



Designation: D8028 – 17

# Standard Test Method for Measurement of Dissolved Gases Methane, Ethane, Ethylene, and Propane by Static Headspace Sampling and Flame Ionization Detection (GC/FID)<sup>1</sup>

This standard is issued under the fixed designation D8028; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers the determination of the dissolved gases methane, ethane, ethylene, and propane in drinking, waste, and ground waters, including domestic wells whether naturally occurring or resulting from commercial activities, or both. This test method has an analytical range from 10  $\mu\text{g/L}$  to 11 000  $\mu\text{g/L}$  for methane, and 10  $\mu\text{g/L}$  to 5000  $\mu\text{g/L}$  for ethane, ethylene, and propane. If a sample has a dissolved gas concentration above the calibration range, the sample would require dilution. Other analytical ranges may be used as long as the instrument calibration encompasses the desired range and demonstrates adequate linearity.

1.2 This test method is applicable to samples collected at a nominal ambient pressure. Samples collected under high pressures, that is, above ambient pressure, may not be accurately analyzed using this method.

1.3 This test method is applicable to a variety of dissolved gases; however, for the present standard, only methane, ethane, ethylene, and propane were validated. In order to validate for a gas not listed in this method, the analyst would need to establish the saturation concentration of the new gas, and establish a valid curve, method detection limits, and demonstration of capability following the procedures outlined in this method.

1.4 It is the analyst's responsibility to ensure the validity of this test method for dissolved gases other than methane, ethane, ethylene, and propane and other sample matrices.

1.5 *Units*—The values stated in SI units are to be regarded as the standard. No other units of measurement are included in this standard.

1.6 A single laboratory study was done in order to establish precision and bias for the surrogate (see Section 16).

1.7 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the*

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D19 on Water and is the direct responsibility of Subcommittee D19.06 on Methods for Analysis for Organic Substances in Water.

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*responsibility of the user of this standard to establish appropriate safety, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.8 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

- D1129 Terminology Relating to Water
- D1193 Specification for Reagent Water
- D8006 Guide for Sampling and Analysis of Residential and Commercial Water Supply Wells in Areas of Exploration and Production (E&P) Operations
- E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods
- E355 Practice for Gas Chromatography Terms and Relationships
- E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

### 2.2 Federal Standards:

- 40 CFR Part 136, Appendix B Definition and Procedure for the Determination of the Method Detection Limit, Revision 1.11<sup>3</sup>
- PA-DEP 3686 Light Hydrocarbons in Aqueous Samples via Headspace and Gas Chromatography with Flame Ionization Detection (GC/FID), Revision 0, April 2012<sup>4</sup>
- SW-846 Test Methods for Evaluating Solid Waste: Physical/

<sup>2</sup> For referenced ASTM standards, visit the ASTM website, [www.astm.org](http://www.astm.org), or contact ASTM Customer Service at [service@astm.org](mailto:service@astm.org). For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

<sup>3</sup> Available from U.S. Government Printing Office, Superintendent of Documents, 732 N. Capitol St., NW, Washington, DC 20401-0001, <http://www.access.gpo.gov>.

<sup>4</sup> Available from Pennsylvania Department of Environmental Protection (PA-DEP), Headquarters, Rachel Carson State Office Building, 400 Market Street, Harrisburg, PA 17101, <http://www.dep.state.pa.us>.

Chemical Methods, Update V, Chapter Four, Revision 5, July 2014<sup>5</sup>

SW-846, Method 5021 Volatile Organic Compounds in Various Sample Matrices Using Equilibrium Headspace Analysis, Update V, Revision 2, July 2014<sup>6</sup>

### 3. Terminology

#### 3.1 Definitions:

3.1.1 For definitions of terms used in this standard, refer to Terminology D1129 and Practice E355.

#### 3.2 Definitions of Terms Specific to This Standard:

3.2.1 *batch, n*—set (group) of up to 20 samples analyzed such that results of analysis of the quality control (QC) samples analyzed with the batch are indicative of the quality of the results of analysis of samples in the batch.

3.2.1.1 *Discussion*—The number of samples in the batch is defined by the task group responsible for the method or as defined by laboratory quality assurance (QA) practices.

3.2.2 *calibration standard, n*—solution containing the analyte(s) of interest at a known concentration either purchased from a certified reference material provider or prepared in-house from materials of known purity and concentration and used to calibrate the measurement system.

3.2.3 *calibration verification standard, CV, n*—defined standard used to verify the accuracy of a calibration in the measurement range of interest.

3.2.3.1 *Discussion*—The CV should be obtained from a certified reference material provider or prepared at the laboratory from a separate source from the calibration standards. This standard may not be used to perform calibrations, only calibration verification.

3.2.4 *field duplicates, n*—two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedure.

3.2.4.1 *Discussion*—Analysis of field duplicates gives an indication of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

3.2.5 *field reagent blank, n*—reagent water placed in a sample container taken to the field along with the samples and treated as a sample in all respects, including exposure to sampling procedures, sampling site conditions, storage, preservation, and all analytical procedures.

3.2.5.1 *Discussion*—The purpose of the field reagent blank is to determine if test method or instrument analytes, or both, or other interferences are present in the field environment.

3.2.6 *initial calibration, ICAL, standard solutions, n*—set of solutions containing the target analytes at concentrations that define the calibration range of the method.

3.2.7 *laboratory control standard, LCS, n*—aliquot of solution with known concentrations of method analytes.

3.2.7.1 *Discussion*—It should be obtained from a certified reference material provider or prepared at the laboratory. The LCS is analyzed using the same sample preparation, analytical method, and QA/QC procedure used for test samples. Its purpose is to determine whether method performance is within accepted control limits.

3.2.8 *laboratory control standard duplicate, LCSD, n*—second aliquot of solution with known concentrations of method analytes. (See 3.2.7.1, *Discussion* for *laboratory control standard*.)

3.2.9 *matrix spike, MS, n*—second aliquot of a sample to which known concentrations of target analyte(s) are added in the laboratory and should be analyzed using the same sample preparation and analytical method used for test samples.

3.2.9.1 *Discussion*—MS should be prepared by diluting the sample with a known concentration of prepared laboratory standard. Its purpose is to determine whether the sample matrix contributes bias to the analytical results.

3.2.10 *method blank, MB, n*—suitable aliquots of reagent water, analyzed using the same sample preparation technique, analytical method, and QA/QC procedure used for test samples.

3.2.10.1 *Discussion*—The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or apparatus.

3.2.11 *method detection limit, MDL, n*—the minimum concentration of an analyte that can be identified, measured, and reported with a 99 % confidence that the analyte concentration is greater than zero.

3.2.11.1 *Discussion*—The confidence level is determined from analysis of a sample in a given matrix containing the analyte(s).

3.2.12 *saturation, n*—point at which a solution contains enough of a dissolved solid, liquid, or gas so that no more will dissolve in the solution at a given temperature and pressure.

3.2.13 *stock standard solution, n*—concentrated solution containing a single certified standard that is a test method analyte prepared in the laboratory with an assayed reference compound.

3.2.13.1 *Discussion*—Stock standard solutions are used to prepare primary dilution standards.

3.2.14 *surrogate analyte, n*—pure analyte(s), which is extremely unlikely to be found in any sample, and is added to the sample aliquot in known amount(s) before extraction and measured with the same procedures used to measure other sample components.

#### 3.3 Acronyms:

3.3.1 *FID, n*—flame ionization detector

3.3.2 *GC, n*—gas chromatograph

3.3.3 *ICAL, adj*—initial calibration

3.3.4 *LCS, n*—laboratory control standard

3.3.5 *LCSD, n*—laboratory control standard duplicate

3.3.6 *MB, n*—method blank

<sup>5</sup> Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, <http://www.epa.gov>.

<sup>6</sup> Available from United States Environmental Protection Agency (EPA), William Jefferson Clinton Bldg., 1200 Pennsylvania Ave., NW, Washington, DC 20460, <http://www.epa.gov>.

- 3.3.7 *MS*, *n*—matrix spike
- 3.3.8 *MSD*, *n*—matrix spike duplicate
- 3.3.9 *PLOT*, *adj*—porous layer open tubular
- 3.3.10 *QA*, *adj*—quality assurance
- 3.3.11 *QC*, *adj*—quality control
- 3.3.12 *PA-DEP*, *n*—Pennsylvania Department of Environmental Protection
- 3.3.13 *RSD*, *n*—relative standard deviation
- 3.3.14 *RSK*, *n*—Robert S. Kerr
- 3.3.15 *UHP*, *adj*—ultra high purity

#### 4. Summary of Test Method

4.1 A headspace is made in the sample vial without exposing the sample to atmosphere. The sample is then stirred or agitated and brought to constant temperature to facilitate partitioning of the dissolved gases into the established headspace. Once temperature control and stirring or agitation parameters are established, EVERY sample, standard, and blank needs to be temperature controlled and stirred or agitated in the exact same way in order to ensure reproducibility. A portion of the headspace is then injected onto the head of a gas chromatographic (GC) column for separation and analysis. Measurement is accomplished using a flame ionization detector (FID).

#### 5. Significance and Use

5.1 This test method covers the determination of the dissolved gases methane, ethane, ethylene, and propane in drinking, waste, and ground waters, including domestic wells; whether naturally occurring or resulting from commercial activities, dissolved gases can be hazardous both to the environment and humans. Due to increased scrutiny of dissolved gases, developing a valid method for the testing of dissolved gases in water has become more imperative. Static headspace sampling is generally applicable for sampling these compounds. However, as these compounds are extremely volatile, a closed sampling system is recommended. This test method can be used for quantitatively determining dissolved gases in ground, waste, and drinking waters.

5.2 This test method is suitable for analysis of domestic drinking water samples from residential and commercial water supply wells prior to oil and gas exploration activities to form a baseline for monitoring potential impacts during exploration; development, including hydraulic fracturing; operation; closure; and reclamation of nearby oil and gas production and injection wells.

#### 6. Interferences

6.1 Impurities in the air, the field sample vials, vial septa, the preservatives, or improper sealing during transport can cause contamination. Field reagent blanks, recommended, and method blanks, required, shall be used to verify proper sampling and handling procedures.

6.2 Contamination or carryover can occur whenever a highly concentrated sample is run. A blank shall be run after a highly concentrated sample to ensure system cleanliness.

6.2.1 A carryover study should be done in order to determine the nominal level of analytes that will be prone to carry over into subsequent samples. From this study, the laboratory shall be required to run blanks after samples containing analytes above the established levels. Otherwise, if a sample is run directly after a high level sample, reference the laboratory carryover study, and displays an analyte of interest, the sample would need to be run again in order to ensure the accuracy of the results.

6.3 The FID is a nonselective detector. If matrix interference caused by sample contamination or compound co-elution occurs, an experienced analyst is required for proper interpretation.

6.4 In order to inhibit analyte loss, samples should be stored in 40-ml vials with polytetrafluoroethylene (PTFE)-lined chlorobutyl septa with no headspace, and placed on ice within 15 minutes of collection. Samples should be transported and kept cooled to approximately 0 to 6°C but not frozen. If any visible headspace exists in a sample vial, it is to be noted in the results report as analyte loss can exist with sample headspace. Samples may be preserved with sulfuric acid in order to extend the expiration date to two weeks from the sampling date.

#### 7. Apparatus

7.1 *Sample containers*, 40-ml screw top vials sealed with PTFE-lined chlorobutyl septa.

7.2 *Water bath*, capable of maintaining water temperature at 20°C ( $\pm 0.5^\circ\text{C}$ ) to prepare calibration and laboratory control standards. Temperatures other than 20°C may be used, as long as the saturated solution concentration at the temperature is known.

7.3 *Digital thermometer*.

7.4 *Gastight syringes*, 10  $\mu\text{l}$  to 2.5 ml.

7.5 *Two gastight syringes fitted with removable needles and Luer lock valves*, 25 ml.

7.6 *Glass-stoppered class A volumetric flasks*, 5 to 100 ml.

7.7 *Stir bars*, (required only for sample agitation through stirring) magnetic stir bars sized to fit in the 40-ml screw-top vials.

7.8 *Ultra high purity (UHP) inert gas*, used to purge the instrument headspace vial to displace any contaminants in the vial. Acceptable gases are helium and nitrogen.

7.9 *Sample Transfer Device*—A transfer device capable of transferring sample or standard from the sample 40-ml vial to a separate 40-ml vial purged with an inert gas such as nitrogen or helium (recommended) and incorporated with a stir bar and surrogate standard. (A stir bar is not needed if sample agitation is done by means other than stirring such as vial shaking.) It is recommended that sample transfer is done with a sealed device/system. See Fig. 1.

NOTE 1—The removable needle needs to be fitted with a Luer lock valve to ensure the sample is not exposed to atmosphere during the sample transfer. See Fig. 1.

7.10 *Sample Agitation*—Samples can be agitated to achieve equilibrium of the dissolved gases in the headspace rapidly.

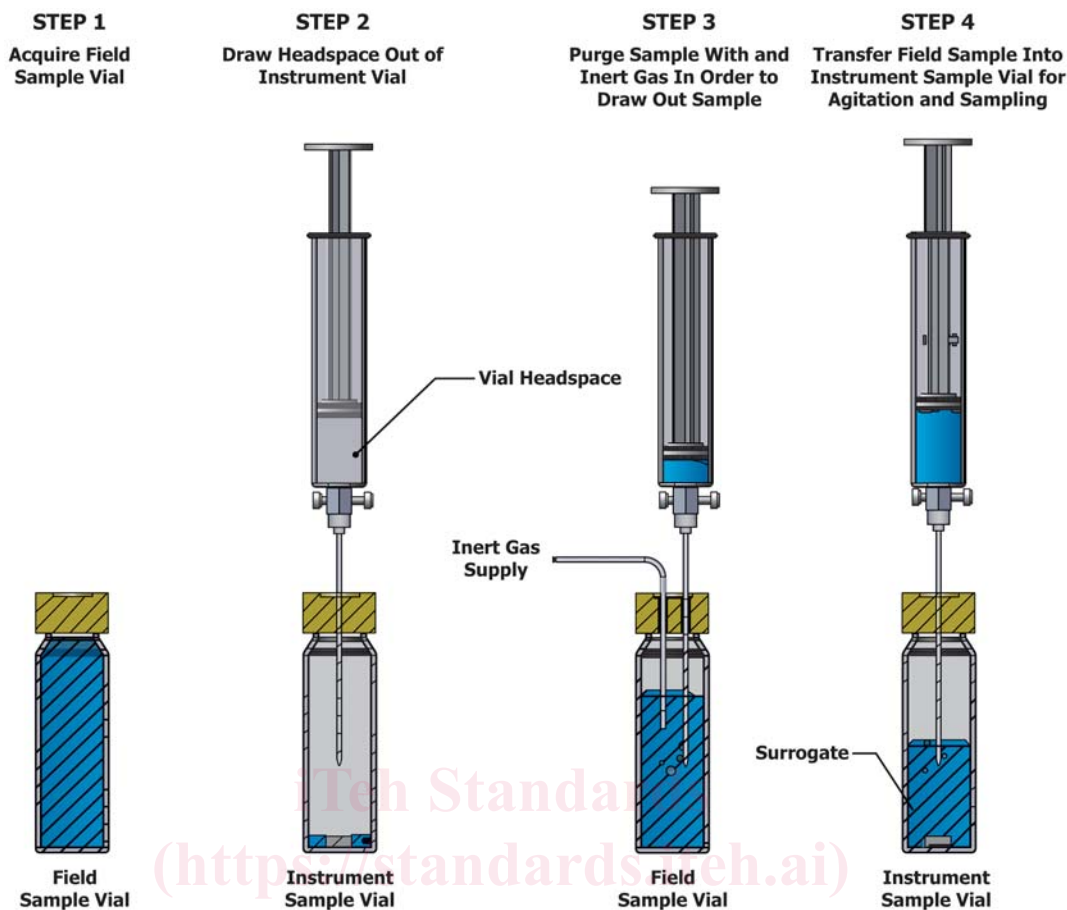


FIG. 1 Sample Transfer Graphic

The sample agitation procedure is discretionary; however, it shall be established that equilibrium of the sample system is achieved with or without an agitation procedure and sample agitation shall be done without exposing the sample to the atmosphere. Furthermore, all sample, standard, spike, and blank agitation shall be done in the exact same manner.

**7.11 Headspace Sampling System**—An automated sampling system capable of performing static headspace can be used as the sample introduction system to the GC. The system must be able to inject the volume necessary to meet the detection limits set forth in this test method. An automated sampling system may be used for the sample transfer, agitation, and headspace sampling as long as it meets all of the manual sample transfer criteria stated above.<sup>7</sup>

**7.12 Gas chromatograph (GC)**, capable of temperature and pressure programming with a split/splitless injection port.

**7.13 Flame Ionization Detector (FID)**—Follow the instrument manufacturer’s recommendations for gases, flow rates, and operation.

**7.14 Capillary or Packed Gas Chromatograph (GC) Column**—Any column that meets the performance specifications of this test method. Sample components are identified by their relative retention time. Because of possible sample matrix interferences, co-elution, and elevated contamination from other compounds, the sample chromatograms can be difficult to analyze. At least a 50 % resolution of the height of the valley between any contaminants and the analyte of interest is required and a retention time window of no greater than 5 % from the daily continuing calibration check is required for identification. Examples of columns found suitable:

**7.14.1 Column 1**, 30-m by 0.53-mm inside diameter (ID) by 20- $\mu$ m, nonpolar porous layer open tubular (PLOT) column incorporating 100 % divinylbenzene.<sup>8</sup>

**7.14.2 Column 2**, 2-m by 1.0-mm ID by 1.6-mm outside diameter (OD) silco, packed column, shin carbon ST 100/120.<sup>9</sup>

<sup>8</sup> A RESTEK QS-BOND PLOT Column (Cat# 19738) was used to develop this test method and generate the precision and bias data presented in Section 16. RESTEK Corporation, Bellefonte, PA 16823. Columns from other vendors that are able to generate similar method performance and that achieve adequate resolution may be used.

<sup>9</sup> RESTEK Shin Carbon ST Column (Cat #19808) was used to develop this test method. RESTEK Corporation, Bellefonte, PA 16823. Columns from other vendors that are able to generate similar method performance and that achieve adequate resolution may be used.

<sup>7</sup> The EST Analytical LGX50 Autosampler was used for the laboratory studies. Autosamplers from other vendors that are able to generate similar method performance and that achieve adequate sampling may be used.

## 8. Reagents and Materials

8.1 *Purity of Reagents*—Reagent-grade chemicals shall be used in all tests. It is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.<sup>10</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

### 8.2 Compressed Gases:

8.2.1 *Helium or Hydrogen*—UHP grade or equivalent, for GC system carrier gas.

8.2.2 *Air*—Zero grade or equivalent, for use as FID fuel gas.

8.2.3 *Hydrogen*—UHP grade or equivalent, for use as FID fuel gas.

8.2.4 *Nitrogen*—UHP grade or equivalent, for sweeping the instrument sample vials.

### 8.3 Waters and Solvents:

8.3.1 *Reagent Grade Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water that meets purity specifications of Specification D1193.

8.3.2 *Methanol*—High purity laboratory control matrix spike (LC-MS) grade or equivalent, for preparation of surrogate working standard.

8.4 *Certified Gas Cylinders*—Purity of 99 % for preparation of stock solutions. Certificate of analysis required.

8.4.1 *Methane*—Primary and secondary source.

8.4.2 *Ethane*—Primary and secondary source.

8.4.3 *Ethylene*—Primary and secondary source.

8.4.4 *Propane*—Primary and secondary source.

8.5 *Stock Standard Solution*—Preparation of the methane, ethane, ethylene, and propane stock standard solutions are prepared fresh and expire after two weeks if preserved, see Appendix X1. The expiration date may be extended if alternate storage conditions for laboratory prepared standards are demonstrated using the process described in Appendix X1. If a certified reference material (CRM) is procured with a certificate of analysis (COA) denoting a different expiration period specified by the manufacturer, the expiration denoted on the CRM can be used.

8.5.1 Set up a recirculating bath set to 20°C ± 0.5°C at 1 atm pressure in a laboratory fume hood.

NOTE 2—The saturation concentration of the solution varies with the temperature of the water and atmospheric pressure; thus, the temperature of the water shall be controlled. Alternative saturation temperatures are acceptable as long as the saturation concentrations are documented.

8.5.2 The saturation concentrations at 20°C and 1 atm pressure of the gases in this test method are as follows:<sup>11,12</sup>

8.5.2.1 *Methane*—23.2 mg/L.

8.5.2.2 *Ethane*—62.0 mg/L.

8.5.2.3 *Ethylene*—149.0 mg/L.

8.5.2.4 *Propane*—76.7 mg/L.

8.5.3 Fill a 500-ml volumetric flask to the neck with water and place it in the recirculating bath ensuring that the reagent grade water in the flask is submerged in the recirculating bath. Let the reagent grade water sit in the bath for long enough for the water to reach 20°C (±0.5°C) using a calibrated digital thermometer.

8.5.4 Connect a flexible piece of tubing to the certified gas cylinder. Then, attach a glass pipette or a frit to the other end of the tubing. Finally, place the pipette/frit at the end of the tubing into the reagent water in the submerged volumetric flask. Tubing should be polyether ether ketone (PEEK), PTFE, or clean copper.

8.5.5 Open the valve of the certified gas cylinder enough to ensure vigorous bubbling of the gas in the water. Bubble the certified gas in the water for at least 30 min to ensure complete saturation.

NOTE 3—200 to 250-ml/min gas flow into 500 ml of water for 30 min is sufficient to ensure saturation. Flow rate, time, and temperature needs to be documented.

8.5.6 Repeat this procedure with a secondary source for the secondary source stock standard solution.

8.5.7 Alternative means of producing or procuring water-based standards of the dissolved gases of known concentration are acceptable provided they meet all quality assurance criteria described in this test method. A CRM with a COA can also be used for the stock solution.

8.6 *Initial Calibration (ICAL) Solutions*—Prepared from the primary stock solution standard.

8.6.1 ICAL solutions are prepared by performing serial dilutions on the primary stock standard solution into a volumetric flask. The dilutions shall be performed while the stock solution is still being purged with the analyte gas to ensure the solution is consistently saturated. These dilutions need to be immediately transferred to a 40-ml vial with PTFE-lined chlorobutyl septa with no headspace until transferred to the instrument sample vial. These solutions shall be refrigerated when not in use.

8.6.2 Alternative means of producing or procuring water-based standards of the dissolved gases of known concentration are acceptable provided they meet all quality assurance criteria described in this test method. A CRM with a COA can also be used to prepare ICAL solutions.

NOTE 4—The temperature of the standards during handling, preparation, and dilution is as important as the temperature during the equilibrium step. All steps for the solution preparation, sample transfer, and dilution steps need to be done at the same approximate temperature. It is recommended that all standard preparation and dilution steps be performed at a temperature of approximately 20 ± 0.5°C to minimize the chance for analyte loss. QC samples should be handled in the exact same manner. Furthermore, after adding the aliquots of stock standard solution to the volumetric flask, the solution needs to be inverted gently three times in order to prevent analyte loss. Also, when transferring the standard solution from the volumetric flask to the 40-ml vial, pour in such a way as

<sup>10</sup> *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

<sup>11</sup> Dean, John A., *Lange's Handbook of Chemistry Fourteenth Edition*, United States of America, McGraw-Hill, Inc., 1972.

<sup>12</sup> *Propane Gas Properties*, <http://encyclopedia.airliquide.com> (accessed Nov. 5, 2011).

to prevent splashing, bubbling, or sample agitation.

8.6.3 There must be at least five calibration points for every curve and separate ICAL solutions should be prepared for each dissolved gas. If multi-analyte standards are available, then multiple analytes can be combined in a single ICAL.

8.6.4 ICAL solutions can be stored up to one week in 40-ml vials with PTFE-lined chlorobutyl septa with no headspace at temperature range of above freezing to 6°C until analysis (see [Appendix X1](#)); two weeks if standard is preserved and a chlorobutyl septa is used (see [Appendix X1](#)).

8.7 *Laboratory Control Standard (LCS) and Laboratory Control Standard Duplicate (LCSD)*—LCS and LCSD solutions are prepared from the primary source stock standard solution.

8.7.1 LCS and LCSD solutions are prepared by performing dilutions on the primary stock standard solution. The LCS solutions need to be prepared while the solution is purging with the analyte to ensure the solution is saturated. LCS and LCSD need to be prepared for each analyte to be analyzed and prepared similar to [8.6.1](#). A CRM with a COA can also be used for an LCS/LCSD solution. As in [8.6.2](#), alternative means of producing or procuring water-based standards of the dissolved gases of known concentration are acceptable provided they meet all quality assurance criteria described in this test method. A CRM with a COA can also be used to prepare ICAL solutions.

8.7.2 LCS and LCSD solutions can be stored up to one week in a 40-ml vial with PTFE-lined chlorobutyl septa, two weeks if preserved, with no headspace at a temperature range of above freezing to 6°C (see [Appendix X1](#)).

8.8 *Calibration Verification (CV) Standard*—CV solutions are prepared from a secondary source stock standard solution.

8.8.1 CV solutions are prepared by performing dilutions on the secondary stock standard solution. The CV solutions need to be prepared while the solution is purging with the analyte to ensure the solution is saturated. CVs need to be prepared for each analyte to be analyzed and prepared similar to [8.6.1](#). A CRM with a COA can also be used for a CV solution. The secondary source can be a different lot CRM or a different saturated solution not used for the calibration verification. As in [8.6.2](#), alternative means of producing or procuring water-

based standards of the dissolved gases of known concentration are acceptable provided they meet all quality assurance criteria described in this test method. A CRM with a COA can also be used to prepare CV solutions.

8.8.2 CV solutions can be stored up to one week in a 40-ml vial with PTFE-lined chlorobutyl septa, two weeks if preserved, with no headspace at a temperature range of above freezing to 6°C (see [Appendix X1](#)).

8.9 *Surrogate Analyte*—A surrogate analyte needs to be added to the instrument headspace vial. The concentration for the surrogate should be in an appropriate concentration of the calibration range and the concentration of the surrogate should remain constant throughout the calibration. The surrogate shall elute during the temperature ramp of the experiment with at least 80 % resolution of the height of the valley between the surrogate and any analyte of interest. The surrogate is used to verify analytical performance of standards, blanks, and samples. An alternate surrogate compound that mimics the analyte properties may also be used.

NOTE 5—For this study, MTBE-d3 was used as the surrogate. However, if there is a likelihood of MTBE in the sample, an alternate surrogate should be used as MTBE and MTBE-d3 do not resolve chromatographically. The MTBE-d3 was procured from a certified reference supplier at a concentration of 2000 µg/ml. MTBE-d3 was chosen as a surrogate due to the fact that it is not a naturally occurring compound, its solubility in water, its ability to come to equilibrium quickly, and because the elution time does not interfere with any of the analytes of interest. The MTBE-d3 was diluted in purge and trap methanol to 1000 µg/ml and 10 µl of the surrogate was added to each sample.

8.10 *Method Blank (MB)*—Fill a prepared instrument sample vial with reagent water for subsequent headspace preparation using the same procedure as the field samples.

## 9. Hazards

9.1 The composition of the field samples is generally unknown and should be treated as a potential health hazard. Proper handling and minimized exposure should be taken into account when handling samples.

9.2 Methane, ethane, ethylene, and propane are all flammable gases. Care shall be taken when handling these gases.

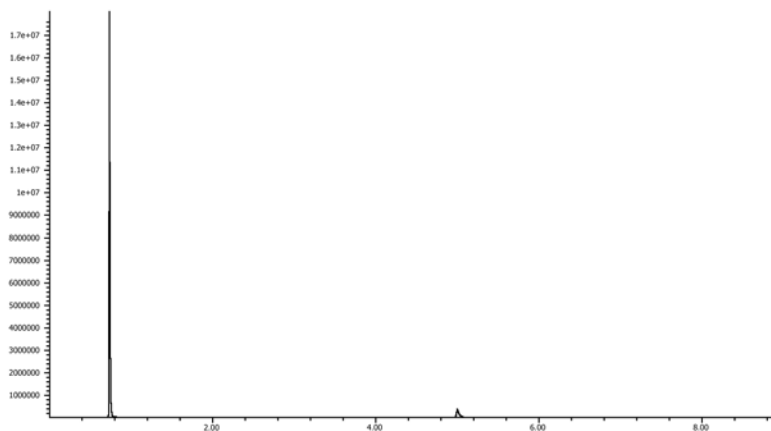


FIG. 2 Methane Standard Chromatogram