Light Hydrocarbons in Aqueous Samples via Headspace and Gas Chromatography with Flame Ionization Detection (GC/FID)

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1.0 Summary of Method

1.1 An aliquot of headspace above an aqueous sample in a closed vessel is injected into a gas chromatograph equipped with a flame ionization detector (GC-FID) for separation and measurement. Analytical results are quantitated using external calibration.

1.2 The calibration curves for each compound are prepared as aqueous solutions, by dilution of saturated aqueous solutions of each gas. Samples are prepared and analyzed in the same manner as the calibration standards.

2.0 Scope and Application

2.1 This method is applicable to the determination of dissolved hydrocarbon gases, in the range of C1 to C3, in aqueous samples but may be expanded provided appropriate method validation techniques are employed.

2.1.1 This method is not amenable to the analysis of non-aqueous samples.

2.1.2 This method has not been evaluated for use with aqueous samples containing residual chlorine or high salinity. Samples containing residual chlorine or high salinity must be appropriately qualified on the final report.

2.2 Table 1 (Section 14) lists the specific compounds included in this method. It may be necessary to include additional compounds that fit into the “light hydrocarbon gas” category. A laboratory wishing to add other compounds must demonstrate acceptable and equivalent method performance through method validation studies and demonstrations of capability.

2.3 The PA-DEP’s Bureau of Laboratories developed the analytical procedure described in this method as an in-house method specific to the DEP’s protocols and procedures. The quality control and method performance have been evaluated and approved by the PA-DEP’s Laboratory Accreditation Program (LAP) in accordance with the provisions of 25 Pa. Code Chapter 252 § 252.307(c) relating to methodology and alternate test procedures.

2.4 Laboratories wishing to use this method to test samples for compliance with the Oil and Gas Act or any other compliance purpose must apply for and be granted accreditation prior to analysis of samples.

2.5 Laboratories using this method must ensure the use of appropriate sampling, analysis, and QA/QC protocols as required by the appropriate regulatory requirements including, but not limited to, 25 Pa. Code Chapter 252, the TNI Standard, the Oil and Gas Act, and/or the Environmental Laboratory Accreditation Act.

2.6 Modifications to this method, such as change in detector (FID), sample delivery technique (headspace), and/or method performance are considered significant method modifications and would require review and approval from the PA-DEP’s LAP prior to analysis and reporting of compliance samples.

2.7 The equipment information and operating conditions in the appendices are provided for reference purposes only and do not imply that the PA-DEP requires their use.

3.0 Definitions

3.1 Sample Duplicate (DUP): A replicate aliquot of the sample, prepared and analyzed at the same dilution, processed along with an under the same conditions as the associated environmental samples, including all steps of the preparation and analytical procedure. DUP sample results provide a measure of analyst and method precision.

3.2 Method Blank (MB): An aliquot of reagent water that is treated exactly as a sample, including exposure to all glassware, equipment, solvents, and reagents that are used with other samples. The MB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.3 Quantitation Limit (QL). May also be referred to as Reporting Limit (RL) or Limit of Quantitation (LOQ). The QL is may not be below the concentration of the lowest level calibration standard, but may be above the lowest calibration standard. Any values reported below the QL are considered estimates and must be reported with appropriate data qualifiers.

3.4 Stock Standard Solution (SSS): A concentrated solution or set of solutions containing the target analytes and stock standard compound(s), and used to prepare the primary dilution standard(s). Stock standard solutions may be purchased from a reputable commercial source or prepared from neat materials.

3.5 Initial Calibration Standard Solutions (ICAL): A set of solutions containing the target analyte(s) at concentrations that define the working range of the instrument. ICAL standards are prepared by dilution of the SSS. ICAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.6 Initial Calibration Verification (ICV): A solution or solutions containing all of the target analytes, but purchased or prepared from a source different from the source of the ICAL standards.

3.7 Continuing Calibration Verification (CCV): Reagent water spiked with a known and verified concentration of all target analytes that has been taken through all preparation and analytical steps in the method. For the purposes of this procedure, the CCV meets the requirement of and can be considered equivalent to a laboratory control sample (LCS).

3.8 Field Duplicate (FDUP): A replicate aliquot of the sample, prepared from the second sample vial and prepared and analyzed at the same dilution, processed along with an under the same conditions as the associated environmental samples, including all steps of the preparation and analytical procedure. FDUP sample results provide a measure of precision of the sampling techniques.

3.9 Batch: Composed of prepared environmental samples that are analyzed together as a group within the same 24-hour period using the same procedures, personnel, lots of reagents and standards.

4.0 Interferences

4.1 Method interferences may be caused by contaminants in solvents, reagents, glass, metal or plasticware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in gas chromatograms. All reagents and apparatus must be routinely demonstrated to be free from interferences under the conditions of the analysis by analysis of MBs.

4.2 The use of high purity reagents and solvents helps to minimize interference problems.

4.3 Contamination by carry-over can occur whenever higher boiling compounds are present in the sample. Analysis of blanks after high concentration samples can reduce carry-over.

4.4 Matrix interferences also may be caused by contaminants that co-elute or are co-extracted from the sample. Complex chromatograms require careful interpretation by an experienced analyst.

4.5 The FID is a non-selective detector, which increases the potential for interference with target analytes. Complex chromatograms should be interpreted by an experienced analyst.

5.0 Safety

5.1 Since the nature of samples submitted to the laboratory for analysis is not known, all samples should be treated as potential health hazards. Analysts must use good judgment and wear appropriate protective equipment when working with samples.

5.2 Material Safety Data Sheets (MSDS) are available from the manufacturer or on-line.

5.3 This procedure uses methane, ethane, and propane gases, which are flammable. Appropriate care must be taken when handling flammable gases.

6.0 Equipment and Supplies

6.1 VOA vials, pre-cleaned 40 mL, amber glass, screw cap, with Teflon lined silicon septa. Used to collect samples.

6.2 Headspace vials, 20 mL, clear glass, with Teflon-lined septa crimp caps. Used for preparation of standards and analysis of samples.

6.3 Microsyringes. Gas tight, with Teflon-tipped plungers, in a variety of volumes. Used for preparing standards and spiking samples.

6.4 Pipets. Class A volumetric, glass, in a variety of volumes. Used for preparing standards and samples.

6.5 Volumetric flasks. Class A, glass, in a variety of volumes. Used for preparing standards and samples.

6.6 Gas chromatography system

6.6.1 Gas chromatograph. Agilent 6890 or equivalent. Must be capable of temperature and pressure programming, and performing splitless injections.

6.6.2 Flame ionization detector. Agilent or equivalent. Must be equipped with makeup gas flow adapters and optimized for use with capillary or packed columns.

6.6.3 Headspace autosampler, Agilent 1888 or equivalent. Must be capable of thermostatting samples.

6.6.4 GC column: Micro-packed column. ShinCarbon ST100/120, 1 mm ID, 1 m length, Restek or equivalent.

6.7 Recirculating water bath: capable of maintaining 20°C. Used for preparation of SSS and all QC standards

7.0 Reagents and Standards

7.1 Compressed gases.

7.1.1 Helium, ultra-high purity (UHP) grade or equivalent. For use as the GC system carrier gas. The helium must be filtered through in-line gas filters to remove hydrocarbons, moisture, and oxygen.

7.1.2 Air, zero grade or equivalent. For use as a fuel gas for the FID. The zero grade air may be supplied from a generator.

7.1.3 Hydrogen, UHP grade or equivalent. For use a fuel gas for the FID. The UHP hydrogen may be supplied from a generator.

7.2 Reagent water, ASTM Type I. For use in preparation of blanks and QC samples and preparation of sample dilutions.

7.3 Certified gas cylinders, ≥ 99.0% purity. For preparation of stock standard solutions. Purchased from a reputable vendor, accompanied by a certificate of analysis. The following gases are needed.

7.3.1 Methane, primary and secondary source.

7.3.2 Ethane, primary and secondary source.

7.3.4 Propane, primary and secondary source.

7.4 Primary Source Stock Standard Solutions (1°SSS)

7.4.1 Preparation of the 1°SSS (methane, ethane, and propane). The 1°SSS are prepared fresh each use, and expire after one day.:

7.4.1.1 Place a 500 mL Erlenmeyer flask inside a recirculating water bath. Fill the flask with reagent water up to the neck. Make certain the water level inside the recirculating water bath is at least 90% of the height of the reagent water inside the flask. Set the water bath temperature to 20°C and allow temperature to stabilize.

7.4.1.2 Attach a piece of flexible plastic tubing to the certified gas cylinder output, and insert a Pasteur pipet into the other end of the tubing. Place the pipet into the Erlenmeyer flask, near the bottom of the vessel. Adjust the gas flow until it is vigorously bubbling, but not splashing. Allow the gas to bubble through the reagent water for a minimum of one hour.

7.4.1.3 Alternatively, commercially available certified 1° SSS may be purchased from a reputable vendor.

7.4.2 Primary Methane Stock Standard (1°MSS). The saturated concentration of methane in water at 20°C and one atmosphere pressure is 23.2 mg/L.

7.4.3 Primary Ethane Stock Standard (1°ESS). The saturated concentration of ethane in water at 20°C and atmospheric pressure is 62.0 mg/L.

7.4.4 Primary Propane Stock Standard (1°PSS). The saturated concentration of propane in water at 20°C and atmospheric pressure is 71.0 mg/L.

7.5 Second Source Stock Standards (2^{nd} SSS). Prepare a 2^{nd} SSS for each gas analyzed. Second SSS are prepared fresh as described in Section 7.4.1 for each use and expire after one day.

7.6 Initial calibration (ICAL) solutions are prepared by dilution of the 1°MSS, 1°ESS or 1°PSS.

7.6.1 ICAL solutions are prepared by taking aliquots of the 1° SSS directly from the Erlenmeyer flask. For each ICAL standard, the gas delivery tube is briefly removed from the 1 °SSS, the appropriate aliquot is taken, and the gas delivery tube is put back into the 1°SSS.

7.6.2 Refer to Table 2 (Section 14) for the preparation procedure and concentrations of the prepared ICAL solutions. ICAL solutions are prepared in the headspace vials, then immediately capped.

7.6.3 ICAL solutions are stored in 20 mL crimp top headspace vials with Teflon-lined septa crimp caps. ICAL solutions may be stored for up to one week and must be stored at ≤ 6°C until analysis. A separate set of ICAL solutions must be prepared for each compound.

7.7. Initial calibration verification (ICV). A 2^{nd} source ICV is prepared by dilution of the 2^{nd} SSS.

7.7.1 Add 2.5 mL of reagent water to a crimp top headspace vial. Using the same procedure explained in Section 7.6, add 2.5 mL of 2^{nd} PSS, 2.5 mL of 2^{nd} ESS, and 2.5 mL of 2^{nd} MSS, in that order, and cap quickly. The ICV expires within one week and is stored at ≤ 6°C until analysis.

7.7.2 Alternatively, prepare ICV standards separately as specified in Table 2.

7.8 Continuing calibration verification (CCV). May be prepared from the 1°SSS or the 2^{nd} SSS. The concentration of the CCVs varies and is prepared at multiple concentrations, including a low-level (within the lower 20% of the ICAL) and a medium or high level.

7.8.1 Prepare additional CCVs as necessary as explained in Section 7.6. CCVs expire within one week and are stored at ≤ 6°C until analysis.

7.8.2 Add 2.5 mL of reagent water to a headspace vial, followed by 2.5 mL each of 1° or 2^{nd} PSS, ESS, and PSS, in that order, and cap quickly.

7.8.3 Alternatively, prepare separate CCV standards as specified in Table 2.

8.0 Sample Collection, Preservation and Storage

8.1 Sample Collection:

8.1.1 Collect grab samples in clean 40 mL amber glass VOA vials with zero headspace directly from the source and in a manner that reduces sample agitation to avoid loss of analyte to volatilization. Immediately cap the VOA vial after collection.

8.1.2 Collect a minimum of 2 and preferably 3 vials for each sample location.

8.1.3 Samples containing headspace > 6 mm in diameter must be rejected or reported with appropriate data qualifiers.

8.1.4 Samples may become contaminated during sampling, shipment, or storage. Field reagent blanks (FRBs) should be sampled and analyzed along with regular unknown samples from the same sampling site if this is a particular concern.

8.1.5 Sample collection techniques can contribute considerable variation into the analytical result obtained during sample analysis. To account for the variation in sampling technique, the Department strongly recommends regular training and consistent sampling techniques for field samplers.

8.1.6 To determine the consistency in sampling, the Department recommends that on a periodic basis, on a pre-determined schedule and when a new field sampler is employed, the laboratory obtain and analyze field duplicates to compare results of the analysis of separate sample vials collected at the same site.

8.2 Sample Preservation. Samples must be temperature preserved via ice or refrigeration at ≤ 6°C immediately at the time of collection.

8.3 Sample Storage. Samples must be stored away from organic vapors or other potential contaminants at ≤ 6°C.

8.4 Holding time (HT). Samples must be analyzed within 7 days of collection.

8.5 Samples collected from chlorinated sources or found to contain residual chlorine must be qualified on the final report. See Section 2.1.2.

9.0 Calibration and Standardization

9.1 Prepare GC for Analysis

9.3.1 Establish headspace conditions comparable to those given in Appendix A.

9.3.2 Establish GC operating conditions comparable to those given in Appendix B. Under these conditions the last compound, propane, elutes in approximately 10 minutes.

9.3.3 Confirm that the baseline is not elevated, all analytes are sufficiently resolved, and that there are no interfering positive or negative peaks, before proceeding.

9.2 Calibration of the GC System

9.2.1 Initial calibration (ICAL). A minimum of five calibration standards is required (nine standards are recommended). One standard must contain each analyte at a concentration at or below the laboratory's quantitation limit/reporting limit. The other standards must contain each target analyte at concentrations that bracket the linear range of the instrument.

9.2.1.1 Prepare the ICAL solutions according to Section 7.0 of this SOP, and analyze them as described in Section 10.0.

9.2.1.2 Calculate the calibration factor (CF) as described in the Section 12 for each target analyte in each of the ICAL standards. Also determine the average CF for each analyte using all the concentration levels.

9.2.1.3 Determine the %RSD for each compound. The %RSD must be ≤20%. If the %RSD is >20% the CF may not be used to quantitate analytical results. Use an alternate calibration routine, such as linear.

9.2.1.4 If using linear regression, the coefficient of determination must be $r^2 \geq 0.995$ using at least five standards.

9.2.1.5 If using quadratic fit the coefficient of determination must be $r^2 \geq 0.999$ using at least six standards that clearly define any non-linear portions of the calibration curve.

10.0. Procedure

10.1 Sample Preparation.

10.1.1 For each sample, to be analyzed, prepare at least 2 labeled crimp top headspace vials. It may be appropriate to prepare and analyze samples at multiple dilutions.

10.1.2 Open a VOA sample vial and quickly transfer 10 mL aliquot of the sample to the first headspace vial. Immediately cap the headspace vial.

10.1.3 Transfer a 2.5 mL aliquot to the second headspace vial and add 7.5 mL of reagent water. Immediately cap each headspace vial.

10.1.4 All samples are analyzed straight and at a 4X dilution in an attempt to limit the number of samples that must be reanalyzed due to high sample concentrations if the upper limit established by the ICAL is below the saturation point.

10.1.5 Prepare sample duplicates with the appropriate frequency of 1 DUP per every 10 samples. The DUP is prepared from the second VOA vial.

10.1.6 Prepare the appropriate number of MBs based on the number of unknown samples to be analyzed, by adding 10 mL of reagent water into a crimp top headspace vial.

10.1.7 Prepare the appropriate number of ICV and CCV/LCS standards based on the number of unknown samples to be analyzed, as outlined in Sections 7.7 and 7.8.

10.2 Sample Analysis. After the instrument has been properly optimized and calibrated, sample analysis can begin. Analyze an aliquot of each sample, blank, standard, and QC sample.

10.2.1 Confirm that the ICV and CCV criteria listed in the calibration and standardization and QC sections of this SOP have been met before proceeding with sample analysis.

10.2.2 If the response for any target analyte exceeds the quantitation range of the instrument as established by the ICAL, either analyze an appropriately diluted sample or report data with appropriate data qualifiers . If a dilution was not already prepared as outlined in Section 10.1, dilute an aliquot of sample with reagent water such that the expected concentration falls near the middle of the calibration range. Analyze the diluted sample.

10.2.3 If not analyzed immediately, dilutions may be stored in tightly sealed headspace vials at ≤ 6°C for up to 7 days from the date of initial collection. **NOTE:** This is not 7 days from the date the analyst prepares the diluted sample.

10.3 Identification and Quantitation of Analytes

10.3.1 Identify sample peaks that are within the RT windows determined by the initial calibration. RT windows either may be calculated for each compound or the default RT window of ± 0.05 minutes may be used.

10.3.2 Using the measured peak area, calculate the concentration of each identified peak in the sample.

11.0 Quality Control (QC)

11.1 Initial calibration verification (ICV). Verify the initial calibration by analyzing an ICV.

11.1.1 The ICV must be analyzed immediately after the ICAL and before analysis of samples. The ICV must be prepared from the 2nd SSS.

11.1.2 Compare the measured concentration of each analyte in the ICV to the true value of the ICV and calculate a percent recovery. The analysis of the ICV must verify that the % recovery is within 80 – 120% of the true value.

11.1.3 If the % recovery of the ICV is not with the acceptable range, perform corrective action until analysis of an ICV meets the acceptable % recovery. It is not acceptable to analyze samples until analysis of an ICV confirms the ICAL. It may be necessary to prepare and analyze a new ICAL.

11.2 Continuing calibration verification (CCV or LCS). The continued precision and accuracy of the ICAL must be monitored through the regular analysis of CCVs.

11.2.1 A CCV must be analyzed after every 10 samples and at the end of the analytical batch. At least once per batch, a low-level CCV must be analyzed at a concentration in the lower 20% of the ICAL.

11.2.3 Calculate the % recovery of the CCV by comparing the measured concentration of each analyte to the true value of the CCV. The analysis of the low-level CCV must verify that

the % recovery is within 60 – 140% of the true value. Mid or high range CCVs must verify that the % recovery is within 80 – 120% of the true value.

11.2.4 If the % recovery is not within the acceptable range, the samples analyzed since the last acceptable CCV (or ICV) must either be re-analyzed or reported with appropriate data qualifier flags.

11.3 Method Blank (MB). Assess possible contamination by analysis of a MB immediately after initial calibration, after every 10 samples and at the end of the analytical batch.

11.3.1 The measured concentration of the MB must be below the QL.

11.3.2 If the concentration of the MB is above the QL, the samples analyzed since the last acceptable MB must either be re-analyzed or reported with appropriate data qualifier flags.

11.4 Sample Duplicates (DUP). Assess precision of the analytical system and sample preparation technique by analyzing sample duplicates with a frequency of 10% of the sample load.

11.5.1 Compare the measured concentration of duplicate sample analyses and calculate the RPD for each target analyte. The RPD must be < 25%.

11.5.2 If the RPD is >25%, the sample must be re-prepared and analyzed or the result must be reported with appropriate data qualifier flags.

12.0 Calculations

Refer to Section 1020 B.11 of Standard Methods for the Examination of Water & Wastewater for appropriate calculations.

13.0 References

13.1 *Sample Preparation and Calculations for Dissolved Gas Analysis in Water Samples Using a GC Headspace Equilibration Technique*, RSKSOP-175, Revision 2, May 2004.

13.2 "Non-Halogenated Organics Using GC/FID", Method 8015D, USEPA OSWER, SW-826, Third Edition, Revision 4, June 2003.

13.3 "Determinative Chromatographic Separations", Method 8000C, USEPA OSWER, SW-846, Third Edition, Revision 3, March 2003.

13.4 "Volatile Organic Compounds in Soils and Other Solid Matrices Using Equilibrium Headspace Analysis", Method 5021, USEPA OSWER, SW-846, Third Edition, Revision 0, December 1996.

13.5 The saturated solution concentrations of methane and ethane may be found in Lange's Handbook of Chemistry, 14th addition, McGraw-Hill.

13.6 The saturated solution concentration of propane may be found on the Air Liquide website at http://encyclopedia.airliquide.com/Encylopedia.asp?GasID=53.

13.7 *Methane, Ethane, and Propane in Aqueous Samples via Headspace and Gas Chromatography with Flame Ionization Detection (GC/FID)*, PA-DEP SOP #BOL 6019, Revision 6.

14.0 Tables and Figures

Table 1: Method Analytes, CAS Numbers, and Quantitation Limits

Compound	CAS No.	QL (µg/L)
Methane	74-82-8	11.6
Ethane	74-84-0	12.4
Propane	74-98-6	14.2

Table 2: Calibration Standard Preparation Scheme

Volume of SSS (mL)	Volume of Reagent Water (mL)	Total Volume (mL)	Methane (µg/L)	Ethane (µg/L)	Propane (µg/L)
10.0	0.0	10.0	23,200	62,000	71,000
7.5	2.5	10.0	17,400	46,500	53,250
5.0	5.0	10.0	11,600	31,000	35,500
2.5	7.5	10.0	5,800	15,500	17,750
1.0	9.0	10.0	2,320	6,200	7,100
0.25	9.75	10.0	580	1,550	1,775
0.05	9.95	10.0	116	310	355
0.010	10.0	10.0	23.2	62.0	71.0
0.005	10.0	10.0	11.6	31.0	35.5
0.002	10.0	10.0	NA	12.4	14.2

Table 3: Summary of Batch QC Requirements

Type of QC	Conc.	Frequency	Acceptance Criteria
Initial calibration (ICAL)	Varies	Initially	%RSD ≤ 20% r^2 ≥ 0.995 linear r^2 ≥ 0.999 quadratic
ICV (2^{nd} Source)	Mid	Immediately after ICAL	80 – 120 %Rec
MB	None	Immediately after ICAL, every 10 samples, end of batch	< QL
CCV	Lower 20% of ICAL	Once per batch	60 – 140 % Rec
CCV	Mid or High	After every 10 samples, end of batch	80 – 120 %Rec
DUP	N/A	10% of samples	RPD < 25%

Appendix A. Operating Conditions for the HP1888 Headspace Sampler

Zone Temps °C

Oven Temp	64
Loop	100
Transfer Line	100

Event Times

GC Cycle Time	14.0 min
Vial Equilibration Time	10.0 min
Pressurization Time	0.10 min
Loop Fill Time	0.20 min
Loop Equilibration Time	0.40 min
Inject Time	1.00 min
Loop Volume	1.0 mL

Vial Parameters

Shake	Low
Vial Pressure	~ 9.5 psi

Appendix B. Operating Conditions for the HP6890 GC/FID

INJECTION PARAMETERS:

Temperature	250°C
Mode	Transfer line
Column flow	Constant pressure @ 20 psi
Carrier gas	He, UHP grade

MISCELLANEOUS:

Detector temperature	250°C
H_2 Flow	30.0 mL/min
Air Flow 400 mL/min	
N_2 Flow	25.0 mL/min

OVEN PROGRAM:

Ramp (°C/Minute)	Temperature (°C)	Hold Time (Minutes)	Step Time (Minutes)
	50	0.0	0.0
10	190	0	14.0
TOTAL RUN TIME:			14.0