

# **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<sub>2</sub>) 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<sub>2</sub> and water vapor. As a guideline, multiply the CO<sub>2</sub> 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<sub>2</sub> and 10 % water vapor, but it would be significant for a source near the detection limit having 10 % CO<sub>2</sub> 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<sub>2</sub> and quantitatively collecting the effluent in a second evacuated canister; then a portion of the CO<sub>2</sub> is reduced to CH<sub>4</sub> 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), CO<sub>2</sub>, and CH<sub>4</sub>; the NMO are oxidized to CO<sub>2</sub>, reduced to CH<sub>4</sub>, 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.

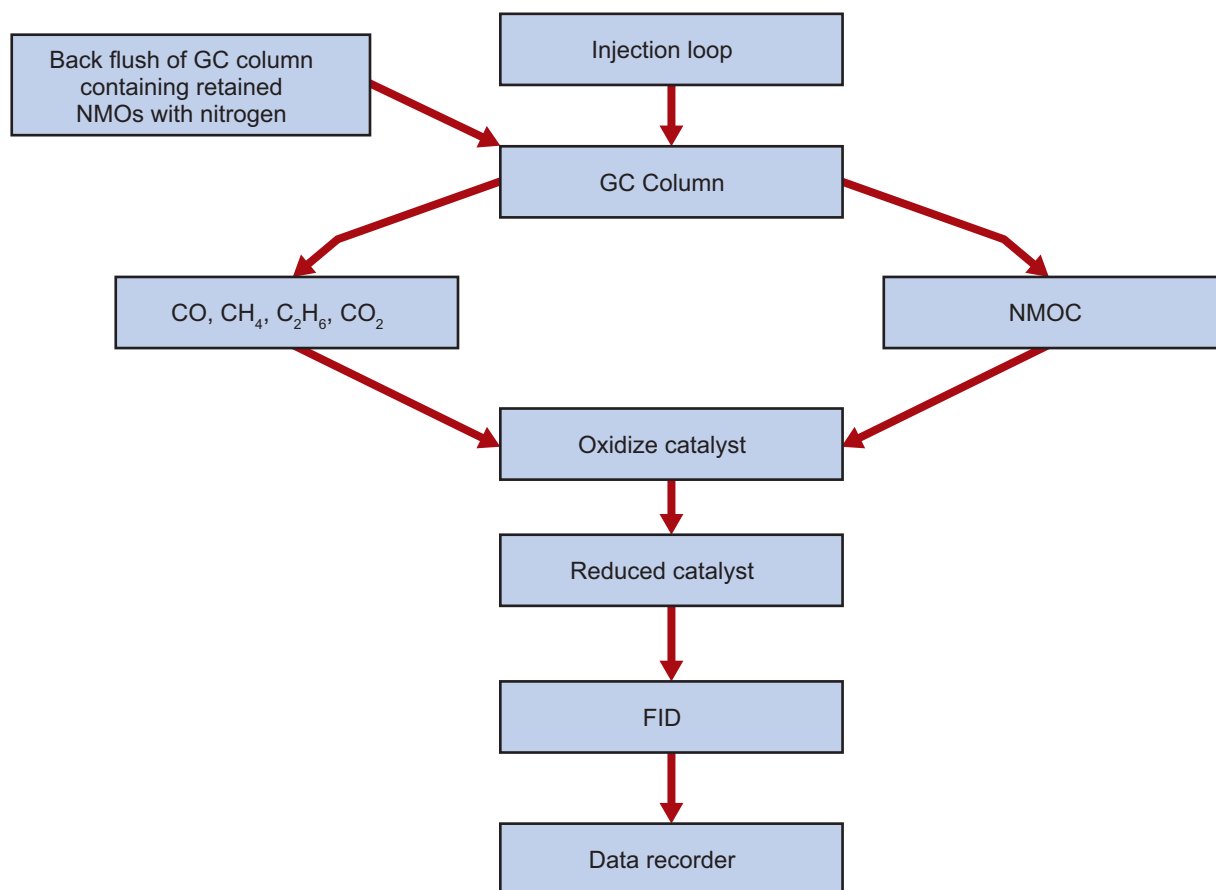
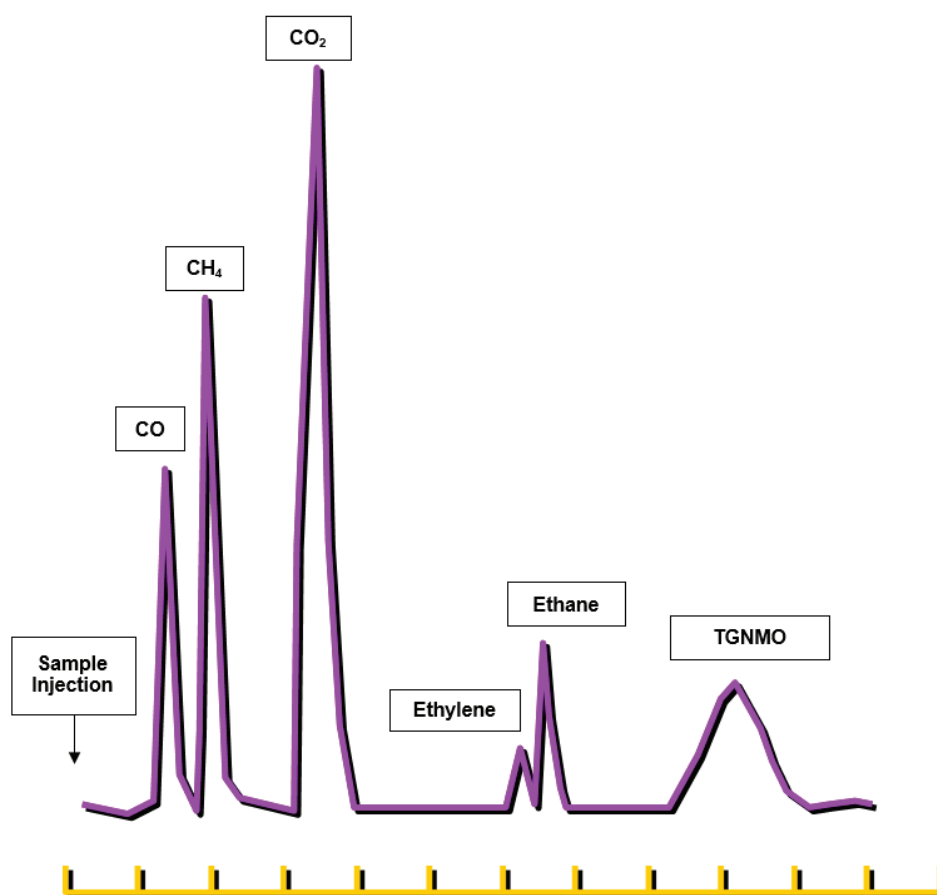


**Figure 1—Analytical Diagram of Gas Chromatograph (CG), Oxidizing and Reducing Catalysts, and Flame Ionization Detector (FID) Specified in FRM 25 Analysis**



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 (<sup>3</sup>/<sub>8</sub> 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 (<sup>3</sup>/<sub>8</sub> 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.

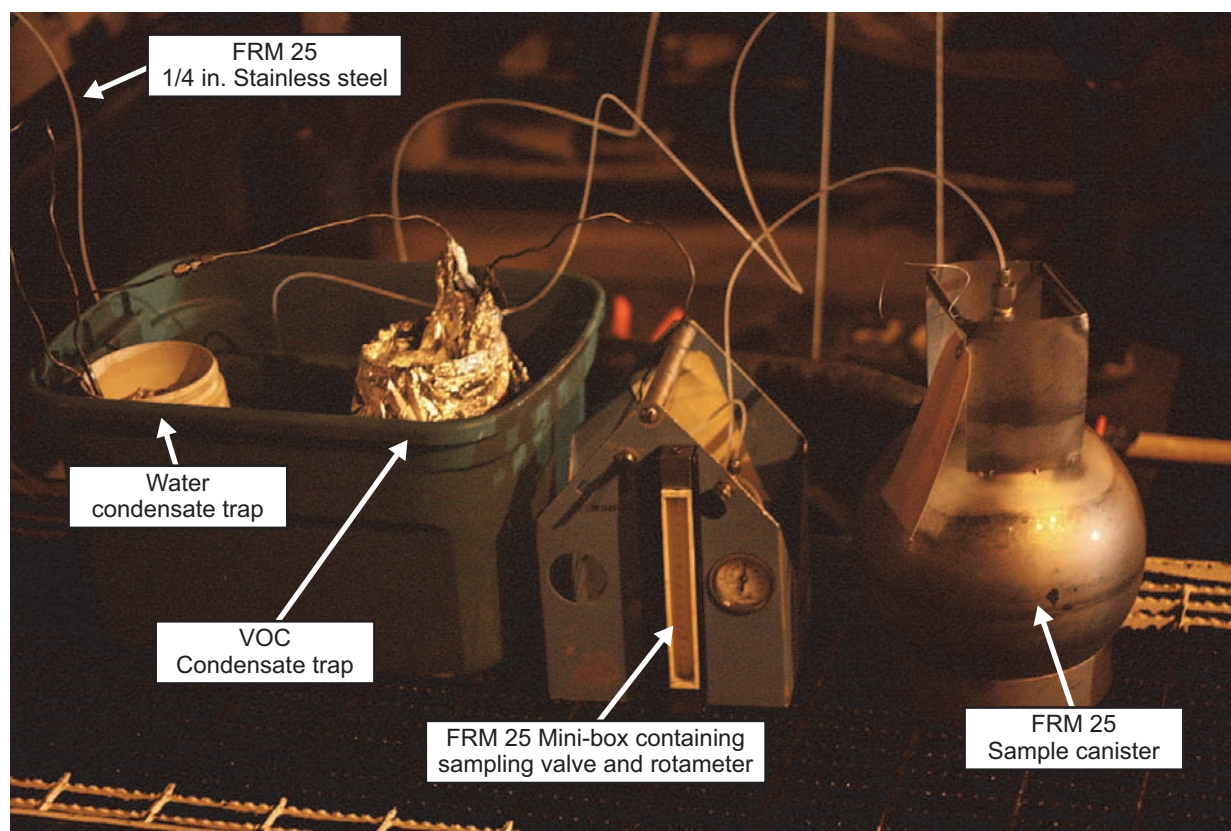


**Figure 3—Typical Time-Integrated Sampling Train Used for Measuring TGNMO, Methane, and Ethane in Air–Vapor Mixture During Filling of a Cargo Vessel with Crude Oil**

## 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 to 100 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.

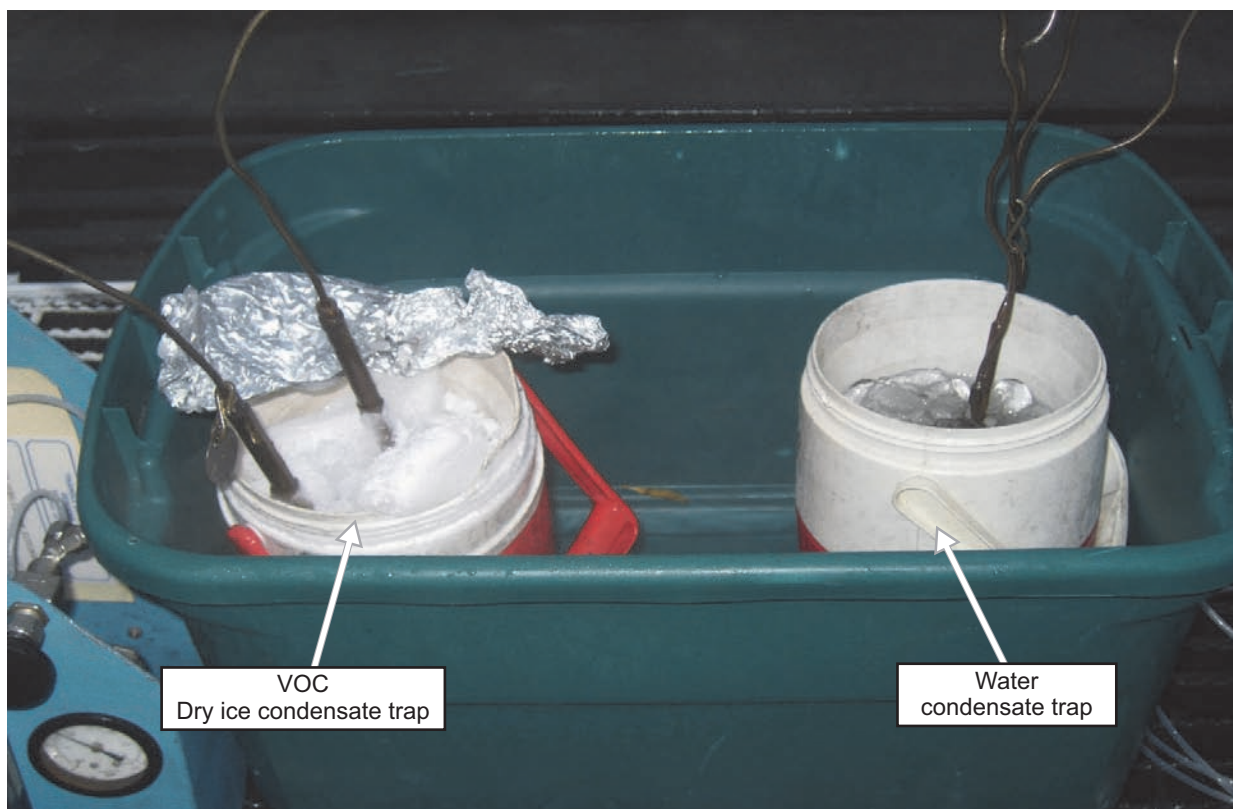


**Figure 4—Close-up View of Water Condensate Trap and VOC Condensate Trap**

## 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  $\frac{1}{4}$  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.

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

| Host Facility                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                | Testing Contractor                                                                                                                                                                                                                                                                                                                                                                                                               | Comments/Check Off                                                                                                                                                                                        |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p>Notifies testing contractor of a candidate vessel and conveys the following information:</p> <ul style="list-style-type: none"> <li>— Location of the vessel</li> <li>— Date(s) of availability</li> <li>— Detail sketch/digital images of anticipated sampling location (vessel hatch or vent stack)</li> <li>— Anticipated time of day that transfer of crude to vessel to occur and length of transfer</li> <li>— Specific safety requirements associated with testing onboard vessel at the intended location, intrinsically safe equipment needs, any harness requirements, safety training requirements, specific equipment grounding requirements, personnel safety equipment needs etc.)</li> <li>— Identify possible lodging arrangements local to the vessel location</li> <li>— Identify local suppliers of dry ice</li> </ul> | <p>Testing contractor should perform the following activities:</p> <ul style="list-style-type: none"> <li>— Develop draft sampling procedures</li> <li>— Identify and meet with analytical laboratory to verify qualifications and verifying that pre-test QA/QC requirements of FRM 25 are performed</li> <li>— Document FRM 25 equipment preparation, calibrated and certification prior to pick-up</li> </ul>                 | <p>Arrange for conference call with host facility and vessel personnel to discuss logistics of vessel and their schedule</p>                                                                              |
|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | <p>Contact host facility and vessel coordinator through conference call to:</p> <ul style="list-style-type: none"> <li>— Confirm the anticipated dates of testing and identification of sampling locations on vessel</li> <li>— Obtain host facility information (i.e. telephone number, receiving address, contact vessel personnel etc.)</li> <li>— Finalize testing schedule based upon loading of crude to vessel</li> </ul> | <p>Verify with project personnel the data quality objectives (DQOs) of the project with regard to quantification of specific analytes (i.e. CO, methane, CO<sub>2</sub>, ethylene, ethane, and TGNMO)</p> |

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

| Host Facility                                                                                                                                                                                              | Testing Contractor                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | Comments/Check Off                                                                                                                                                                                                                                                                                                                                           |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <p>Vessel Activities:</p> <ul style="list-style-type: none"> <li>— Makes any necessary arrangements with respect to the host facility with support for equipment logistics and manpower support</li> </ul> | <p>Testing arrangements through host facility:</p> <ul style="list-style-type: none"> <li>— Travel arrangements for testing contractor</li> <li>— Acquiring certified testing equipment and shipment to host facility</li> <li>— Finalize sampling rate/time and number of test needed to characterize emissions during filling of vessel</li> <li>— Determine FRM 25 number of traps and canisters needed for project completion</li> <li>— Determine type/number of spare parts needed to have available during testing</li> </ul>                                                                                                                                                                         | <p>Perform pre-test calibration of FRM 25 testing equipment:</p> <ul style="list-style-type: none"> <li>— Sample canister volume determination</li> <li>— Calibration of thermocouples</li> <li>— Calibration of rate meter</li> <li>— Certification clean of water trap/cryogenic trap/canister components</li> <li>— Leak check sampling system</li> </ul> |
|                                                                                                                                                                                                            | <p>Confirms with host facility that the testing is scheduled</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |                                                                                                                                                                                                                                                                                                                                                              |
|                                                                                                                                                                                                            | <p>Vessel activities:</p> <ul style="list-style-type: none"> <li>— Prepare the sampling location(s) for testing (vessel hatch or vent stack)</li> <li>— If applicable, provide covers for hatches to prevent air in-leakage</li> </ul>                                                                                                                                                                                                                                                                                                                                                                                                                                                                       |                                                                                                                                                                                                                                                                                                                                                              |
|                                                                                                                                                                                                            | <p>Travels to test site:</p> <ul style="list-style-type: none"> <li>— Identify logistics and location at host facility for equipment unpacking, set-up, calibration etc.</li> <li>— Pick-up dry ice from local supplier</li> <li>— Put on all safety equipment as specified by vessel/project health and safety plan (HSP)</li> <li>— Assemble the testing apparatus and haul to sampling location(s)</li> <li>— Assemble the probe support at the sampling location(s)</li> <li>— Verify that all equipment is properly positioned and ready for use</li> <li>— Record water and cryogenic trap numbers and canister numbers for each specific sampling event onto field test data sheets (FTDS)</li> </ul> | <p>Pre-test items:</p> <ul style="list-style-type: none"> <li>— Attend health and safety meeting with host facility and vessel personnel</li> <li>— Perform pre-test meeting with host facility and vessel personnel covering monitoring objectives, equipment, personnel needs, anticipated schedule, process data needed during testing etc.</li> </ul>    |

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

| Host Facility                                                                                                                                                     | Testing Contractor                                                                                                                                                                                                                                                                                                                                                                                                                           | Comments/Check Off                                                         |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------------------|
| Vessel Documentation:<br>— Acquire needed process/transfer date during testing of crude into vessel<br>— Record process data at required intervals during testing | — Perform pre-test leak check of sampling systems using dummy canisters<br>— Purge sample line to water condensate trap with external vacuum canister for approximately 10 min<br>— Reconnect sample line to water condensate trap<br>— Place ice water/dry ice around individual condensate traps<br>— Evacuate canisters off site to –29 in. Hg, leak check and connect to sampling train<br>— 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<br>— Begin sampling at specified flow-rate for a pre-determined sampling time by opening the canister valve to “open” position<br>— Record sampling parameters i.e. flow rate, ambient temperature, ambient pressure etc.) during testing on the FTDS                                                                    | Contact vessel personnel during filling to record appropriate process data |
| 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<br>— Record final sampling data on FTDS                                                                                                                                                                                                                                                                                                        |                                                                            |

**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:<br>— Disconnect the water (optional) and cryogenic traps from the sampling train<br>— Plug the ends of the traps and immerse in cryogen for transport to analytical laboratory<br>— Checks and records the final vacuum in the sample canisters and record on FTDSs<br>— Prepare all sampling components (i.e. water traps, cryogenic traps, and canisters) for shipment to analytical laboratory, completing chain-of-custody (COC) | Perform post-test meeting with host and vessel personnel |

**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 <sub>2</sub> ?                                                                                               |     |    |
| 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**

| Item                                   | Item Name                           | Purpose or Function                                                                                                          | Yes/No |
|----------------------------------------|-------------------------------------|------------------------------------------------------------------------------------------------------------------------------|--------|
| <b>Field Apparatus</b>                 |                                     |                                                                                                                              |        |
| 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                                                                        |        |
| <b>Laboratory Analytical Apparatus</b> |                                     |                                                                                                                              |        |
| 8                                      | Condensate recovery system          | A system which will heat and maintain the condensate collection tube at 200 °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, O <sub>2</sub> containing less than 1 ppm CO <sub>2</sub> 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 % CO <sub>2</sub> in air to check NMO and FID linearity                                       |        |
| 20                                     | NMO system checks                   | A nominal cylinder mixture of 50 ppm CH <sub>4</sub> , 50 ppm CO, 20 ppm propane, and 2 % CO with the balance gas being air  |        |

