

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

API TECHNICAL REPORT 2574
FIRST EDITION, AUGUST 2016



AMERICAN PETROLEUM INSTITUTE

Special Notes

API publications necessarily address problems of a general nature. With respect to particular circumstances, local, state, and federal laws and regulations should be reviewed.

Neither API nor any of API's employees, subcontractors, consultants, committees, or other assignees make any warranty or representation, either express or implied, with respect to the accuracy, completeness, or usefulness of the information contained herein, or assume any liability or responsibility for any use, or the results of such use, of any information or process disclosed in this publication. Neither API nor any of API's employees, subcontractors, consultants, or other assignees represent that use of this publication would not infringe upon privately owned rights.

API publications may be used by anyone desiring to do so. Every effort has been made by the Institute to assure the accuracy and reliability of the data contained in them; however, the Institute makes no representation, warranty, or guarantee in connection with this publication and hereby expressly disclaims any liability or responsibility for loss or damage resulting from its use or for the violation of any authorities having jurisdiction with which this publication may conflict.

API publications are published to facilitate the broad availability of proven, sound engineering and operating practices. These publications are not intended to obviate the need for applying sound engineering judgment regarding when and where these publications should be utilized. The formulation and publication of API publications is not intended in any way to inhibit anyone from using any other practices.

Any manufacturer marking equipment or materials in conformance with the marking requirements of an API standard is solely responsible for complying with all the applicable requirements of that standard. API does not represent, warrant, or guarantee that such products do in fact conform to the applicable API standard.

Classified areas may vary depending on the location, conditions, equipment, and substances involved in any given situation. Users of this Technical Report should consult with the appropriate authorities having jurisdiction.

Users of this Technical Report should not rely exclusively on the information contained in this document. Sound business, scientific, engineering, and safety judgment should be used in employing the information contained herein.

API is not undertaking to meet the duties of employers, manufacturers, or suppliers to warn and properly train and equip their employees, and others exposed, concerning health and safety risks and precautions, nor undertaking their obligations to comply with authorities having jurisdiction.

Information concerning safety and health risks and proper precautions with respect to particular materials and conditions should be obtained from the employer, the manufacturer or supplier of that material, or the material safety data sheet.

All rights reserved. No part of this work may be reproduced, translated, stored in a retrieval system, or transmitted by any means, electronic, mechanical, photocopying, recording, or otherwise, without prior written permission from the publisher. Contact the Publisher, API Publishing Services, 1220 L Street, NW, Washington, DC 20005.

Copyright © 2016 American Petroleum Institute

Foreword

Nothing contained in any API publication is to be construed as granting any right, by implication or otherwise, for the manufacture, sale, or use of any method, apparatus, or product covered by letters patent. Neither should anything contained in the publication be construed as insuring anyone against liability for infringement of letters patent.

Suggested revisions are invited and should be submitted to the Standards Department, API, 1220 L Street, NW, Washington, DC 20005, standards@api.org.

Contents

	Page
1 Scope	1
1.1 Applicability	1
1.2 Principle	1
2 Field Sampling Apparatus	2
2.1 General	2
2.2 Sampling Probe	2
2.3 Water Condensate Trap	3
2.4 VOC Condensate Trap	3
2.5 Metering Valve and Rate Meter	4
2.6 Sample Canister	4
2.7 Mercury Manometer or Absolute Pressure Gauge	5
2.8 Vacuum Pump	5
3 Sampling Reagents	5
4 Time-Integrated Field Sampling Procedure	5
4.1 Sampling Train Assembly	5
4.2 Sample Train Operation	12
4.3 Sample Train Recovery	13
5 Instantaneous Field Sampling Procedure	14
5.1 Sampling Train Preparation	14
5.2 Sampling Train Operation	14
5.3 Sampling Train Recovery	14
6 Nomenclature and Calculations	14
6.1 General	14
6.2 Nomenclature	15
6.3 Calculations	16
Annex A (informative) Federal Reference Method 25 (FRM 25) Determination of Total Gaseous Nonmethane Organic Emissions as Carbon (Abridged and Modified)	18
Annex B (informative) Protocol for Sampling and Analysis of Vapors from Marine Loading of Crude Oil: Field Testing for Proof-of-Principle	34
Annex C (informative) Analytical Sample Canister Identification	45
Annex D (informative) Laboratory Analytical Results	46
Bibliography	48
Figures	
1 Analytical Diagram of Gas Chromatograph (CG), Oxidizing and Reducing Catalysts, and Flame Ionization Detector (FID) Specified in FRM 25 Analysis	2
2 Analytical Chromatogram Associated With FRM 25 Analysis for Quantifying TGNMO, Methane, and Ethane Emissions in an Air-Vapor Mixture	3
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	4
4 Close-up View of Water Condensate Trap and VOC Condensate Trap	5
B.1 Meteorological Data: New Orleans Lakefront, LA	36
B.2 Meteorological Data: Baton Rouge, LA	36
B.1 Barge Hatch with Sampling Probes	37

B.2 TGNMOC Concentration (ppm) vs Time (hours) 39
B.3 Methane Concentration (ppm) vs Time (hours) 39
B.4 Ethane Concentration (ppm) vs Time (hours) 40

Tables

1 Various Project Activities to be Completed by Host Facility and Testing Contractor 6
2 Various Project (Sampling) Activities to be Completed by Host Facility and Testing Contractor 8
3 Various Project (Clean up) Activities to be Completed by Host Facility and Testing Contractor 8
4 QC Checklist Associated with Sampling and Analytical Event 9
5 QC Checklist for Equipment and Reagents 10
6 Field Test Data Sheet (FTDS) 11
**B.1 Results for Only Location at Which Both Grab Samples and a Valid Integrated Sample
Were Obtained 40**
B.2 Results From Other Sample Locations 41
**B.3 Summary of Data Comparing Grab Sample Average Results to All Integrated Sample
Results Average 41**
B.4 Barge A 43
B.5 Barge B 44

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 (CO₂) 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 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.

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 CO₂ and quantitatively collecting the effluent in a second evacuated canister; then a portion of the CO₂ is reduced to CH₄ and measured by a flame ionization detector (FID). The organic content of the field sample canister fraction is