Field Testing Protocol for Characterization of Total Gaseous Nonmethane Organics (TGNMO), Methane, and Ethane in Air–Vapor Mixture During Filling of a Cargo Vessel with Crude Oil

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Field Testing Protocol for Characterization of Total Gaseous Nonmethane Organics (TGNMO), Methane, and Ethane in air–vapor Mixture During Filling of a Cargo Vessel with Crude Oil

1 Scope

1.1 Applicability

This method applies to the measurement of volatile organic compounds (VOC) as total gaseous nonmethane organics (TGNMO), methane and ethane from the air–vapor mixture that is expelled during filling of a cargo vessel with crude oil. This protocol utilizes a modified version of U.S. EPA Federal Reference Method 25 (FRM 25) entitled: *"Determination of Total Gaseous Nonmethane Organic Emissions as Carbon."* Annex A contains an abridged and modified version of FRM 25 to meet specific project quality objectives (PQOs).While the field testing in support of this protocol (see Annex B, Annex C, and Annex D) was performed only for the loading of crude oil into barges, the method could be suitable for loading of any volatile organic liquid into any type of vessel or compartment from which vapors are exhausted through a single vent opening where the field sampling can take place.

The objective of this field testing protocol is to provide standardized testing methodology for quantifying TGNMO, methane and ethane emissions in the air–vapor mixture that is expelled from cargo compartments during filling with crude oil.

The characteristics and composition of the air–vapor mixture expelled from a cargo vessel into the atmosphere during filling with crude oil is dependent upon the characteristics of the crude oil, including such variables as volatility, temperature, etc. The changing characteristics of the exhausted air–vapor mixture can affect the application of FRM 25 in quantifying the concentration of TGNMO, methane, and ethane in the air–vapor mixture. This field testing protocol provides guidance on utilizing various configurations of FRM 25 in the characterization process. They are:

- Time-Integrated Sampling: The traditional FRM 25 sampling train configuration is used but modified by adding a water condensate trap in front of the volatile organic compound (VOC) condensate trap to drop out the water content found in the air-vapor mixture. The water condensate trap prevents freezing of the VOC condensate trap by the water molecules which would lead to reduced gas flow through the sampling system.
- Instantaneous Sample: In this configuration, the FRM 25 condensate trap(s) [i.e. water and VOC traps] are removed from the sampling train and instantaneous samples of the air–vapor mixture are acquired periodically during the filling process, utilizing a pre-evacuated canister.

When carbon dioxide (CO_2) and water vapor are present together in the air–vapor mixture, they can produce a positive bias in the sample. The magnitude of the bias depends on the concentrations of CO_2 and water vapor. As a guideline, multiply the CO_2 concentration, expressed as volume percent, times the water vapor concentration. If this product does not exceed 100, the bias can be considered insignificant. For example, the bias is not significant for a source having 10 % CO_2 and 10 % water vapor, but it would be significant for a source near the detection limit having 10 % CO_2 and 20 % water vapor.

1.2 Principle

An emission sample from the air–vapor mixture is withdrawn at a constant rate through an unheated stainless-steel sampling probe, a water-chilled condensate trap, and a dry ice condensate trap by means of an evacuated sample canister. After sampling is completed, the concentrations of TGNMO, methane, and ethane are determined by independently analyzing the condensate traps and sample canister fractions and combining the analytical results. The organic content of the condensate trap fractions are determined by oxidizing the nonmethane organics (NMO) to CO_2 and quantitatively collecting the effluent in a second evacuated canister; then a portion of the CO_2 is reduced to CH_4 and measured by a flame ionization detector (FID). The organic content of the field sample canister fraction is

measured by injecting a portion of the field sample canister into a gas chromatographic column to separate the NMO from carbon monoxide (CO), CO₂, and CH₄; the NMO are oxidized to CO₂, reduced to CH₄, and measured by a FID. In this manner, the variable response of the FID associated with different types of organics is eliminated. Figure 1 outlines the analytical scheme while Figure 2 illustrates the response of the FID to analysis of a field sample.

2 Field Sampling Apparatus

2.1 General

The sampling system consists of a probe, a water condensate trap, a VOC condensate trap, a flow control system, and a sample canister. The TGNMO sampling equipment can be constructed from commercially available components and components fabricated in a machine shop. Figure 3 documents a typical sampling system. The equipment required is listed in 2.2 to 2.8.

2.2 Sampling Probe

The sampling probe is constructed of a 6.4 mm ($^{1}/_{4}$ in.) OD stainless steel tube. An inverted stainless steel funnel can be attached to the tip of the probe. The probe is unheated and is attached to the water condensate trap. The probe can be of various lengths to accommodate various sampling locations.



Figure 1—Analytical Diagram of Gas Chromatograph (CG), Oxidizing and Reducing Catalysts, and Flame Ionization Detector (FID) Specified in FRM 25 Analysis



NOTE The above chromatogram represents an overlay of separate chromatographic analyses of the sample canister and trap required for quantification of target analytes as specified in Federal Reference Method 25 (FRM 25).

Figure 2—Analytical Chromatogram Associated With FRM 25 Analysis for Quantifying TGNMO, Methane, and Ethane Emissions in an Air–Vapor Mixture

2.3 Water Condensate Trap

air–vapor gas streams in the cargo compartment can contain liquid droplets of water or have very high relative humidity. Under these conditions, it is advisable to attach a water condensate trap between the probe outlet and the inlet of the VOC condensate trap. The water condensate trap is a 9.5 mm (³/₈ in.) 316 stainless steel tubing bent into a U-shape (approximately 10 in. in length). The tubing is not packed but is hollow. During sampling, the trap is immersed in a water/ice mixture contained in a small cooler to reduce the temperature of the gas stream for removal of water from the air–vapor mixture. The water condensate trap is illustrated in Figure 4.

2.4 VOC Condensate Trap

The VOC condensate trap is similar in construction to the water condensate trap. The VOC condensate trap is a 9.5 mm ($^{3}/_{8}$ in.) 316 stainless steel tubing bent into a U-shape (approximately 10 in. in length). The tubing is packed with coarse quartz wool, to a density of approximately 0.11 g/mL before bending. During sampling, the trap is immersed in dry ice contained in a small cooler to reduce the temperature of the gas stream to -50 °C in order to condense the VOCs in the air–vapor mixture. The very volatile VOCs in the air–vapor mixture pass through the trap and are captured in an evacuated canister downstream of the condensate trap. The dry ice VOC condensate trap is illustrated in Figure 4.



Figure 3—Typical Time-Integrated Sampling Train Used for Measuring TGNMO, Methane, and Ethane in Air–Vapor Mixture During Filling of a Cargo Vessel with Crude Oil

2.5 Metering Valve and Rate Meter

A stainless steel metering valve (sampling valve) is inserted into the sampling system for starting and stopping sample flow through the sampling train. A rate meter, which is a rotameter or equivalent, indicates the flow of sample gas (i.e. 5 mL/min to100 mL/min) through the sampling system. The metering valve and rate meter are contained in the mini-box of the sampling train, as illustrated in Figure 3.

2.6 Sample Canister

The final component of the sampling train is the stainless steel or aluminum canister with a specified volume of 4.2 L. It is preferable to use a larger canister, such as 8.3 L, for time-integrated sampling, in order to minimize the likelihood of having to change canisters during the sampling period. The canister is pre-cleaned before using in the field. The canister captures those very volatile VOCs (i.e. methane, ethane, ethylene, and propane) which are typically C3s and less. However, other organic and inorganic compounds can be trapped in the canister during sampling. The canister also serves as the pump in the sampling system. Before sampling, the canister is evacuated to at least 10 mm Hg vacuum, as measured by a portable vacuum gauge, by way of a heavy-duty vacuum pump. Once evacuated, the canister is inserted into the sample train by attaching it to a three-way valve located in the mini-box. When the three-way valve is moved to the sample position, the air–vapor gas sample is pulled through the probe, through the water condensate trap, through the VOC condensate trap, through the flow control valve and rate meter, and into the evacuated canister. In general, VOCs with >3 or more carbons are retained in the VOC cryogenic trap while the VOCs with less than three carbons are retained in the canister. After a prescribed sampling time, the canister and trap are recovered and sent to the laboratory for analysis.



Figure 4—Close-up View of Water Condensate Trap and VOC Condensate Trap

2.7 Mercury Manometer or Absolute Pressure Gauge

Capable of measuring pressure to within 1 mm Hg in the range of 0 mm to 900 mm.

2.8 Vacuum Pump

Capable of evacuating to an absolute pressure of 10 mm Hg. Used for evacuating canisters prior to field use.

3 Sampling Reagents

- Crushed dry ice.
- Crushed ice.

4 Time-Integrated Field Sampling Procedure

4.1 Sampling Train Assembly

4.1.1 Position the sampling train close to the vent opening of the cargo compartment during filling operations. Extend the ¹/4 in. sampling probe (with an inverted funnel attached, if one is used) a few inches down into the cargo compartment (if sampling at an open hatch, in the centroid of the hatch a few inches below the opening of the hatch; if sampling at a vent stack, near the centroid of the stack at a position below the flame arrestor). The probe inlet shall be above the highest level that the crude oil will reach during filling. Guide wires can be used to support the probe

system. The sample gas is then extracted through the unheated stainless steel probe to the sampling train next to the cargo compartment vent opening.

Quality assurance/quality control (QA/QC) activities are important in quantifying the concentration of TGNMO, methane, and ethane in the air–vapor mixture that is expelled from cargo compartments during the filling with crude oil. Table 1, Table 2, Table 3, Table 4 and Table 5 provide guidance and checklists which should be incorporated into any sampling program to ensure that accurate and reliable data are acquired.

Host Facility	Testing Contractor	Comments/Check Off
Notifies testing contractor of a candidate vessel and conveys the following information:	Testing contractor should perform the following activities:	Arrange for conference call with host facility and vessel personnel to discuss logistics
- Location of the vessel	Develop draft sampling procedures	or vesser and their schedule
 Date(s) of availability Detail sketch/digital images of anticipated sampling location (vessel hatch or vent stack) Anticipated time of day that transfer of crude to vessel to occur and length of transfer Specific safety requirements associated with testing onboard vessel at the intended location, intrinsically safe equipment needs, any harness requirements, safety training requirements, personnel safety equipment needs etc.) Identify possible lodging arrangements local to the vessel location 	 Identify and meet with analytical laboratory to verify qualifications and verifying that pre-test QA/QC requirements of FRM 25 are performed Document FRM 25 equipment preparation, calibrated and certification prior to pick-up 	
 Identify local suppliers of dry ice 		
	Contact host facility and vessel coordinator through conference call to:	Verify with project personnel the data quality objectives (DQOs) of the project with
	 Confirm the anticipated dates of testing and identification of sampling locations on vessel 	regard to quantification of specific analytes (i.e. CO, methane, CO_2 , ethylene, ethane, and TGNMO)
	 Obtain host facility information (i.e. telephone number, receiving address, contact vessel personnel etc.) 	
	 Finalize testing schedule based upon loading of crude to vessel 	

Table 1—Various Project Activities to be Completed by Host Facility and Testing Contractor

6

Table 1—Various Project Activities to be Completed by Host Facility and Testing Contractor (Continued)

Host Escility	Tosting Contractor	Commonts/Chock Off
		Comments/Check Off
Vessel Activities:	Testing arrangements through host facility:	Perform pre-test calibration of FRM 25 testing equipment:
respect to the host facility with support for equipment logistics and manpower support	contractor	 — Sample canister volume determination
	 Acquiring certified testing equipment and shipment to host facility 	 Calibration of thermocouples
	 Finalize sampling rate/time and number of test needed to characterize emissions during filling of vessel 	 Calibration of rate meter
	 Determine FRM 25 number of traps and canisters needed for project completion 	 Certification clean of water trap/cryogenic trap/ canister components
	 Determine type/number of spare parts needed to have available during testing 	 Leak check sampling system
	Confirms with host facility that the testing is scheduled	
	Vessel activities:	
	 Prepare the sampling location(s) for testing (vessel hatch or vent stack) 	
	 If applicable, provide covers for hatches to prevent air in-leakage 	
	Travels to test site:	Pre-test items:
	 Identify logistics and location at host facility for equipment unpacking, set-up, calibration etc. 	 Attend health and safety meeting with host facility and vessel personnel
	 Pick-up dry ice from local supplier 	 Perform pre-test meeting with bost facility and
	 Put on all safety equipment as specified by vessel/project health and safety plan (HSP) 	vessel personnel covering monitoring objectives, equipment, personnel
	 Assemble the testing apparatus and haul to sampling location(s) 	schedule, process data needed during testing etc.
	 Assemble the probe support at the sampling location(s) 	
	 Verify that all equipment is properly positioned and ready for use 	
	 Record water and cryogenic trap numbers and canister numbers for each specific sampling event onto field test data sheets (FTDS) 	

Host Facility	Testing Contractor	Comments/Check Off
Vessel Documentation:	 Perform pre-test leak check of sampling systems using dummy canisters 	
Acquire needed process/transien date during testing of crude into vessel Record process data at required	 Purge sample line to water condensate trap with external vacuum canister for approximately 10 min 	
intervals during testing	 Reconnect sample line to water condensate trap 	
	 Place ice water/dry ice around individual condensate traps 	
	 Evacuate canisters off site to –29 in. Hg, leak check and connect to sampling train 	
	 Record initial vacuum of canister into FTDS 	
Vessel operator notifies testing contractor when filling begins		
	 Assemble FRM 25 sampling train containing certified clean water trap (optional), VOC condensate trap and canister 	Contact vessel personnel during filling to record appropriate process data
	 Begin sampling at specified flow-rate for a pre- determined sampling time by opening the canister valve to "open" position 	
	 Record sampling parameters i.e. flow rate, ambient temperature, ambient pressure etc.) during testing on the FTDS 	
Vessel operator notifies testing contractor when filling is complete		
	 At the end of filling, stop FRM 25 sampling by closing the canister valve to "off" position 	
	 Record final sampling data on FTDS 	

Table 2—Various Project (Sampling) Activities to be Completed by Host Facility and Testing Contractor

Table 3—Various Project (Clean up) Activities to be Completed by Host Facility and Testing Contractor

Host Facility	Testing Contractor	Comments/Check Off		
Vessel personnel provides all process data from test to Testing Contractor	 Performs final field-related functions: Disconnect the water (optional) and cryogenic traps from the sampling train Plug the ends of the traps and immerse in cryogen for transport to analytical laboratory Checks and records the final vacuum in the sample canisters and record on FTDSs 	Perform post-test meeting with host and vessel personnel		
	 Prepare all sampling components (i.e. water traps, cryogenic traps, and canisters) for shipment to analytical laboratory, completing chain-of-custody (COC) 			

Table 4—QC Checklist Associated with Sampling and Analytical Event

Question/Topic	Yes	No
Was a pre-site visit required and properly performed?		
Have sampling team members had official FRM 25 training and experience?		
Has contractor been informed of calibration data required on-site?		
Is obtaining a concentration of non-speciated gaseous organic compounds as carbon the object of the sampling and analysis?		
Are there sufficient amounts of carbon dioxide and water in the sample gas that the product of their percentage concentrations exceeds 100 and may cause interference to FRM 25?		
Have newly prepared water and condensate traps been checked for contaminants prior to use?		
Has the sample canister(s) been leak checked either in the lab or in the field?		
Was the sample canister vacuum checked?		
Was the required pretest leak check performed in accordance with FRM 25?		
Is a second sample canister available in the event a sample canister change has to be made prior to obtaining the minimum sample volume?		
Was the sample canister vacuum recorded immediately after the sampling was terminated?		
Is the trap packed and shipped to the lab in dry ice?		
Were the water and condensate traps flushed with zero air after sampling?		
Has a catalyst oxidation efficiency check been performed in accordance with FRM 25?		
Was the condensate trap purge confirmed to be less than 5 ppm of CO_2 ?		
Were two audit samples, if required, analyzed along with the collected samples		
For compliance testing, did the audit sample analysis results agree to within 20 % of the known concentration?		

Table 5—QC Checklist for Equipment and Reagents

ltem	Item Name Purpose or Function		
		Field Apparatus	
1	Apparatus calibration documentation	Verification of method required calibrations	
2	Training certifications	Verification of competency of sampling personnel	
3	Probe	Typical ¹ /4 in. stainless steel, unheated	
4	Water trap	A U-tube stainless steel tube for removing sample water	
5	VOC condensate trap	A quartz wool packed, U-shaped stainless steel tube for removing sample condensable VOCs	
6	Acquisition and metering system	Sampling rate meter and control valve located in mini-box	
7	Sample canister	A stainless steel canister of a minimum volume of 4 L	
		Laboratory Analytical Apparatus	
8	Condensate recovery system	A system which will heat and maintain the condensate collection tube at 200 $^\circ\mathrm{C}$	
9	Oxidation catalyst	A 19 % chromia packed on alumina pellets contained in a $^{3/\!8}$ in. Inconel $600^{\$}$ tubing	
10	Reduction catalyst	A 100 mesh nickel powder packed into an Inconel tubing	
11	NDIR detector	A nondispersive infrared detector (NDIR) to monitor the CO, within 0 % to 5 %, exiting the condensate trap during combustion	
12	NMO analyzer	A GC with back-flush capability and utilizing the oxidation and reduction catalyst and a flame ionization detector (FID)	
13	Mercury manometer	Measurement of vacuum pressure of collection vessel prior to and subsequent to sample collection	
14	Data recording system	A system to record the output of the FID	
15	Sample injection system	A ten port GC sample injection valve interfaced with the NIVIO monitor	
16	Barometer	To measure atmospheric pressure to within 1 mm Hg	
17	Carrier gases	Zero grade helium, ${\rm O}_2$ containing less than 1 ppm ${\rm CO}_2$ and 99.999 % hydrogen	
18	Calibration gases	Calibration of NMO analyzer using 20 ppm, 200 ppm, and 3000 ppm of propane-in-air	
19	Linearity gases	Nominal 50 ppm, 500 ppm, and 1 $\%~\text{CO}_2$ in air to check NMO and FID linearity	
20	NMO system checks	A nominal cylinder mixture of 50 ppm CH_4 , 50 ppm CO , 20 ppm propane, and 2 % CO with the balance gas being air	

4.1.2 Obtain clean water and VOC traps from the laboratory. Before its initial use and after each subsequent use, all condensate traps (both water and VOC traps) and canisters shall be thoroughly cleaned and checked to ensure that they are not contaminated. Both cleaning and checking can be accomplished by installing the trap in the condensate recovery system and treating it as if it were a sample as specified in FRM 25. The trap should be heated as described in A.5.1.4. A trap can be considered clean when the CO₂ concentration in its effluent gas drops below 10 ppm. This check is optional for traps that have been used to collect samples which were then recovered according to the procedure (see A.5.1.4). The canisters are "certified" clean (i.e. <10 ppm TGNMO) by analyzing their content according to FRM 25 (see Annex A). Obtain the laboratory "certificate" for both the traps and canisters from the laboratory and document on the field test data sheet (FTDS), Table 6.

Table 6—Field Test Data Sheet (FTDS)

General Information	
Facility	Sample Location
Location	Vessel Number
Date	Facility
Run Information	
Barometric Pressure ("Hg)	Ambient Temperature (°F)

Barometric Pressure ("Hg)_____ Pre-test Canister Vacuum (<10 mm Hg)_____ Pre-test Purge Performed?_____ Calculated Flow Rate (mL/min)_____ All Canisters Certified Clean? Ambient Temperature (°F)_____ Post Test Canister Vacuum (mm Hg)_____ Probe Positioned/Sealed?_____ All Traps Certified Clean?_____ Sampling Train Leak Check Acceptable?

Com	Components Identification				
Water Trap (Optional)	VOC Condensate Trap	Canister	Canister Vacuum mm Hg	Setting mL	Comments
	Com Water Trap (Optional)	Components Identific Water Trap (Optional) VOC Condensate Trap	Components Identification Water Trap (Optional) VOC Condensate Trap Canister Image: Construction of the second structure of the s	Components Identification Canister Canister Vacuum mm Hg Water Trap (Optional) VOC Condensate Trap Canister Canister Image: State of the sta	Components Identification Canister Trap (Optional) VOC Condensate Trap Canister Canister Vacuum mm Hg Flow Meter Setting mL Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Setting ml Image: Seting Image: Setting ml

4.1.3 The sample canisters shall be shipped under pressure to keep them clean. In the deployment area, using a high efficiency pump, evacuate the sample canister(s) to 10 mm Hg absolute pressure or less. Close the sample canister valve, and allow the canister to sit for 60 min. After 60 min, attach a vacuum gauge to the sample canister. The sample canister is acceptable if no change in canister vacuum is noted. The results of the canister vacuum test are recorded on the FTDS, Table 6. Obtain the needed traps and record their identification on the FTDS.

4.1.4 Transport the sample canister(s), the water and cryogenic traps, the mini-box and other materials to the sampling location.

4.1.5 Position the unheated stainless-steel probe near the sampling location. Plug the ends of the probe with aluminum foil. Assemble the sampling equipment at the sampling location. Measure the initial vacuum in the sample canister once again to verify that the canister has not leaked during transport. Record this vacuum, the ambient temperature, and the barometric pressure at this time on the FTDS. Close the sample canister valve and assemble the sampling system.

4.1.6 Unplug the condensate traps by removing the brass end caps. Using a connector, connect the two traps together, with the water condensate trap first followed by the VOC condensate trap (see Figure 3 and Figure 4). Immerse the first condensate trap body (i.e. water trap) in the water condenser, then immerse the second condensate trap body (i.e. VOC trap) in the dry ice.

Caution-Use gloves when handling dry ice.

Use small pellets of dry ice around the trap and pack the trap well before sampling.

NOTE The better the contact between the ice and trap, the better the heat transfer and the better the organics are trapped. If all of the heavy organics, especially oxygenated compounds, are retained in the VOC trap then better analytical results are acquired.

Keep the brass caps from the traps in a clean area and do not allow them to come in contact with pump oil, vacuum grease, or other contaminants.

Record the water and dry ice traps tags as identification of the components used during the sample run on the FTDS.

The point where the inlet tube joins the trap body should be 2.5 cm to 5 cm above the top of the dry ice. Cover the traps with foil to prevent sunlight from warming the traps.

4.1.7 Record "general information" of the test facility on the FTDS. Also record "run information" on the FTDS. See Table 6.

4.2 Sample Train Operation

4.2.1 Calculate or measure the approximate volume of the sampling train from the probe tip to the sample canister valve. After assembling the sampling train, plug the probe tip, and make certain that the sample canister valve is closed. Using a "T-connection," attach a "blank canister" to the sampling train along with a portable vacuum gauge. Open the "blank canister" valve and evacuate the sampling system from the probe tip to the "blank canister" to an absolute pressure of 10 mm Hg or less, as indicated by the portable vacuum gauge. Close the "blank canister" valve, wait a minimum period of 5 min, and recheck the indicated vacuum. Calculate the maximum allowable pressure change based on a leak rate of 1 % of the sampling rate. If the measured pressure change exceeds the calculated limit, correct the problem before beginning sampling. Record the results of the leak check on the FTDS. Unplug the probe tip, and place the probe into a pre-determined position at the sampling location (if sampling at an open hatch, in the centroid of the hatch a few inches below the opening of the hatch; if sampling at a vent stack, near the centroid of the stack at a position below the flame arrestor). The probe inlet shall be above the highest level that the crude oil will reach during filling. Seal the sample port sufficiently to minimize air inleakage around the probe.

4.2.2 Connect a "purge canister" to the "T-connect" on the probe line. Using the "purge canister," purge the sample probe for approximately 3 min. Close the "purge canister" valve and disconnect from the sampling system. Plug the "T-connect" with a fitting to prevent gas from escaping from the sample line.

4.2.3 Allow the water and VOC traps to equilibrate in their individual baths for approximately 10 min.

4.2.4 Connect the sample canister to the outlet of the mini-box by way of a PTFE line. Record the sample canister identification number on the FTDS.

4.2.5 To begin sampling, open the sample canister valve. Set the flow rate to approximately 12 mL/min using the rate meter in the mini-box. Record the clock time, date, sampling location, etc. on the FTDS. Also record component identification (i.e. water trap, dry ice trap, and canister) numbers on the FTDS.

4.2.6 Adjust the flow rate as necessary to maintain a constant rate (± 10 %) throughout the duration of the sampling period. Record the sample canister vacuum and flow meter setting at 30 min intervals on the FTDS. Intervals may be as long as 60 min if logistical constraints prevent more frequent monitoring of the sample train. During sampling, check the water condenser level and the dry ice level around the condensate trap. Add ice water and dry ice if necessary.

Monitor both the sample flow and the canister vacuum with the rate meter and gauge on the mini-box.

NOTE The vacuum gauge is a good monitor of the sample run.

If the sample canister vacuum does not drop sufficiently, the sample flow may not be correct.

4.2.7 Sampling is complete at the end of the filling operation.

If sampling had to be stopped before the filling operation is complete because a constant flow rate could not be maintained, proceed as follows. After closing the sample canister valve, remove the used sample canister from the sampling train (without disconnecting other components of the sampling train). Take another evacuated and leak-checked sample canister, measure and record the canister vacuum, and attach the new canister to the sampling train. After the new canister is attached to the sample train, proceed with the sampling until the filling operation has completed. Record sample canister identification on the FTDS. Also, if the traps freeze, preventing flow to be maintained, then warm up the inlet to each trap until flow is maintained.

4.3 Sample Train Recovery

4.3.1 After sampling is completed, close the sample canister flow control valve. Record the final canister vacuum on the FTDS. Record the final ambient temperature and barometric pressure on the FTDS.

4.3.2 Disconnect the sample canister from the sample system. Disconnect both the water and the condensate traps from the sampling system. Tightly seal both arms of the water and condensate traps with clean brass caps and pack in dry ice in a cooler.

4.3.3 Record the identification of the water condenser trap, the dry ice condenser trap and the sample canister(s) on the FTDS.

4.3.4 Store the traps packed in dry ice until the samples are returned to the laboratory for analysis. Ensure that the same test run number is properly identified on the condensate traps and the sample canister(s) and also recorded on the FTDS.

4.3.5 Complete "chain-of-custody" for the sample run and store with the samples in the deployment area.

5 Instantaneous Field Sampling Procedure

5.1 Sampling Train Preparation

5.1.1 Cleaning Sampling Equipment (Laboratory Certification)

Before its initial use and after each subsequent use, the canister(s) should be thoroughly cleaned and checked to ensure that they are not contaminated. Both cleaning and checking can be accomplished by installing the canister(s) in the FRM 25 sample analytical system and treating them as if they were a sample. A canister is clean when the TGNMO concentration is below 10 ppm. Obtain from the laboratory a "certificate" indicating that the canister(s) have been cleaned to the stated specification.

5.1.2 Sample Canister(s) Evacuation and Leak Check

Evacuate the sample canister(s) to 10 mm Hg absolute pressure or less. Then close the sample canister valve, and allow the canister to sit for 60 min. The canister is acceptable if no change in canister vacuum is noted. The evacuation and leak check is conducted in the field. The results of the leak check are recorded on the FTDS.

5.1.3 Pre-test Vacuum Check of Sample Canister

Just before assembly, measure the canister vacuum using an absolute pressure gauge. Record this vacuum, the ambient temperature, and the barometric pressure on the FTDS. Close the sample canister valve.

5.1.4 Pre-test Purge of Probe

Unplug the probe tip, and place the probe into a pre-determined position at the sampling location (if sampling at an open hatch, in the centroid of the hatch a few inches below the opening of the hatch; if sampling at a vent stack, near the centroid of the stack at a position below the flame arrestor). The probe inlet has to be above the highest level that the crude oil will reach during filling. Attach a pre-evacuated "purge canister" to the outlet of the probe and pull the air–vapor mixture in the cargo compartment through the probe for approximately 2 min. At the end of the purge, remove the "purge canister", and connect the probe to the sample canister.

5.2 Sampling Train Operation

5.2.1 Record the clock time, date, sampling location etc. on the FTDS. To begin sampling, open the sample canister valve. One will hear the rush of air–vapor mixture into the canister. The sample time is approximately 15 s to 30 s.

5.2.2 Once sampling is complete, close the sample canister valve. Note on the FTDS the canister ID, sample location, and sample time.

5.3 Sampling Train Recovery

5.3.1 Verify that the sample canister valve is closed. Disconnect the sample canister from the probe and store in a safe area. Complete any necessary field notes on the FTDS.

5.3.2 Complete a "chain-of-custody" for each sample canister and return to laboratory for analysis.

6 Nomenclature and Calculations

6.1 General

All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge or manometer pressure.

6.2 Nomenclature

С	TGNMO concentration of the effluent, ppm C equivalent
Cc	calculated condensable organic (condensate trap) concentration of the effluent, ppm C equivalent
$C_{\sf cm}$	measured concentration (NMO analyzer) for the condensate trap ICV, ppm CO ₂
Ct	calculated non-condensable organic concentration (sample canister) of the effluent, ppm C equivalent
$C_{\sf tm}$	measured concentration (NMO analyzer) for the sample canister, ppm NMO
F	sampling flow rate, mL/min
FID	flame ionization detector
FTDS	field test data sheet
GC	gas chromatograph
ICV	intermediate collection vessel
L	volume of liquid injected, μL
М	molecular weight of the liquid injected, g/g-mole
m _c	TGNMO mass concentration of the effluent, mg C/dsm ³
n	number of data points
N	carbon number of the liquid compound injected ($N = 12$ for decane; $N = 6$ for hexane)
NDIR	nondispersive infrared
NMO	nonmethane organics
P_{b}	barometric pressure, cm Hg
P_{f}	final pressure of the intermediate collection vessel, mm Hg absolute
P_{ti}	gas sample canister pressure before sampling, mm Hg absolute
Pt	gas sample canister pressure after sampling, but before pressurizing, mm Hg absolute
P_{tf}	final gas sample canister pressure after pressurizing, mm Hg absolute
q	total number of analyzer injections of intermediate collection vessel during analysis (where $k =$ injection number, 1 q)
r	total number of analyzer injections of sample canister during analysis (where $j =$ injection number, 1 r)
TGNMO	total gaseous nonmethane organics
T_{f}	final temperature of intermediate collection vessel, K
T _{ti}	sample canister temperature before sampling, K
Tt	sample canister temperature at completion of sampling, K
$T_{\sf tf}$	sample canister temperature after pressurizing, K
V	sample canister volume, m ³
VOC	volatile organic compounds
Vs	gas volume sampled, dsm ³
Vt	sample train volume, mL
Vv	intermediate collection vessel volume, m ³
xi	individual measurements
\overline{x}	mean value
θ	leak check period, min
ΔP	allowable pressure change, cm Hg

6.3 Calculations

6.3.1 Allowable Pressure Change

For the pretest leak check, calculate the allowable pressure change.

$$\Delta P = 0.01 \ \frac{FP_{b}\theta}{V_{t}}$$

6.3.2 Sample Volume

For each test run, calculate the gas volume sampled.

$$V_{\rm s} = 0.3857 V \left(\frac{P_{\rm t}}{T_{\rm t}} - \frac{P_{\rm ti}}{T_{\rm ti}}\right)$$

6.3.3 Non-condensable Organics

For each sample canister, determine the concentration of nonmethane organics (ppm C).

$$C_{t} = \left(\frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_{t}}{T_{t}} - \frac{P_{ti}}{T_{ti}}}\right) \left(\frac{1}{r} \sum_{j=1}^{r} C_{tm_{j}}\right)$$

6.3.4 Condensable Organics

For each condensate trap determine the concentration of organics (ppm C).

$$C_{\rm c} = 0.3857 \frac{V_{\rm v} P_{\rm f}}{V_{\rm s} T_{\rm f}} \left(\frac{1}{q} \sum_{k=1}^{q} C_{\rm cm_k}\right)$$

6.3.5 TGNMO

To determine the TGNMO concentration for each test run, use the following equation.

 $C = C_t + C_c$

6.3.6 TGNMO Mass Concentration

To determine the TGNMO mass concentration as carbon for each test run, use the following equation.

 $m_{\rm c} = 0.4993C$

6.3.7 Percent Recovery

To calculate the percent recovery for the liquid injections to the condensate recovery and conditioning system, use the following equation.

% Recovery = 1.604 (*M*/*L*) (V_V/P) (P_f/T_f) (C_{cm}/N)

6.3.8 Relative Standard Deviation

To calculate the relative standard deviation, RSD, use the following equation:

$$\mathsf{RSD} = \frac{100}{\bar{x}} \sqrt{\frac{\sum (x_i - \bar{x})^2}{n - 1}}$$

Annex A

(informative)

Federal Reference Method 25 (FRM 25) Determination of Total Gaseous Nonmethane Organic Emissions as Carbon (Abridged and Modified)

A.1 Applicability and Principle

A.1.1 Applicability

This method applies to the measurement of volatile organic compounds (VOC) as total gaseous nonmethane organics (TGNMO) as carbon in source emissions. The minimum detectable for the method is 50 ppm as carbon.

When carbon dioxide (CO₂) and water vapor are present together in the stack, they can produce a positive bias in the sample. The magnitude of the bias depends on the concentrations of CO₂ and water vapor. As a guideline, multiply the CO₂ concentration, expressed as volume percent, times the water vapor concentration. If this product does not exceed 100, the bias can be considered insignificant. For example, the bias is not significant for a source having 10 % CO₂ and 10 % water vapor, but it would be significant for a source near the detection limit having 10 % CO₂ and 20 % water vapor.

A.1.2 Principle

An emission sample is withdrawn from the source at a constant rate through an unheated sampling probe, a water condenser, a VOC condenser and a flow control module by means of an evacuated sample canister. After sampling is completed, the concentrations of TGNMO, methane, and ethane are determined by independently analyzing the condensate trap(s) and sample canister fractions and combining the analytical results. The organic content of the condensate trap(s) fractions are determined by oxidizing the nonmethane organics (NMO) to CO₂ and quantitatively collecting the effluent in an evacuated vessel; then a portion of the CO₂ is reduced to CH₄ and measured by a flame ionization detector (FID). The organic content of the sample canister fraction is measured by injecting a portion of the sample into a gas chromatographic column to separate the NMO from carbon monoxide (CO), CO₂, and CH₄; the NMO are oxidized to CO₂, reduced to CH₄, and measured by an FID. In this manner, the variable response of the FID associated with different types of organics is eliminated.

A.2 Apparatus

A.2.1 Field Sampling Apparatus

A.2.1.1 General

The sampling system consists of an unheated probe, a water condensate trap, a VOC condensate trap, a flow control system, and a sample canister. The TGNMO sampling equipment can be constructed from commercially available components and components fabricated in a machine shop. The equipment required is given in A.2.1.2 to A.2.1.8.

A.2.1.2 Unheated Probe

The unheated sampling probe is constructed of a 6.4 mm ($^{1}/_{4}$ in.) OD stainless steel tube. An inverted stainless steel funnel may be attached to the tip of the probe. The probe is unheated and is attached to the water condensate trap. The probe can be of various lengths to accommodate various sampling locations.

A.2.1.3 Water Condensate Trap

Air–vapor gas streams in the cargo compartment may contain liquid droplets of water or have very high relative humidity. Under these conditions, it is advisable to attach a water condensate trap between the probe outlet and the inlet of the VOC condensate trap. The water condensate trap is a 9.5 mm (³/₈ in.) 316 stainless steel tubing bent into a U-shape (approximately 10 in. in length). The tubing is not packed but is hollow. During sampling, the trap is immersed in a water/ice mixture contained in a small cooler to reduce the temperature of the gas stream for removal of water from the air–vapor mixture.

A.2.1.4 VOC Condensate Trap

The VOC condensate trap is similar in construction to the water condensate trap. The VOC condensate trap is a 9.5 mm ($^{3}/_{8}$ in.) 316 stainless steel tubing bent into a U-shape (approximately 10 in. in length). The tubing is packed with coarse quartz wool, to a density of approximately 0.11 g/mL before bending. During sampling, the trap is immersed in dry ice contained in a small cooler to reduce the temperature of the gas stream to -50 °C in order to condense the VOCs in the air–vapor mixture. The very volatile VOCs in the air–vapor mixture pass through the trap and are captured in an evacuated canister downstream of the condensate trap.

A.2.1.5 Metering Valve and Rate Meter

A stainless steel metering valve (sampling valve) is inserted into the sampling system for starting and stopping sample flow through the sampling train. A rate meter, which is a rotameter or equivalent, indicates the flow of sample gas (i.e. 5 mL/min - 100 mL/min) through the sampling system. The metering valve and rate meter are contained in the mini-box of the sampling train.

A.2.1.6 Sample Canister

The final component of the sampling train is the stainless steel or aluminum canister with a specified volume of 4.2 L. It is preferable to use a larger canister, such as 8.3 L, for time-integrated sampling, in order to minimize the likelihood of having to change canisters during the sampling period. The canister is pre-cleaned before using in the field. The canister captures those very volatile VOCs (i.e. methane, ethane, ethylene, and propane) which are typically C3s and less. However, other organic and inorganic compounds can be trapped in the canister during sampling. The canister also serves as the pump in the sampling system. Before sampling, the canister is evacuated to at least 10 mm Hg vacuum, as measured by a portable vacuum gauge, by way of a heavy-duty vacuum pump. Once evacuated, the canister is inserted into the sample train by attaching it to a three-way valve located in the mini-box. When the three-way valve is moved to the sample position, the air–vapor gas sample is pulled through the probe, through the water condensate trap, through the VOC condensate trap, through the flow control valve and rotameter, and into the evacuated canister. In general, VOCs with >3 or more carbons are retained in the VOC cryogenic trap while the VOCs with less than three carbons are retained in the canister. After a prescribed sampling time, the canister and trap are recovered and sent to the laboratory for analysis.

A.2.1.7 Mercury Manometer or Absolute Pressure Gauge

Capable of measuring pressure to within 1 mm Hg in the range of 0 mm to 900 mm.

A.2.1.8 Vacuum Pump

Capable of evacuating to an absolute pressure of 10 mm Hg. Used for evacuating canisters prior to field use.

A.2.2 Laboratory System Apparatus

A.2.2.1 Condensate Recovery Apparatus

A.2.2.1.1 General

The system for the recovery of the organics captured in the condensate trap(s) consists of a heat source, oxidation catalyst, nondispersive infrared (NDIR) analyzer, and an intermediate collection vessel (ICV). The system shall be capable of proper oxidation and recovery, as specified in Section A.5. The following major components given in A.2.2.1.2 to A.2.2.1.11 are required as part of the condensate recovery apparatus.

A.2.2.1.2 Heat Source

Sufficient to heat the condensate trap (including connecting tubing) to a temperature of 200 °C. A system using both a heat gun and an electric tube furnace is recommended.

A.2.2.1.3 Heat Tape

Sufficient to heat the connecting tubing between the water trap and the oxidation catalyst to 100 °C.

A.2.2.1.4 Oxidation Catalyst

A suitable length of 9.5 mm ($^{3}/_{8}$ in.) OD Inconel 600[®] tubing packed with 15 cm (6 in.) of 3.2 mm ($^{1}/_{8}$ in.) diameter 19 % chromia on alumina pellets. The catalyst material is packed in the center of the catalyst tube with quartz wool packed on either end to hold it in place. The catalyst tube shall be mounted vertically in a 650 °C tube furnace.

A.2.2.1.5 Water Trap

Leak proof, capable of removing moisture from the gas stream.

A.2.2.1.6 Syringe Port

A 6.4 mm (¹/4 in.) OD stainless steel tee fitting with a rubber septum placed in the side arm.

A.2.2.1.7 NDIR Detector

Capable of indicating CO_2 concentration in the range of zero to 5 %, to monitor the progress of combustion of the organic compounds from the condensate trap.

A.2.2.1.8 Flow Control Valve

Stainless steel, to maintain the trap conditioning system near atmospheric pressure.

A.2.2.1.9 Intermediate Collection Vessel (ICV)

Stainless steel or aluminum, equipped with a female quick connect. Canisters with nominal volumes of at least 6 L are recommended.

A.2.2.1.10 Mercury Manometer or Absolute Pressure Gauge

Capable of measuring pressure to within 1 mm Hg in the range of 0 mm to 900 mm.

A.2.2.1.11 Syringe

A 10 mL gas-tight, glass syringe equipped with an appropriate needle.

A.2.2.2 NMO Analyzer ¹

A.2.2.2.1 General

The NMO analyzer is a gas chromatograph (GC) with back flush capability for NMO analysis and is equipped with an oxidation catalyst, reduction catalyst, and FID. This semi-continuous GC/FID analyzer shall be capable of:

- 1) separating CO, CO₂, and CH₄, from NMO;
- 2) reducing the CO_2 to CH_4 and quantifying as CH_4 ; and
- 3) oxidizing the NMO to CO_2 , reducing the CO_2 to CH_4 and quantifying as CH_4 according to Section A.5.

The analyzer consists of the following major components given in A.2.2.2.2 to A.2.2.2.5.

A.2.2.2.2 Oxidation Catalyst

A suitable length of 9.5 mm ($^{3}/_{8}$ in.) OD Inconel 600[®] tubing packed with 5.1 cm (2 in.) of 19 % chromia on 3.2 mm ($^{1}/_{8}$ in.) alumina pellets. The catalyst material is packed in the center of the tube supported on either side by quartz wool. The catalyst tube must be mounted vertically in a 650 °C furnace.

A.2.2.2.3 Reduction Catalyst

A 7.6 cm (3 in.) length of 6.4 mm (¹/₄ in.) OD Inconel tubing fully packed with 100-mesh pure nickel powder. The catalyst tube must be mounted vertically in a 400 °C furnace.

A.2.2.2.4 Separation Column(s)

A 30 cm (1 ft) length of 3.2 mm (¹/₈ in.) OD stainless steel tubing packed with 60/80 mesh Unibeads[™] 1S followed by a 61 cm (2 ft) length of 3.2 mm (¹/₈ in.) OD stainless steel tubing packed with 60/80 mesh Carbosieve[®] G. The Carbosieve[®] and Unibeads[™] columns must be baked separately at 200 °C with carrier gas flowing through them for 24 hours before initial use.

A.2.2.2.5 Sample Injection System

A 10-port GC sample injection valve fitted with a sample loop properly sized to interface with the NMO analyzer (1 cm³ loop recommended).

A.2.2.3 FID

A.2.2.3.1 General

An FID meeting the following specifications given in A.2.2.3.2 to A.2.2.3.4 is required.

A.2.2.3.2 Linearity

A linear response (±5 %) over the operating range as demonstrated by the procedures established in A.6.3.4.

A.2.2.3.3 Range

A full scale range of 10 ppm to 50,000 ppm CH₄. Signal attenuators shall be available to produce a minimum signal response of 10 % of full scale.

¹ The registered terms in this Annex are used as examples only, and do not constitute an endorsement of these products by API.

A.2.2.3.4 Data Recording System

Analog strip chart recorder or digital integration system compatible with the FID for permanently recording the analytical results.

A.2.3 Other Analysis Apparatus

A.2.3.1 Barometer

Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 1 mm Hg.

A.2.3.2 Thermometer

Capable of measuring the laboratory temperature to within 1 °C.

A.2.3.3 Vacuum Pump

Capable of evacuating to an absolute pressure of 10 mm Hg.

A.2.3.4 Syringes

10 μ L and 50 μ L liquid injection syringes.

A.2.3.5 Liquid Sample Injection Unit

316 SS U-tube fitted with an injection septum.

A.3 Reagents

A.3.1 Sampling

The following are required for sampling:

- a) crushed dry ice;
- b) crushed ice.

A.3.2 NMO Analysis

The following gases are needed.

- a) **Carrier gases**: zero grade helium (He) and oxygen (O₂) containing less than 1 ppm CO₂ and less than 0.1 ppm C as hydrocarbon.
- b) Fuel gas: zero grade hydrogen (H₂), 99.999 % pure.
- c) Combustion gas: Zero grade air or O₂ as required by the detector.

A.3.3 Condensate Trap Analysis

The following gases are needed.

a) Carrier gas: zero grade air, containing less than 1 ppm C.

- b) **Auxiliary O₂**: zero grade O₂ containing less than 1 ppm C.
- c) **Hexane**: ACS grade, for liquid injection.
- d) Decane: ACS grade, for liquid injection.

A.3.4 Calibration

A.3.4.1 General

For all calibration gases, the manufacturer must recommend a maximum shelf life for each cylinder (i.e. the length of time the gas concentration is not expected to change more than ± 5 % from its certified value). The date of gas cylinder preparation, certified organic concentration, and recommended maximum shelf life must be affixed to each cylinder before shipment from the gas manufacturer to the buyer. The following calibration gases given in A.3.4.2 to A.3.4.5 are required.

A.3.4.2 Oxidation Catalyst Efficiency Check Calibration Gas

Gas mixture standard with nominal concentration of 1 % methane in air.

A.3.4.3 FID Linearity and NMO Calibration Gases

Three gas mixture standards with nominal propane concentrations of 20 ppm, 200 ppm, and 3000 ppm, in air.

A.3.4.4 CO₂ Calibration Gases

Three gas mixture standards with nominal CO₂ concentrations of 50 ppm, 500 ppm, and 1 %, in air.

NOTE Total NMO of less than 1 ppm required for 1 % mixture.

A.3.4.5 NMO Analyzer System Check Calibration Gases

Four calibration gases are needed as follows.

- 1) **Propane mixture**: gas mixture standard containing (nominal) 50 ppm CO, 50 ppm CH₄, 2 % CO₂, and 20 ppm C₃H₈, prepared in air.
- 2) Hexane: gas mixture standard containing (nominal) 50 ppm hexane in air.
- 3) Toluene: gas mixture standard containing (nominal) 20 ppm toluene in air.
- 4) Methanol: gas mixture standard containing (nominal) 100 ppm methanol in air.

A.4 Procedure

A.4.1 Field Sampling Time-Integrated Procedure

A.4.1.1 Sampling Train Assembly

A.4.1.1.1 The sampling train is positioned close to the vent opening of the cargo compartment during filling operations. The ¹/4 in. unheated sampling probe (with an inverted funnel attached, if one is used) is extended a few inches down into the cargo compartment (if sampling at an open hatch, in the centroid of the hatch a few inches below the opening of the hatch; if sampling at a vent stack, near the centroid of the stack at a position below the flame arrestor.). The probe inlet has to be above the highest level that the crude oil will reach during filling. Guide wires can

be used to support the probe system. The sample gas is then extracted through the unheated stainless steel probe to the sampling train next to the cargo compartment vent opening.

A.4.1.1.2 Obtain "certified" clean water and VOC traps from the laboratory. Before its initial use and after each subsequent use, all condensate traps (both water and VOC traps) and canisters shall be thoroughly cleaned and checked to ensure that they are not contaminated. Both cleaning and checking can be accomplished by installing the trap in the condensate recovery system and treating it as if it were a sample. The trap should be heated as described in A.5.1.4. A trap may be considered clean when the CO₂ concentration in its effluent gas drops below 10 ppm. This check is optional for traps that have been used to collect samples which were then recovered according to the procedure in A.5.1.4. The canisters are "certified" clean (i.e. <10 ppm TGNMO) by analyzing their content according to FRM 25. Obtain the laboratory "certificate" for both the traps and canisters from the laboratory and document on the field test data sheet (FTDS).

A.4.1.1.3 The sample canisters are shipped under pressure to keep them clean. In the deployment area, using a high efficiency pump, evacuate the sample canister(s) to 10 mm Hg absolute pressure or less. Close the sample canister valve, and allow the canister to sit for 60 min. After 60 min, attach a vacuum gauge to the sample canister. The sample canister is acceptable if no change in canister vacuum is noted. The results of the canister vacuum test are recorded on the FTDS. Obtain the needed traps and record their identification on the FTDS.

A.4.1.1.4 Transport the sample canister(s), the water and cryogenic traps, the mini-box and other materials to the sampling location.

A.4.1.1.5 Position the stainless-steel probe near the sampling location. Plug the ends of the probe with aluminum foil. Assemble the sampling equipment at the sampling location. Measure the initial vacuum in the sample canister once again to verify that the canister has not leaked during transport. Record this vacuum, the ambient temperature, and the barometric pressure at this time on the FTDS. Close the sample canister valve and assemble the sampling system.

A.4.1.1.6 Unplug the condensate traps by removing the brass end caps. Using a connector, connect the two traps together, with the water trap first followed by the VOC trap. Immerse the first condensate trap body (i.e. water trap) in the water condenser, then immerse the second condensate trap body (i.e. VOC trap) in the crushed dry ice.

NOTE Keep the brass caps from the traps in a clean area and do not allow them to come in contact with pump oil, vacuum grease, or other contaminants.

Record the water and dry ice traps tags as identification of the components used during the sample run on the FTDS.

NOTE Use gloves when handling dry ice. Use small pellets of dry ice around the trap and pack the trap well before sampling. The better the contact between the ice and trap the better the heat transfer and the better the organics are trapped. If all of the heavy organics, especially oxygenated compounds, are retained in the VOC trap then better analytical results are acquired.

The point where the inlet tube joins the trap body should be 2.5 cm to 5 cm above the top of the dry ice. Cover the traps with foil to prevent sunlight from warming the traps.

A.4.1.1.7 Record "General Information" of the test facility on the FTDS. Also record "Run Information" on the FTDS.

A.4.1.2 Sample Train Operation

A.4.1.2.1 Calculate or measure the approximate volume of the sampling train from the probe tip to the sample canister valve. After assembling the sampling train, plug the probe tip, and make certain that the sample canister valve is closed. Using a "T-connection," attach a "blank canister" to the sampling train along with a portable vacuum gauge. Open the "blank canister" valve and evacuate the sampling system from the probe tip to the "blank canister" to an absolute pressure of 10 mm Hg or less, as indicated by the portable vacuum gauge. Close the "blank canister" valve, wait a minimum period of 5 min, and recheck the indicated vacuum. Calculate the maximum allowable

pressure change based on a leak rate of 1 % of the sampling rate. If the measured pressure change exceeds the calculated limit, correct the problem before beginning sampling. The results of the leak check are recorded on the FTDS. Unplug the probe tip, and place the probe into a pre-determined position at the sampling location (if sampling at an open hatch, in the centroid of the hatch a few inches below the opening of the hatch; if sampling at a vent stack, near the centroid of the stack at a position below the flame arrestor.). The probe inlet shall be above the highest level that the crude oil will reach during filling. Seal the sample port sufficiently to minimize air entering around the probe.

A.4.1.2.2 Connect a "purge canister" to the "T-connect" on the probe line. Using the "purge canister" purge the sample probe for approximately 3 min. Close the "purge canister" valve and disconnect from the sampling system. Plug the "T-connect" with a fitting to prevent gas from escaping from the sample line.

A.4.1.2.3 Allow the traps to equilibrate in their individual baths for approximately 10 min.

A.4.1.2.4 Connect the sample canister to the outlet of the mini-box by way of a PTFE line. Record the sample canister identification number on the FTDS.

A.4.1.2.5 To begin sampling, open the sample canister valve. Set the flow rate to approximately 12 mL/min using the rate meter in the mini-box. Record the clock time, date, sampling location etc. on the FTDS. Also record component identification (i.e. water trap, dry ice trap, and canister) numbers on the FTDS.

A.4.1.2.6 Adjust the flow rate as necessary to maintain a constant rate $(\pm 10 \%)$ throughout the duration of the sampling period. Record the sample canister vacuum and flow meter setting at 30 min intervals on the FTDS. Intervals may be as long as 60 min if logistical constraints prevent more frequent monitoring of the sample train. During sampling, check the water condenser level and the dry ice level around the condensate trap. Add ice water and dry ice if necessary.

Monitor both the sample flow and the canister vacuum with the rate meter and gauge on the mini-box. The vacuum gauge is a good monitor of the sample run. If the sample canister vacuum does not drop sufficiently, the sample flow may not be correct.

A.4.1.2.7 Sampling is complete at the end of the filling operation.

If sampling had to be stopped before the filling operation is complete because a constant flow rate could not be maintained, proceed as follows. After closing the sample canister valve, remove the used sample canister from the sampling train (without disconnecting other components of the sampling train). Take another evacuated and leak checked sample canister, measure and record the canister vacuum, and attach the new canister to the sampling train. After the new canister is attached to the sample train, proceed with the sampling until the filling operation has completed. Record sample canister identification on the FTDS. Also, if the traps freeze, preventing flow to be maintained, then warm up the inlet to each trap until flow is maintained.

A.4.1.3 Sample Train Recovery

A.4.1.3.1 After sampling is completed, close the sample canister flow control valve. Record the final canister vacuum on the FTDS. Record the final ambient temperature and barometric pressure on the FTDS.

A.4.1.3.2 Disconnect the sample canister from the sample system. Disconnect both the water and the condensate traps from the sampling system. Tightly seal both arms of the water and condensate traps with clean brass caps and pack in dry ice in a cooler.

A.4.1.3.3 Record the identification of the water condenser trap, the dry ice condenser trap and the sample canister(s) on the FTDS.

A.4.1.3.4 Store the traps packed in dry ice until the samples are returned to the laboratory for analysis. Ensure that the same test run number is properly identified on the condensate traps and the sample canister(s) and also recorded on the FTDS.

A.4.1.3.5 Complete "chain-of-custody" for the sample run and store with the samples in the deployment area.

A.4.2 Field Sampling Instantaneous Procedure

A.4.2.1 Sampling Train Preparation

A.4.2.1.1 Obtaining Clean Canisters (Laboratory Certification)

Before its initial use and after each subsequent use, the canister(s) should be thoroughly cleaned and checked to ensure that they are not contaminated. Both cleaning and checking can be accomplished by installing the canister(s) in the FRM 25 sample analytical system and treating them as if they were a sample. A canister is clean when the TGNMO concentration is below 10 ppm. Obtain from the laboratory a "certificate" indicating that the canister(s) have been cleaned to the stated specification.

A.4.2.1.2 Sample Canister(s) Evacuation and Leak Check

Evacuate the sample canister(s) to 10 mm Hg absolute pressure or less. Then close the sample canister valve, and allow the canister to sit for 60 min. The canister is acceptable if no change in canister vacuum is noted. The evacuation and leak check is conducted in the field. The results of the leak check are recorded on the FTDS.

A.4.2.1.3 Pre-test Vacuum Check of Sample Canister

Just before assembly, measure the canister vacuum using an absolute pressure gauge. Record this vacuum, the ambient temperature, and the barometric pressure on the FTDS. Close the sample canister valve.

A.4.2.1.4 Pre-test Purge of Probe

Unplug the probe tip, and place the probe into a pre-determined position at the sampling location (if sampling at an open hatch, in the centroid of the hatch a few inches below the opening of the hatch; if sampling at a vent stack, near the centroid of the stack at a position below the flame arrestor). The probe inlet has to be above the highest level that the crude oil will reach during filling. Attach a pre-evacuated "purge canister" to the outlet of the probe and pull the air–vapor mixture in the cargo compartment through the probe for approximately 2 min. At the end of the purge, remove the "purge canister" and connect the probe to the sample canister.

A.4.2.2 Sampling Train Operation

A.4.2.2.1 Record the clock time, date, sampling location etc. on the FTDS. To begin sampling, open the sample canister valve. One will hear the rush of air–vapor mixture into the canister. The sample time is approximately 15 s to 30 s.

A.4.2.2.2 Once sampling is complete, close the sample canister valve. Note on the FTDS the canister ID, sample location, and sample time.

A.4.2.3 Sampling Train Recovery

A.4.2.3.1 Verify that the sample canister valve is closed. Disconnect the sample canister from the probe and store in a safe area. Complete any necessary field notes on the FTDS.

A.4.2.3.2 Complete a "chain-of-custody" for each sample canister and return to laboratory for analysis.

A.5 Analysis

A.5.1 Condensate Trap(s) Recovery

A.5.1.1 General

Set the carrier gas flow rate, and heat the catalyst to its operating temperature to condition the apparatus.

A.5.1.2 Daily Performance Checks

A.5.1.2.1 General

Each day before analyzing any samples, perform the following tests given A.5.1.2.2 to A.5.1.2.4.

A.5.1.2.2 Leak Check

With the carrier gas inlets and the flow control valve closed, install a clean condensate trap in the system, and evacuate the system to 10 mm Hg absolute pressure or less. Close the vacuum pump valve and turn off the vacuum pump. Monitor the system pressure for 10 min. The system is acceptable if the pressure change is less than 2 mm Hg.

A.5.1.2.3 System Background Test

Adjust the carrier gas and auxiliary oxygen flow rate to their normal values of 100 mL/min and 150 mL/min, respectively, with the sample recovery valve in vent position. Using a 10 mL syringe withdraw a sample from the system effluent through the syringe port. Inject this sample into the NMO analyzer, and measure the CO_2 content. The system background is acceptable if the CO_2 concentration is less than 10 ppm.

A.5.1.2.4 Oxidation Catalyst Efficiency Check

Conduct a catalyst efficiency test. If the criterion of this test cannot be met, make the necessary repairs to the system before proceeding.

A.5.1.3 Condensate Trap(s) CO₂ Purge and Sample Canister Pressurization

After sampling is completed, the condensate trap(s) will contain condensed water and organics and a small volume of sampled gas. This gas from the source may contain a significant amount of CO_2 which must be removed from the condensate trap(s) before the sample is recovered. This is accomplished by purging the condensate trap(s) with zero air and collecting the purged gas in the original sample canister.

Begin with the sample canister and condensate trap(s) from the test run to be analyzed. Set the four-port valve of the condensate recovery system in the CO_2 purge position. With the sample canister valve closed, attach the sample canister to the sample recovery system. With the sample recovery valve in the vent position and the flow control valve fully open, evacuate the manometer or pressure gauge to the vacuum of the sample canister. Next, close the vacuum pump valve, open the sample canister valve, and record the canister pressure.

Attach the dry-ice cooled condensate trap to the recovery system, and initiate the purge by switching the sample recovery valve from vent to collect position. Adjust the flow control valve to maintain atmospheric pressure in the recovery system. Continue the purge until the CO_2 concentration of the trap effluent is less than 5 ppm. CO_2 concentration in the trap effluent should be measured by extracting syringe samples from the recovery system and analyzing the samples with the NMO analyzer. This procedure should be used only after the NDIR response has reached a minimum level. Using a 10 mL syringe, extract a sample from the syringe port prior to the NDIR, and inject this sample into the NMO analyzer. Repeat procedure for the water condensate trap.

After the completion of the CO_2 purge, use the carrier gas bypass valve to pressurize the sample canister to approximately 1060 mm Hg absolute pressure with zero air.

A.5.1.4 Recovery of the Condensate Trap(s) Samples

Attach the intermediate collection vessel (ICV) to the sample recovery system. With the sample recovery valve in a closed position, between vent and collect, and the flow control and ICV valves fully open, evacuate the manometer or gauge, the connecting tubing, and the ICV to 10 mm Hg absolute pressure. Close the flow control and vacuum pump valves.

Begin auxiliary oxygen flow to the oxidation catalyst at a rate of 150 mL/min, switch the four-way valve to the trap recovery position and the sample recovery valve to collect position. The system should now be set up to operate. After the manometer or pressure gauge begins to register a slight positive pressure, open the flow control valve. Adjust the flow control valve to maintain atmospheric pressure in the system within 10 %.

Now, remove the condensate trap from the dry ice, and allow it to warm to ambient temperature while monitoring the NDIR response. If after 5 min the CO₂ concentration of the catalyst effluent is below 10,000 ppm, discontinue the auxiliary oxygen flow to the oxidation catalyst. Begin heating the trap by placing it in a furnace preheated to 200 °C. Once heating has begun, carefully monitor the NDIR response to ensure that the catalyst effluent concentration does not exceed 50,000 ppm. Whenever the CO₂ concentration exceeds 50,000 ppm, supply auxiliary oxygen to the catalyst at the rate of 150 mL/min. Begin heating the tubing that connected the heated sample box to the condensate trap only after the CO₂ concentration falls below 10,000 ppm. This tubing may be heated in the same oven as the condensate trap or with an auxiliary heat source such as a heat gun. Heating temperature must not exceed 200 °C. If a heat gun is used, heat the tubing slowly along its entire length from the upstream end to the downstream end, and repeat the pattern for a total of three times. Continue the recovery until the CO₂ concentration drops to less than 10 ppm as determined by syringe injection as described under the condensate trap CO₂ purge procedure.

After the sample recovery is completed, use the carrier gas bypass valve to pressurize the ICV to approximately 1060 mm Hg absolute pressure with zero air.

A.5.2 Analysis For TGNMOs

A.5.2.1 General

Before putting the NMO analyzer into routine operation, conduct an initial performance test. Start the analyzer, and perform all the necessary functions in order to put the analyzer into proper working order; then conduct the performance test according to the procedures established in A.6.3. Once the performance test has been successfully completed and the CO_2 and NMO calibration response factors have been determined, proceed with sample analysis as follows.

A.5.2.2 Daily Operations and Calibration Checks

Before and immediately after the analysis of each set of samples or on a daily basis (whichever occurs first), conduct a calibration test according to the procedures established in A.6.4. If the criteria of the daily calibration test cannot be met, repeat the NMO analyzer performance test (A.6.3) before proceeding.

A.5.2.3 Operating Conditions

The carrier gas flow rate is 29.5 mL/min He and 2.2 mL/min O_2 . The column oven is heated to 85 °C. The order of elution for the sample from the column is CO, CH₄, CO₂, and NMO.

A.5.2.4 Analysis of Recovered Condensate Sample

Purge the sample loop with sample, and then inject the sample. Under the specified operating conditions, the CO₂ in the sample will elute in approximately 100 s. As soon as the detector response returns to baseline following the CO₂ peak, switch the carrier gas flow to back flush, and raise the column oven temperature to 195 °C as rapidly as possible. A rate of 30 °C/min has been shown to be adequate. Record the value obtained for the condensable organic material (C_{cm}) measured as CO₂ and any measured NMO. Return the column oven temperature to 85 °C in preparation for the next analysis. Analyze each sample in triplicate, and report the average C_{cm} .

A.5.2.5 Analysis of Sample Canister

Perform the analysis as described in A.5.2.4, but record only the value measured for NMO (C_{tm}).

A.6 Calibration and Operational Checks

A.6.1 General

Maintain a record of performance of each item.

A.6.2 Initial Performance Check of Condensate Recovery Apparatus

A.6.2.1 General

Perform the tests given in A.6.2.2 to A.6.2.4 before the system is first placed in operation, after any shutdown of 6 months or more, and after any major modification of the system, or at the specified frequency.

A.6.2.2 Carrier Gas and Auxiliary O₂ Blank Check

Analyze each new tank of carrier gas or auxiliary O_2 with the NMO analyzer to check for contamination. Treat the gas cylinders as noncondensable gas samples, and analyze according to the procedure in A.5.2.4. Add together any measured CH₄, CO, CO₂, or NMO. The total concentration must be less than 5 ppm.

A.6.2.3 Catalyst Efficiency Check

With a clean condensate trap installed in the recovery system, replace the carrier gas cylinder with the high level methane standard gas cylinder (A.3.4.2). Set the four-port valve to the recovery position, and attach an ICV to the recovery system. With the sample recovery valve in vent position and the flow control and ICV valves fully open, evacuate the manometer or gauge, the connecting tubing, and the ICV to 10 mm Hg absolute pressure. Close the flow control and vacuum pump valves.

After the NDIR response has stabilized, switch the sample recovery valve from vent to collect. When the manometer or pressure gauge begins to register a slight positive pressure, open the flow control valve. Keep the flow adjusted so that atmospheric pressure is maintained in the system within 10 %. Continue collecting the sample in a normal manner until the ICV is filled to a nominal gauge pressure of 300 mm Hg. Close the ICV valve, and remove the ICV from the system. Place the sample recovery valve in the vent position, and return the recovery system to its normal carrier gas and normal operating conditions. Analyze the ICV for CO_2 using the NMO analyzer; the catalyst efficiency is acceptable if the CO_2 concentration is within 2 % of the methane standard concentration.

A.6.2.4 System Performance Check

Construct a liquid sample injection unit. Insert this unit into the condensate recovery and conditioning system in place of a condensate trap, and set the carrier gas and auxiliary O_2 flow rates to normal operating levels. Attach an evacuated ICV to the system, and switch from system vent to collect. With the carrier gas routed through the injection unit and the oxidation catalyst, inject a liquid sample [see liquids listed in 1 to 4 below] into the injection port. Operate

the trap recovery system as described in A.5.1.4. Measure the final ICV pressure, and then analyze the vessel to determine the CO_2 concentration. For each injection, calculate the percent recovery.

The performance test is acceptable if the average percent recovery is 100 ± 10 % with a relative standard deviation of less than 5 % for each set of triplicate injections as follows:

- 1) 50 µL hexane,
- 2) 10 µL hexane,
- 3) 50 µL decane,
- 4) 10 µL decane.

A.6.3 Initial NMO Analyzer Performance Test

A.6.3.1 General

Perform the tests given in A.6.3.2 to A.6.3.5 before the system is first placed in operation, after any shutdown longer than 6 months, and after any major modification of the system.

A.6.3.2 Oxidation Catalyst Efficiency Check

Turn off or bypass the NMO analyzer reduction catalyst. Make triplicate injections of the high level methane standard (A.3.4.2). The oxidation catalyst operation is acceptable if the FID response is less than 1 % of the injected methane concentration.

A.6.3.3 Reduction Catalyst Efficiency Check

With the oxidation catalyst unheated or bypassed and the heated reduction catalyst bypassed, make triplicate injections of the high level methane standard (A.3.4.2). Repeat this procedure with both catalysts operative. The reduction catalyst operation is acceptable if the response under both conditions agree within 5 %.

A.6.3.4 Analyzer Linearity Check and NMO Calibration

While operating both the oxidation and reduction catalysts, conduct a linearity check of the analyzer using the propane standards specified in A.3.4.3. Make triplicate injections of each calibration gas, and then calculate the average response factor (area/ppm C) for each gas, as well as the overall mean of the response factor values. The instrument linearity is acceptable if the average response factor of each calibration gas is within 2.5 % of the overall mean value and if the relative standard deviation for each set of triplicate injections is less than 2 %. Record the overall mean of the propane response factor values as the NMO calibration response factor (RF_{NMO}).

Repeat the linearity check using the CO_2 standards specified in A.3.4.4. Make triplicate injections of each gas, and then calculate the average response factor (area/ppm C) for each gas, as well as the overall mean of the response factor values. Record the overall mean of the response factor values as the CO_2 calibration response factor (RF_{CO2}). Linearity is acceptable if the average response factor of each calibration gas is within 2.5 % of the overall mean value and if the relative standard deviation for each set of triplicate injections is less than 2 %. The RF_{CO2} must be within 10 % of the RF_{NMO} .

A.6.3.5 System Performance Check

Check the column separation and overall performance of the analyzer by making triplicate injections of the calibration gases listed in A.3.4.5. The analyzer performance is acceptable if the measured NMO value for each gas (average of triplicate injections) is within 5 % of the expected value.

A.6.4 NMO Analyzer Daily Calibration

A.6.4.1 CO₂ Response Factor

Inject triplicate samples of the high level CO_2 calibration gas (A.3.4.4), and calculate the average response factor. The system operation is adequate if the calculated response factor is within 5 % of the RF_{CO2} calculated during the initial performance test (A.6.3). Use the daily response factor (DRF_{CO2}) for analyzer calibration and the calculation of measured CO_2 concentrations in the ICV samples.

A.6.4.2 NMO Response Factors

Inject triplicate samples of the mixed propane calibration cylinder (A.3.4.5, Item 1), and calculate the average NMO response factor. The system operation is adequate if the calculated response factor is within 5 % of the RF_{NMO} calculated during the initial performance test (A.6.3). Use the daily response factor (DRF_{NMO}) for analyzer calibration and calculation of NMO concentrations in the sample canisters.

A.6.5 Sample Canister and ICV Volume

The volume of the gas sampling canisters used must be determined. Determine the canister and ICV volumes by weighing them empty and then filled with deionized distilled water; weigh to the nearest 5 g, and record the results. Alternatively, measure the volume of water used to fill them to the nearest 5 mL.

A.7 Nomenclature and Calculations

A.7.1 General

All equations are written using absolute pressure; absolute pressures are determined by adding the measured barometric pressure to the measured gauge or manometer pressure.

A.7.2 Nomenclature

С	TGNMO concentration of the effluent, ppm C equivalent
Cc	calculated condensable organic (water or condensate trap) concentration of the effluent, ppm C equivalent
$C_{\sf cm}$	measured concentration (NMO analyzer) for the condensate trap ICV, ppm CO ₂
Ct	calculated non-condensable organic concentration (sample canister) of the effluent, ppm C equivalent
$C_{\sf tm}$	measured concentration (NMO analyzer) for the sample canister, ppm NMO
F	sampling flow rate, mL/min
FID	flame ionization detector
FTDS	field test data sheet
GC	gas chromatograph
ICV	intermediate collection vessel
L	volume of liquid injected, μL
M	molecular weight of the liquid injected, g/g-mole
m _C	TGNMO mass concentration of the effluent, mg C/dsm ³
n	number of data points
N	carbon number of the liquid compound injected ($N = 12$ for decane; $N = 6$ for hexane)
NDIR	nondispersive infrared
NMO	nonmethane organics

P_{b}	barometric pressure, cm Hg
P_{f}	final pressure of the intermediate collection vessel, mm Hg absolute
P_{ti}	gas sample canister pressure before sampling, mm Hg absolute
Pt	gas sample canister pressure after sampling, but before pressurizing, mm Hg absolute
P_{tf}	final gas sample canister pressure after pressurizing, mm Hg absolute
q	total number of analyzer injections of intermediate collection vessel during analysis (where k = injection number, 1 q)
r	total number of analyzer injections of sample canister during analysis (where $j =$ injection number, 1 r)
T_{f}	final temperature of intermediate collection vessel (ICV), K
TGNMO	total gaseous nonmethane organics
T _{ti}	sample canister temperature before sampling, K
Tt	sample canister temperature at completion of sampling, K
$T_{\sf tf}$	sample canister temperature after pressurizing, K
V	Sample canister volume, m ³
VOC	volatile organic compounds
Vs	gas volume sampled, dsm ³
Vt	sample canister volume, mL
V_{V}	intermediate collection vessel (ICV) volume, m ³
xi	individual measurements
\overline{x}	mean value
θ	leak check period, min
ΔP	allowable pressure change, cm Hg.

A.7.3 Calculations

A.7.3.1 Allowable Pressure Change

For the pretest leak check, calculate the allowable pressure change:

$$\Delta P = 0.01 \ \frac{FP_{\rm b}\theta}{V_{\rm t}}$$

A.7.3.2 Sample Volume

For each test run, calculate the gas volume sampled:

$$V_{\rm s} = 0.3857 V \left(\frac{P_{\rm t}}{T_{\rm t}} - \frac{P_{\rm ti}}{T_{\rm ti}}\right)$$

A.7.3.3 Non-condensable Organics

For each sample canister, determine the concentration of nonmethane organics (ppm C):

$$C_{t} = \left(\frac{\frac{P_{tf}}{T_{tf}}}{\frac{P_{t}}{T_{t}} - \frac{P_{ti}}{T_{ti}}}\right) \left(\frac{1}{r} \sum_{j=1}^{r} C_{tm_{j}}\right)$$

A.7.3.4 Condensable Organics

For each condensate trap determine the concentration of organics (ppm C):

$$C_{\rm c} = 0.3857 \, \frac{V_{\rm v} P_{\rm f}}{V_{\rm s} T_{\rm f}} \left(\frac{1}{q} \sum_{k=1}^{q} C_{\rm cm_k}\right)$$

A.7.3.5 TGNMO

To determine the TGNMO concentration for each test run, use the following equation:

$$C = C_{\mathsf{t}} + C_{\mathsf{c}}$$

A.7.3.6 TGNMO Mass Concentration

To determine the TGNMO mass concentration as carbon for each test run, use the following equation:

 $m_{\rm C} = 0.4993C$

A.7.3.7 Percent Recovery

To calculate the percent recovery for the liquid injections to the condensate recovery and conditioning system, use the following equation.

% Recovery = 1.604 (*M/L*) (V_V/P) (P_f/T_f) (C_{cm}/N)

A.7.3.8 Relative Standard Deviation

To calculate the relative standard deviation, use the following equation:

$$RSD = \frac{100}{\bar{x}} \sqrt{\frac{\sum (x_i - \bar{x})^2}{n - 1}}$$

Annex B

(informative)

Protocol for Sampling and Analysis of Vapors from Marine Loading of Crude Oil: Field Testing for Proof-of-Principle

B.1 Background

The purpose of this test program was to develop a protocol for collecting vapor samples during the loading of marine vessels with crude oil and other petroleum liquids. The intention was to develop a protocol for general use by parties interested in measuring the concentrations of methane, ethane, and total hydrocarbons in the vapors displaced during the loading of marine vessels.

The test program proposed was based on EPA Federal Reference Method 25 (FRM 25), *Determination of Total Gaseous Nonmethane Organic Emissions as Carbon*. FRM 25 uses gas chromatography (GC) to separate carbon monoxide, methane, carbon dioxide, ethane and ethylene from the nonmethane organic compounds in the sample so they do not create a positive bias to the final analysis of the total gaseous nonmethane organic compounds (TGNMOC) fraction. Thus FRM 25 is believed to be well suited to this study, in that an objective of the protocol is to measure the methane and ethane concentrations separately from the aggregate of other hydrocarbons.

Modifications were made to FRM 25 in order to adapt it to the particular application of sampling during the loading of marine vessels. These modifications included not using a heated probe, so as to avoid any non-intrinsically safe components. Instead, the length of the probe was limited so as to minimize the potential for condensation in the probe. Furthermore, the sample was drawn entirely by the evacuated canister, without use of a pump, also to avoid any non-intrinsically safe components. Another modification was the use of an ice bath, in addition to the cryogenic (dry-ice) bath. The purpose of the ice bath was to remove moisture from the sample prior to the dry-ice bath. The resulting sampling train is intrinsically safe, and separates water and carbon dioxide from the sample stream in order to avoid the problems reported in other studies pertaining to interference from these compounds.

Sampling in which vapors were drawn continuously through the modified FRM 25 sampling train into an evacuated canister throughout the loading period is referred to in this report as "integrated sampling," in that this sampling process is effectively integrated over time. Sampling in which vapors were pulled directly into an evacuated canister that was opened only briefly, without employing the modified FRM 25 sampling train, is referred to as "grab sampling."

The report given in this annex summarizes the results of the field study that was undertaken as a proof-of-principle exercise in support of the protocol development. The purpose of this report is to describe the field sampling that took place, and to present a summary of analysis results from laboratory testing of the samples captured in the field. The proof-of-principle field study included capturing periodic grab samples during the loading process, in addition to the integrated samples obtained by means of the modified FRM 25 sampling train. Both the grab samples and the integrated samples were then analyzed in a laboratory in accordance with FRM 25.

B.2 Field Conditions

The facility that participated in this study is a terminal on the Mississippi River near St. James, Louisiana that receives crude oil by ocean-going vessel, stores the crude oil in storage tanks on shore, and subsequently loads the crude oil into barges for transport further up river.

Certain of the conditions for this loading activity were not ideal for the study. The barges each had 8 cargo compartments, approximately 10 ft deep. The displaced vapors were not manifolded to a single vent stack, but rather each compartment vented directly to the atmosphere. Filling rates were adjusted from compartment to compartment during the course of loading, such that the barge did not become unduly tilted due to uneven distribution of load. Thus

the rate of vapor discharge out of a given compartment was variable. Furthermore, vapors were vented through open hatches, rather than through vent stacks, which complicated efforts to obtain a representative sample.

In addition, the crude oil being loaded exhibited very low volatility, with a reported Reid vapor pressure (RVP) of 0.50 psi. In that this is well below the lower bound of the scope of the correlation for obtaining true vapor pressure (TVP) from RVP², there is more uncertainty in this value than would be the case for a lighter crude oil. The prior cargo in the barges was "slurry oil", which is a very heavy fuel oil. The term "slurry oil" is conventionally applied to the stream from the bottom of the fractionator in a fluid catalytic cracking (FCC) unit, composed of heavy oil and residual catalyst particles. Slurry oil is typically pumped through a slurry settler, where catalyst particles are settled out. The oil removed from the top of the slurry settler, called clarified slurry oil or decant oil, is likely the stock that had been previously transported in the barges.

The period of opportunity for sampling was during one loading operation, during which two barges were being loaded simultaneously. The equipment brought to the site was sufficient to set up four modified FRM 25 sampling trains. Two compartments on each barge were arbitrarily selected for the FRM continuous, integrated sampling, and grab samples were taken periodically at one of these locations on each barge. The barges were designated A and B, and the compartments were assigned designations as shown below, with P indicating the port side and S indicating the starboard side of each barge.

Barge A		Bar	ge B
A-1-P	A-1-S	B-1-P	B-1-S
A-2-P	<u>A-2-S</u>	B-2-P	B-2-S
<u>A-3-P</u>	A-3-S	<u>B-3-P</u>	B-3-S
A-4-P	A-4-S	B-4-P <u>B-4-S</u>	

The compartments arbitrarily selected for sampling are summarized below.

Barge	Compartment	Compartment Integrated Sampling	
^	A-3-P	Х	Х
A	A-2-S	Х	
D	B-3-P	Х	Х
В	B-4-S	Х	

Loading began at approximately midnight on February 19, 2011, and continued until approximately 9:00 am on February 20, 2011. Checking of the integrated sampling trains occurred on a half-hour schedule and collection of grab samples occurred on an hourly schedule throughout the period of loading.

Meteorological data from regional weather stations are summarized in Table B.1 and Table B.2.

While there was no official rainfall in the area, conditions on the river were damp and misty throughout the night and early morning hours.

² EPA's AP-42 Figure 7.1-13 for obtaining TVP from RVP is not applicable below 2 psi RVP. [U.S. Environmental Protection Agency, 7.1 "Organic Liquid Storage Tanks," in *Compilation of Air Pollutant Emission Factors*, USEPA Report No. AP-42, November 2006.]

Time (CST)	Temp.	Humidity	Sea Level Pressure	Wind Speed	Conditions
12:53 AM	61.0 °F	87 %	30.12 in	8.1 mph	Clear
1:53 AM	60.1 °F	90 %	30.11 in	6.9 mph	Clear
2:53 AM	61.0 °F	90 %	30.09 in	10.4 mph	Clear
3:53 AM	60.1 °F	93 %	30.08 in	6.9 mph	Clear
4:53 AM	60.1 °F	93 %	30.08 in	5.8 mph	Clear
5:53 AM	61.0 °F	93 %	30.08 in	9.2 mph	Clear
6:53 AM	60.8 °F	94 %	30.11 in	6.9 mph	Clear
7:53 AM	64.9 °F	87 %	30.10 in	8.1 mph	Clear

Table B.1—Meteorological Data: New Orleans Lakefront, LA

Table B.2—Meteorological Data: Baton Rouge, LA

Time (CST)	Temp.	Humidity	Sea Level Pressure	Wind Speed	Conditions
12:53 AM	61.0 °F	83 %	30.12 in	3.5 mph	Clear
1:53 AM	59.0 °F	93 %	30.10 in	3.5 mph	Clear
2:53 AM	54.0 °F	100 %	30.08 in	Calm	Clear
3:53 AM	52.0 °F	97 %	30.07 in	3.5 mph	Partly Cloudy
4:15 AM	55.4 °F	94 %	30.07 in	3.5 mph	Mostly Cloudy
4:34 AM	59.0 °F	100 %	30.07 in	3.5 mph	Overcast
4:53 AM	60.1 °F	100 %	30.07 in	5.8 mph	Overcast
5:02 AM	60.8 °F	100 %	30.07 in	9.2 mph	Overcast
5:36 AM	60.8 °F	100 %	30.08 in	6.9 mph	Overcast
5:53 AM	61.0 °F	100 %	30.08 in	9.2 mph	Patches of Fog
6:53 AM	61.0 °F	100 %	30.09 in	4.6 mph	Patches of Fog
7:53 AM	63.0 °F	97 %	30.09 in	5.8 mph	Mostly Cloudy

B.3 Overview of the Field Testing

As noted above, the barge compartments did not vent through a common header, but rather each compartment vented through a hatch. The hatches were 42 inches in diameter, and extended 12 in. above the deck. A smaller oval hatch was constructed into the lid of each 42-in. hatch, extending another 6 in. above the deck. The oval hatches were 24 in. long and 16 in. wide. A typical hatch is shown in Figure B.1.

Figure B.1 shows the oval hatch open, with a piece of wood across the opening through which the stainless steel probes are mounted. A portion of the sampling train is visible to the left. Separate probes were used for the integrated sample and the grab sample, so as to not interrupt the integrated sample when taking the grab sample.

The sampling train involved a ¼ in. stainless steel probe extending down into the barge compartment. The tip of the probe was positioned approximately at the level of the deck. An inverted stainless steel funnel was attached to the tip



Figure B.1—Barge Hatch with Sampling Probes

of the probe. Sample vapors were drawn into the probe and through the modified FRM 25 sampling train by the vacuum in the evacuated sample canister. The modified FRM 25 sampling train is shown in Figure 3.

The water condensate trap consisted of U-shaped tubing in an ice water bath, for trapping water, and the VOC condensate trap consisted of U-shaped tubing in a container packed with dry ice, for trapping condensable volatile organic compounds (VOCs). After passing through these traps, the sample passed through the mini-box containing a three-way valve, a vacuum gauge, and a rotameter. The three-way valve accommodated purging of the sampling train prior to pulling vapors into the sample canister, the gauge measured the vacuum in the sample canister, and the rotameter measured the rate of flow. The assembly and operation of the sampling train are described in more detail in the protocol.

The integrated sampling trains were in operation from commencement of loading until completion. An initial calculation was performed to determine a flow rate that would allow a single canister to be used for the integrated sample at each location. The loading operation was anticipated to be complete within 10 h. A target flow rate of 12 mL/min was selected so as to still have ample vacuum in an 8.3 L canister to pull vapors through the sampling train after 10 h.

Inspection of the four sampling trains was undertaken on approximately a one-half hour cycle, during which the vacuum and flow readings were checked for any indications of problems in the sampling. On every other inspection cycle, grab samples were obtained from two of the locations, and thus the grab samples were obtained approximately hourly. Barge A finished loading approximately one-half hour earlier than Barge B.

A summary of the sample canisters collected is shown in Annex C. A few observations concerning difficulties in the field are evident from a review of the field notes and the canister identifications.

— A-3-P: The attempt at an integrated sample from location A-3-P was hampered by the canister losing vacuum too quickly. Whereas a single canister was sufficient for each of the other three locations, the canisters lost vacuum so quickly at location A-3-P that a succession of 4 canisters were used with the integrated sampling train at this location. Sampling periods were as follows:

Integrated samples. 23:59 - 8:24 (succession of 4 canisters - data disregarded)

Grab samples. 00:45 – 7:35 (8 hourly samples).

 A-2-S: This location had an integrated sampling train, but no grab samples. There were no evident problems. Sampling period was as follows:

Integrated samples. 0:03 - 8:25 (1 canister).

B-3-P: The first canister used with the integrated sampling train was deemed to have a problem an hour into the loading process, and the canister was replaced. Thus the integrated sample from this location was missing the first hour of sampling. Also, there was a question concerning the grab sample obtained at 2:50 am, and a second grab sample was collected at that time. Laboratory analysis showed the first sample to have trivial concentration of vapors, and thus only the second sample was included in the compiled data. Sampling periods were as follows:

Integrated samples. 1:04 – 8:53 (1 canister)

Grab samples. 00:57 - 7:58 (8 hourly samples - a duplicate at one hour was disregarded).

 B-4-S: This location had an integrated sampling train, but no grab samples. There were no evident problems. Sampling period was as follows:

Integrated samples. 0:12 - 8:55 (1 canister).

B.4 Laboratory Results

Results from the laboratory analyses are presented in Annex D. Given the relatively trivial values from the canisters used for the integrated sample for location A-3-P, those results were neglected. Similarly, the first grab sample for the third hour at location B-3-P was neglected. All other data were included in the laboratory results summarized graphically in Figure B.2, Figure B.3, and Figure B.4.

A visual appraisal of the graphical displays of results shows the integrated sample results (represented by straight lines) to fall generally within the range of grab sample results (represented by markers). The grab samples show a general upward trend of concentration over time, as would be expected. There is, however, notable variation among the results. The extent to which this variation is due to actual variation in vapor concentration at different barge compartments versus error in the sampling and analysis procedure is not known.

The results are summarized numerically in Table B.1, Table B.2 and Table B.3.

Both the trend and the absolute values of the two sets of results are reasonably similar.

The data may also be summarized by comparing the average of all the grab sample results to the average of all the integrated sample results, as shown below Table B.3.

It is apparent that, expressed as a percent to one significant figure, the results for the two sampling methods match.



Figure B.2—TGNMOC Concentration (ppm) vs Time (hours)



Figure B.3—Methane Concentration (ppm) vs Time (hours)



Figure B.4—Ethane Concentration (ppm) vs Time (hours)

Table B.1—Results for Only Location at Which Both Grab Samples and a Valid
Integrated Sample Were Obtained

Barge B	Cor			
Location B-3-P	Methane	Ethane	TGNMOC	Total
Grab Samples Averages	755	919	19831	21505
Integrated Sample	833	1077	24708	26618

Barge A Location A-3-P							
Grob Samplas	Co						
Grab Samples	Methane	Ethane	TGNMOC	Total			
Average:	544	844	19221	20609			
Integrated Samples							
data quality issues							
	Barge	A Location A-2-	S				
Grab Samples							
none taken at this loc	ation						
	Co						
Integrated Sample	Methane	Ethane	TGNMOC	Total			
	289	389	11368	12046			
	Barge	B Location B-4-	S				
Grab Samples							
none taken at this loc	none taken at this location						
Concentration (ppm)							
Integrated Sample	Methane	Ethane	TGNMOC	Total			
	812	657	12622	14091			

Table B.2—Results From Other Sample Locations

Table B.3—Summary of Data Comparing Grab Sample Average Results to All Integrated Sample Results Average

Both Barges							
	Methane	Methane Ethane TGNMOC		Total			
Grab Samples							
Average (ppm):	649	881	19526	21057			
Average (%):	0.1	0.1	2	2			
Integrated Samples							
Average (ppm):	645	708	16233	17585			
Average (%):	0.1	0.1	2	2			

B.5 Methane Concentration

One of the objectives of the study was to check for measurable levels of methane in crude oil. The crude oil loaded during the field study was from the Captain field in the North Sea. This Captain crude oil is initially stored in the North Sea production field in a floating production, storage, and offloading (FPSO) vessel, from which it is transported by shuttle tanker to a shore-based terminal at Nigg, Scotland. The crude oil is then transferred to ocean-going tankers for passage across the Atlantic Ocean. The travel time to the St. James, LA terminal is about 14 to 16 days. The Captain crude oil that was loaded during this testing program had been stored in two tanks at the St. James terminal, and then blended in a third tank prior to loading onto the barges.

As noted previously, the Captain field produces a low volatility crude oil, with RVP of 0.5 psi reported by the St. James terminal. The operator of the Captain field provided the following properties for Captain crude oil:

- oil gravity: 19 to 21 API
- crude oil:100 mbopd (Area A and Area B)
- produced water: 240 mbwpd
- gas capacity: 14 mmscfd
- gas injection: 12 mmscfd
- water injection: 240 mbwpd
- produced water: (all produced water is re-injected)

The crude oil and gas capacity may be expressed as gas-to-oil ratio (GOR) in terms of cubic meters of gas produced per liter of crude oil. Conversion of 14 mmscfd to cubic meters (per day) and 100 mbopd to liters (per day) gives a GOR of $0.025 \text{ m}^3/\text{L}$ for Captain crude oil. As a point of comparison, EPA's NESHAP rule for Oil and Natural Gas Production (40 *CFR* Part 63 Subpart HH) defines "black oil" as having an initial producing GOR less than $0.31 \text{ m}^3/\text{L}$ and an API gravity less than 40, and it specifies that these criteria must be exceeded in the definition of "storage vessel with the potential for flash emissions."

It is evident that Captain crude oil is significantly lower in gas content and heavier in density than crude oils that are deemed to have the potential for flash emissions when stored in an atmospheric storage vessel. Furthermore, the crude oil being loaded during the field study had experienced multiple transfers and extensive transportation at nominally atmospheric conditions. This crude oil, then, would have been deemed "black oil" as produced, and it was further "stabilized" by the transfers and transportation that occurred downstream from the production field.

As shown in the summaries below (see Tables B.4 and B.5), there were levels of methane in the vapor ranging from 2 % to 6 % of total hydrocarbons, and the sum of methane and ethane was in the range of 6 % to 10 %. This is within the range reported in EPA's AP-42 Section 5.2, where the sum of methane and ethane in the vapors from the loading of crude oil are given as ranging from 0 % to 45 %, with a typical value of 15 %.³ Thus the field study confirmed that methane can be present in the vapors from even low GOR, heavy crude oils that have been transported extensively and transferred multiple times.

³ These values for the range and typical levels of the sum of methane and ethane are documented in a 1984 report that is available from EPA's website. This report involved measurements at the docks of 31 domestic refineries owned by 8 different oil companies (the "8-31 Marine Emissions Study"), with data collected from the loading of 63 individual tank compartments. http://www.epa.gov/ttn/chief/old/ap42/ch05/s02/reference/ref_03c05s02_jan1995.pdf

Location A-3-P							
Grab Samples	Co	ncentration (p	pm)	Percent	of Hydrocarbo	n Vapors	
Time	Methane	Ethane	TGNMOC	Methane	Ethane	TGNMOC	
(00:45)	395	525	15,623	2 %	3 %	94 %	
(01:39)	512	685	19,272	3 %	3 %	94 %	
(02:35)	543	750	21,877	2 %	3 %	94 %	
(03:38)	563	828	23,117	2 %	3 %	94 %	
(04:38)	551	854	25,476	2 %	3 %	95 %	
(05:40)	553	908	20,905	2 %	4 %	93 %	
(06:35)	576	1003	13,422	4 %	7 %	89 %	
(07:35)	656	1201	14,073	4 %	8 %	88 %	
Averages:	544	844	19,221	3 %	4 %	93 %	
Integrated Samples data quality issues							
		L	-ocation A-2-S				
Grab Samples							
none taken at this locat	tion						
	Co	ncentration (p	pm)	Percent	of Hydrocarbo	n Vapors	
Integrated Sample	Methane	Ethane	TGNMOC	Methane	Ethane	TGNMOC	

Table B.4—Barge A

B.6 Conclusion

289

389

The field study demonstrated that the modified FRM 25 protocol for collecting time-integrated samples achieved reasonable agreement with hourly grab samples. The field study also confirmed the presence of methane and ethane in vapors displaced from the loading of crude oil.

11368

2 %

3 %

94 %

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Table B.5—Barge B

Location B-4-S								
Grab Samples								
none taken at this location								
	Concentration (ppm)				Percent of Hydrocarbon Vapors			
Integrated Sample	Methane	Ethane	TGNMOC		Methane	Ethane	TGNMOC	
	812	657	12,622		6 %	5 %	90 %	

Location B-3-P							
Grab Samples	Co	oncentration (pp	om)		Percent	of Hydrocarbor	N Vapors
Time	Methane	Ethane TGNMOC			Methane	Ethane	TGNMOC
(00:57)	476	533	15,355		3 %	3 %	94 %
(01:52)	586	435	8634		6 %	5 %	89 %
(02:51)	658	810	16,119		4 %	5 %	92 %
(03:49)	757	934	22,334		3 %	4 %	93 %
(04:48)	893	1105	23,891		3 %	4 %	92 %
(05:50)	969	1241	26,819		3 %	4 %	92 %
(06:41)	831	1094	22,879		3 %	4 %	92 %
(07:58)	869	1197	22,619		4 %	5 %	92 %
Averages:	755	919	19,831		4 %	4 %	92 %
	Co	oncentration (pp	om)		Percent	of Hydrocarbor	N Vapors
Integrated Sample	Methane	Ethane	TGNMOC		Methane	Ethane	TGNMOC
	833	1077	24,708		3 %	4 %	93 %

Annex C (informative)

Analytical Sample Canister Identification

Barge A	Barge A	Barge B	Barge B
Sample Location	Sample Location	Sample Location	Sample Location
A-3-P	A-2-S	B-3-P	B-4-S
Grab Sample Canisters ID/Time	Grab Sample Canisters ID/Time	Grab Sample Canisters ID/Time	Grab Sample Canisters ID/Time
104 (00:45)	NA	123 (00:57)	NA
256 (01:39)		247 (01:52)	
204 (02:35)		115 (02:50)	
200 (03:38)		120 (02:51)	
182 (04:38)		237 (03:49)	
208 (05:40)		235 (04:48)	
140 (06:35)		189 (05:50	
270 (07:35)		275 (06:41)	
		266 (07:58)	
Time-Integrated Canisters ID/Time	Time-Integrated Canister ID/Time	Time-Integrated Canister ID/Time	Time-Integrated Canister ID/Time
244 (23:59-02:13)	238 (00:03-08:25)	132 (01:04-08:53)	216 (00:12-08:55)
203 (02:13-04:35)			
152 (04:35-06:31)			
192 (06:31-08:24)			
CO ₂ Trap ID	CO ₂ Trap ID	CO ₂ Trap ID	CO ₂ Trap ID
DE	BJX	AHH	AAJ
Water Trap ID	Water Trap ID	Water Trap ID	Water Trap ID
C16	C13	C35	C63

Annex D (informative)

Laboratory Analytical Results

BARGE A

Sample Location A-3-P	Concentration, ppm							
Grab Sample Canister ID/Time	со	CH₄	CO ₂	Ethane	Ethylene	Non- Condensibles (Canister)	Condensibles (Water/CO ₂ Traps)	Total Gaseous Non-Methane Organic Compounds (TGNMOCs)
104 (00:45)	<35	395	949	525	24	15,623	NA	15,623
256 (01:39)	<24	512	1159	685	21	19,272	NA	19,272
204 (02:35)	<15	543	1235	750	21	21,877	NA	21,877
200 (03:38)	<20	563	1330	828	24	23,117	NA	23,117
182 (04:38)	<22	551	1373	854	20	25,476	NA	25,476
208 (05:40)	<19	553	1423	908	19	20,905	NA	20,905
140 (06:35)	<28	576	1687	1003	21	13,422	NA	13,422
270 (07:35)	<16	656	1784	1201	20	14,073	NA	14,073
Time-Integrated Canister ID/Time								
244 (23:59-02:13)	<15	15	6631	13	<6	353	439	799
203 (02:13-04:35)	<11	16	517	19	<5	319	NA	376
152 (04:35-06:31)	<13	24	562	29	<5	550	NA	547
192 (06:31-08:24)	<13	21	535	28	<6	550	NA	550
CO ₂ /Water Trap ID								
DE/C16	<15	15		13	<6	360	439	799

BARGE A	1
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Sample Location A-2-S	Concentration, ppm							
Grab Sample Canister ID/Time	со	CH₄	CO ₂	Ethane	Ethylene	Non- Condensibles (Canister)	Condensibles (Water/CO ₂ Traps)	Total Gaseous Non-Methane Organic Compounds (TGNMOCs)
NA	NA	NA	NA	NA	NA	NA	NA	NA
FRM 25 Time-Integrated Canister/Water/CO ₂ Trap ID/Time								
238/C13/BJX (00:03-08:25)	<27	289	9587	389	17	4542	6826	11,368

Sample Location B-3-P		Concentration, ppm						
Grab Sample Canister ID/Time	со	CH₄	CO ₂	Ethane	Ethylene	Non- Condensibles (Canister)	Condensibles (Water/CO ₂ Traps)	Total Gaseous Non-Methane Organic Compounds (TGNMOCs)
123 (00:57)	<37	476	749	533	39	15,355	NA	15,355
247 (01:52)	<14	586	566	435	45	8634	NA	8634
115 (02:50)	<9	<5	<5	<4	<4	13	NA	13
120 (02:51)	<23	658	997	810	42	16,119	NA	16,119
237 (03:49)	<20	757	1095	934	41	22,334	NA	22,334
235 (04:48)	<18	893	1239	1105	41	23,891	NA	23,891
189 (05:50)	<20	969	1330	1241	42	26,819	NA	26,819
275 (06:41)	<14	831	1187	1094	36	22,879	NA	22,879
266 (07:58)	<20	869	1248	1197	37	22,619	NA	22,619
FRM 25 Time- Integrated Canister/Water/ CO ₂ Trap ID/Time								
132/C35/AHH (01:04-08:53)	<20	833	9192	1077	41	11,693	13,016	24,708

BARGE B

BARGE B

Sample Location B-4-S	Concentration, ppm							
Grab Sample Canister ID/Time	со	CH₄	CO ₂	Ethane	Ethylene	Non- Condensibles (Canister)	Condensibles (Water/CO ₂ Traps)	Total Gaseous Non-Methane Organic Compounds (TGNMOCs)
NA	NA	NA	NA	NA	NA	NA	NA	NA
FRM 25 Time- Integrated Canister/Water/ CO ₂ Trap ID/Time								
216/C63/AAJ (00:12-08:55)	<17	812	5605	657	36	6772	5850	12,622

Bibliography

- [1] Federal Reference Method 25 (FRM 25), Code of Federal Regulations, 40 CFR Part 60.
- [2] Salo, Albert E., Samuel Witz, and Robert D. MacPhee, "Determination of Solvent Vapor Concentrations by Total Combustion Analysis: A Comparison of Infrared with Flame Ionization Detectors," Paper No. 7533.2, presented at the 68th Annual Meeting of the Air Pollution Control Association, Boston, MA, June 15–20, 1975. 14 p.
- [3] Salo, Albert E., William L. Oaks, and Robert D. MacPhee, "Measuring the Organic Carbon Content of Source Emissions for Air Pollution Control" Paper No. 74190, presented at the 67th Annual Meeting of the Air Pollution Control Association, Denver, Colorado. June 913, 1974, 25 p.



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