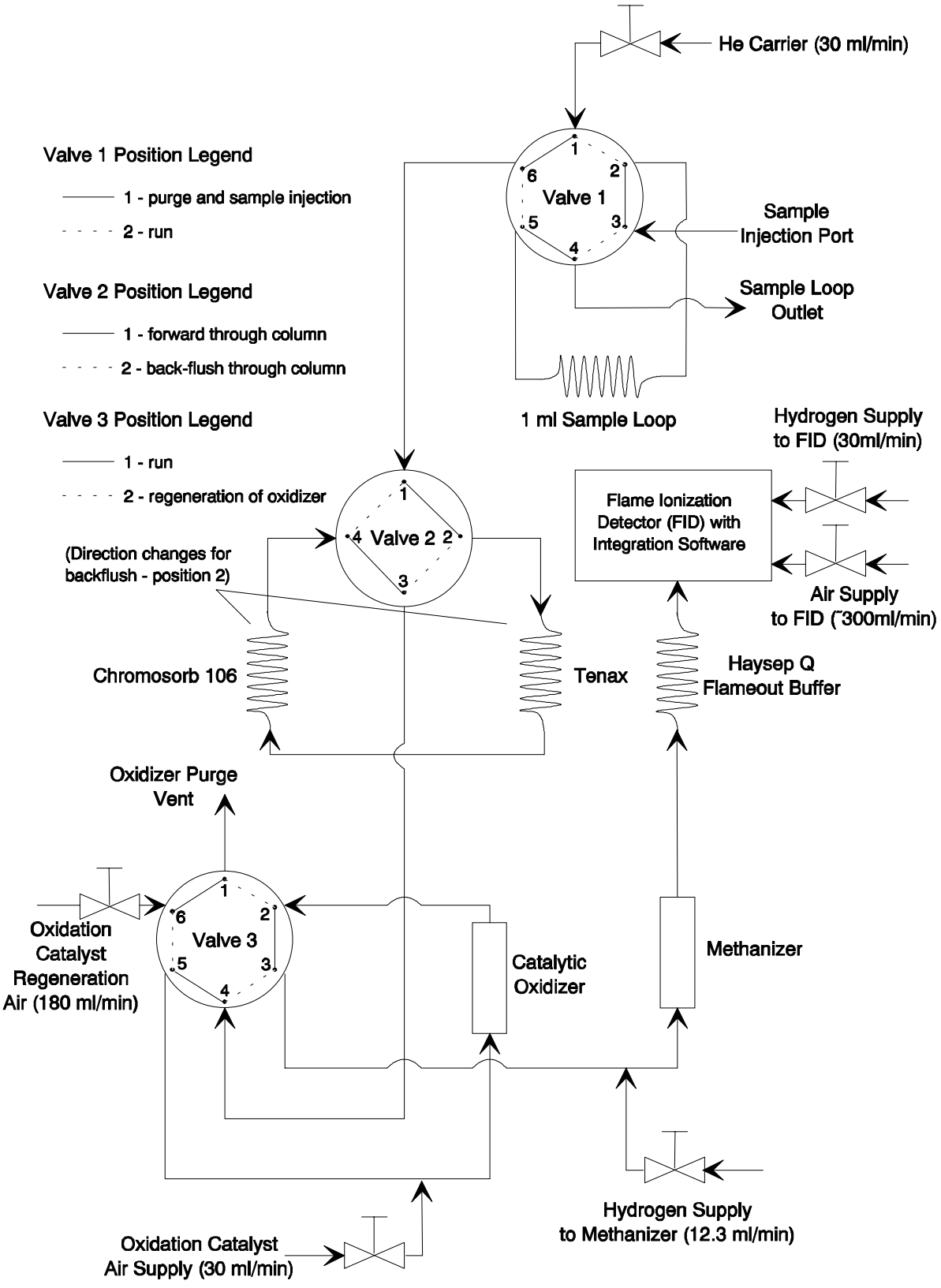

Figure 25.3-7 Equipment Diagram for TCA Analysis on Canisters

Equipment Operation for TCA Analysis on Canisters

Step #	Time	Valve 1 Position	Valve 2 Position	Valve 3 Position	Description
1	0	1	1	1	Verify Temperatures and Valve Positions
2	0	1	1	1	Inject Sample
3	after inj.	2	1	1	Switch Carrier Flow Through Sample Loop
4	0-8 min.	2	1	1	Observe CO_2, CH_4, Ethane Elute
5	8 min	2	2	1	Switch to Backflush Mode
6	8-15 min	2	2	1	Increase Column Oven Temp by 50^{o}C/min for 2 min, Hold at 150 ^{o}C for 5 min
7	Over-night	2	2	2	Increase Column Oven Temp to 190 ^{o}C to Regenerate Oxidation Catalyst

Figure 25.3-8 Equipment Operation for TCA Analysis on Canisters

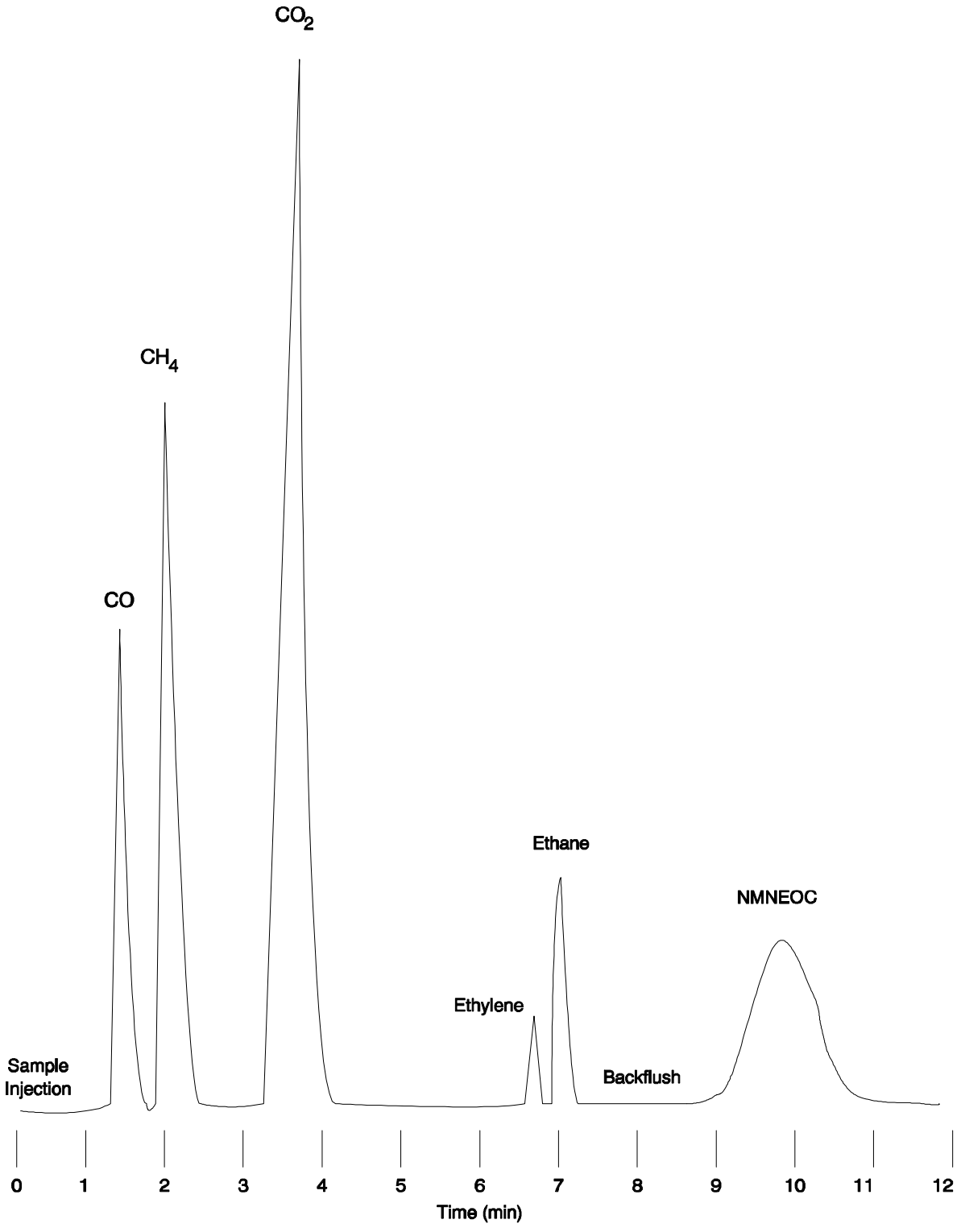

Figure 25.3-9 Example Chromatogram for TCA Analysis on Canisters

METHOD 25.3

DETERMINATION OF LOW CONCENTRATION NON-METHANE NON-ETHANE ORGANIC COMPOUND EMISSIONS FROM CLEAN FUELED COMBUSTION SOURCES

Section 5 of 5

5. Engineering Calculations and Reporting

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation.

5.1 Data Quality Checks

The results of the duplicate sampling for NMNEOC must not deviate more than 20% from the average of the two values in order to meet the precision criteria. The results of the duplicate sampling for carbon monoxide and carbon dioxide must not deviate more than 20% from the average of the two values in order to meet the leak indicator criteria. Field observations of occurrences that may cause sample bias may be used to invalidate one of the duplicate samples in the case that the 20% precision criteria is not satisfied. Individual results cannot, however, be discarded solely on the basis that the results disagree or that the results are higher than anticipated. Contamination cannot be used to invalidate the sample without substantial evidence that contamination occurred. Alternatively the lower value can be discarded for a worst case evaluation.

5.2 VOC Molecular Weight per Carbon Ratio

In order to convert the lab results as carbon to actual mass emissions as VOC. A molecular weight per carbon ratio must be either measured, calculated or assumed. Although a qualitative analytical speciation of the VOC using an approved method is preferable, it is sometimes not easily accomplished, and other times not feasible due to

partitioning of the sample into gaseous and condensable fractions. Other times the ratio can be calculated based on the VOC formulation of materials consumed in, for example, a coating or printing operation. In these situations, it is acceptable to use information provided in Material Data Safety Sheets (MSDS), if considered accurate. The use of MSDS information is generally, however, not considered as sufficiently accurate for calculating capture efficiencies. It is acceptable for calculating destruction efficiencies since the molecular weight per carbon ratio cancels out of the calculation when it is assumed that the ratio remains constant across the control device. In many cases the ratio can be considered as represented by a surrogate compound that is representative of the VOC encountered in the process. In the absence of any of the aforementioned information, common practice has dictated the use of a default ratio of hexane which is 14.36 lb/lb-mol C. Table 25.3-2 lists several general categories of molecular weight per carbon ratios which have been deemed as acceptable for the specified applications. Several specific examples are given below:

a. For Coating and Printing Processes:

Most Preferred: Volatile Carbon Analysis from SCAQMD Protocol for Determination of VOC Capture Efficiency

Calculation: 12 lb/lb mol x % VOC weighted average / % volatile carbon weighted average (all percents by weight)

Example: Coating #1 VOC = 50%, % volatile carbon = 40%, usage = 100 lb/hr
Coating #2 VOC = 80%, % volatile carbon = 60%, usage = 10 lb/hr

$$MW/C = \frac{12 \text{ lb/lb-mol} \times [(50\% \times 100 \text{ lb/hr}) + (80\% \times 10 \text{ lb/hr})]}{[(40\% \times 100 \text{ lb/hr}) + (60\% \times 10 \text{ lb/hr})]}$$

$$= 15.13 \text{ lb/lb-molC}$$

b. For Coating and Printing Processes: 2nd Choice- MSDS or Formulation Information

MSDS formulation is usually given as weight percent of the total coating/solvent

Calculation: $MW/C = \Sigma(MW \times mol\ frac)/ \Sigma(carbon\# \times mol\ frac)$

Example: Coating #1 VOC formulation = 10% benzene, 20% formaldehyde

usage = 10 lb/hr

Coating #2 VOC formulation = 30% butanol, 40% ethylene glycol monoethyl ether (a.k.a. EGMEE, Cellosolve; 2-Ethoxyethanol), usage = 100 lb/hr

Benzene Usage = (10% x 10 lb/hr) / 100 = 1 lb/hr

Formaldehyde Usage = (20% x 10 lb/hr) / 100 = 2 lb/hr

Butanol Usage = (30% x 100 lb/hr) / 100 = 30 lb/hr

EGMEE Usage = (40% x 100 lb/hr) / 100 = 40 lb/hr

$MW_{benzene}$ = 78 lb/lb-mol, $C\#_{benzene}$ = 6

$MW_{formaldehyde}$ = 30 lb/lb-mol, $C\#_{formaldehyde}$ = 1

$MW_{butanol}$ = 74 lb/lb-mol, $C\#_{butanol}$ = 4

MW_{EGMEE} = 90 lb/lb-mol, $C\#_{EGMEE}$ = 4

$mol\ frac_i = (usage_i / MW_i) / \Sigma(usage_i / MW_i)$

$\Sigma(usage_i / MW_i) = (1\ lb/hr_{benzene} / 78\ lb/lb\text{-}mol_{benzene})$
$+ (2\ lb/hr_{formaldehyde} / 30\ lb/lb\text{-}mol_{formaldehyde})$
$+ (30\ lb/hr_{butanol} / 74\ lb/lb\text{-}mol_{butanol})$
$+ (40\ lb/hr_{EGMEE} / 90\ lb/lb\text{-}mol_{EGMEE})$
$= 0.929\ lb\text{-}mol_{VOC}/hr$

$mol\ frac_{benzene} = (1\ lb/hr_{benzene} / 78\ lb/lb\text{-}mol_{benzene}) / 0.929 = 0.014$

$mol\ frac_{form} = (2\ lb/hr_{form} / 30\ lb/lb\text{-}mol_{form}) / 0.929 = 0.072$

$mol\ frac_{butanol} = (30\ lb/hr_{butanol} / 74\ lb/lb\text{-}mol_{butanol}) / 0.929 = 0.436$

$mol\ frac_{EGMEE} = (40\ lb/hr_{EGMEE} / 90\ lb/lb\text{-}mol_{EGMEE}) / 0.929 = 0.478$

$$MW/C = \frac{(78 \times 0.014) + (30 \times 0.072) + (74 \times 0.436) + (90 \times 0.478)}{(6\ C \times 0.014) + (1\ C \times 0.072) + (4\ C \times 0.436) + (4\ C \times 0.478)}$$

$MW/C = 20.6\ lb/lb\text{-}molC$

c. If the permit or other emissions limit is specified as a specific compound:

Calculation: MW/C# of specified compound

Example: Permit limit is specified as emissions in units of VOC as Hexane

MW = 86.17 lb/lb-mol

C# = 6.000

MW/C = 86.17 lb/lb-mol / 6.000 C

MW/C = 14.36 lb/lb-mol

d. For Combustion of Only Natural Gas Only:

Calculation: MW/C# of Methane or Hexane. Methane is preferable when either a worst case emission rate is desired or formaldehyde by-products may be present due to incomplete combustion. Incomplete combustion may be indicated by unusually high levels of methane or carbon monoxide.

Example: as Methane.

MW = 16.04 lb/lb-mol

C# = 1.000

MW/C = 16.04 lb/lb-mol / 1.000 C

MW/C = 16.04 lb/lb-mol

e. For fugitive emissions from petroleum processing operations:

Calculation: MW/C# of propane or other compounds if known

Example: as propane

MW = 44.10 lb/lb-mol

C# = 3.000

MW/C = 44.10 lb/lb-mol / 3.000 C

MW/C = 14.70 lb/lb-mol

e. For processes that use strictly petroleum distillates:

Calculation: ((14 x C#) +2) / C#

Example: for an average carbon number of 8.

MW/C = ((14 x 8) +2) / 8

MW/C = 14.3 lb/lb-mol

In absence of any information regarding the composition of the VOC, generally the molecular weight per carbon ratio of hexane is assumed (14.36 lb/lb-molC). As for the general range of molecular weight to carbon ratios for most VOC mixtures encountered, formaldehyde (30.03 lb/lb-molC) and methanol (32.04 lb/lb-molC) represent the upper bounds, while benzene represents the lower bound (13.02 lb/lb-molC). In applications where the molecular weight per carbon ratio is either difficult to determine as above or in dispute, a worst case scenario can be used for compliance purposes .

5.3 Bias Correction Factor

During the USEPA's Office of Air Quality Planning and Standards (OAQPS) evaluation of this source test method, it was determined that a bias correction factor must be applied to all results achieved by this method. This correction factor of 1.086 was determined according to USEPA Method 301 for validating test methods and was based on the results of the validation testing. The calculation is performed as follows:

Corrected Conc. (ppmC) = Total VOC (ppmC as determined in Section 4.11) x 1.086

5.4 VOC Mass Emission Rate Calculation

The individual VOC mass emission rates are determined using the following quantities for each duct or stack where both a concentration and corresponding flow rate are determined:

C - Average Corrected Concentration of Non-Methane Non-Ethane Organic Compounds (NMNEOC) from the Method 25.3 sampling pairs reported in ppmC;

Q - Volumetric flow rate as determined by SCAQMD Methods 1.1 through 4.1 in dry standard cubic feet per minute;

MW - Molecular Weight per Carbon Ratio as determined in Section 5.2 in lb/lb-mol C;

The VOC mass emissions rate in pounds per hour can then be calculated as follows:

VOC Mass Emission Rate (lb/hr) = $1.583 \times 10^{-7} \times MW \times C \times Q$

These calculations can be performed by using the calculation sheet in Figure 1. If multiple emission points are present, the VOC mass emission rate must be calculated separately as above and added together for a total VOC mass emission rate.

Application	Method	Calculation	MW/C Ratio	Typical Range
Coating and Printing Operations	% Volatile Carbon Analysis from SCAQMD Protocol for Determination of VOC Capture Efficiency	12 lb/lb mol x % VOC weighted average / % volatile carbon weighted average	Varies	13-32 lb/lb-mol C
Coating and Printing Operations	MSDS Information	Σ(MW x mol frac)/ Σ(carbon# x mol frac)	Varies	13-32 lb/lb-mol C
When Permit Specifies Compound to be Reported as:	Specified Compound	MW/C#	Varies	13-32 lb/lb-mol C
Natural Gas/Fuel Gas Combustion	Assume Hexane	MW/C#	14.36 lb/lb-mol C	14.36 lb/lb-mol C
Natural Gas/Fuel Gas Combustion for Worst Case or Incomplete Combustion	Assume Methane (although non-VOC, sometimes used, accounts for formaldehyde formation)	MW/C#	16.04 lb/lb-mol C	16.04 lb/lb-mol C
Fugitive Emissions from Petroleum Processing Operations	Assume Propane	MW/C#	14.70 lb/lb-mol C	14.70 lb/lb-mol C
Ethanol Only Processes (ethanol combustion, investment casting, flexographic processes)	Assume Ethanol	MW/C#	23.03 lb/lb-mol C	23.03 lb/lb-mol C
Processes That Use Strictly Petroleum Distillates	Average Carbon Number	$\frac{((14 \times C\#) + 2)}{C\#}$	Varies	14-15 lb/lb-mol C
Processes where the Formulation of the VOC is Known	VOC Formulation	Σ(MW x mol frac)/ Σ(carbon# x mol frac)	Varies	13-32 lb/lb-mol C
In Absence of Information for Applying Any of the Above	Assume Hexane	MW/C#	14.36 lb/lb-mol C	14.36 lb/lb-mol C

Figure 25.3-10 Molecular Weight per Carbon Ratios

Test No._____ Date _____

SOURCE TEST CALCULATIONS

Duct Identification	Flow Rate (dscfm)	NMNEOC Conc. (ppm)	VOC Mass Rate (lb/hr)
#1 #2 #3 #4			
TOTAL		N/A	

WHERE:

VOC Mass Rate =

1.583×10^{-7} x (Flow Rate dscfm) x (NMNEOC ppm) (MW per Carbon Ratio lb/lb-mol C)

FIGURE 25.3-11
VOC MASS EMISSION RATE CALCULATION