



Determination of Trace Oxygenated Hydrocarbons in Gaseous, LPG and Liquid Hydrocarbon Streams by GC

UOP Method 960-20

Scope

This method is for determining trace levels of select oxygenated hydrocarbons, with boiling points up to 138°C, in refinery gas streams, C₄ liquefied petroleum gas (LPG), light isomerate and naphtha. Mono-oxygenated hydrocarbons determined include C₁ through C₅ alcohols, and C₂ through C₆ carbonyls and ethers. Formaldehyde, if present, is not determined by this method. Di-oxygenated hydrocarbons determined include C₂ through C₄ methyl esters and 1,4-dioxane. The range of quantitation for each individual oxygenate in liquid streams is 0.2 to 250 mass-ppm (mg/kg) and in gas/LPG streams is 1.0 to 250 mass-ppm (mg/kg). Inorganic compounds containing oxygen, such as water, carbon monoxide, carbon dioxide or heteroatoms such as nitrogen, chlorine or sulfur are not determined. Unsaturated oxygenated hydrocarbons may be detected but are not identified. Certain oxygenated hydrocarbons are not separated and are reported as composites. Some sulfur and nitrogen compounds are known to elute in the oxygenate region of the chromatogram.

References

- ASTM Practice D1265, "Standard Practice Sampling Liquefied Petroleum (LP) Gases (Manual methods)," www.astm.org
- ASTM Method D1657, "Density or Relative Density of Light Hydrocarbons by Pressure Hydrometer," www.astm.org
- ASTM Method D2163, "Analysis of Liquefied Petroleum (LP) Gases and Propene Concentrates by Gas Chromatography," www.astm.org
- ASTM Method D2598, "Calculation of Certain Physical Properties of Liquefied Petroleum (LP) Gases from Compositional Analysis," www.astm.org
- ASTM Method D4052, "Density and Relative Density of Liquids by Digital Density Meter," www.astm.org
- ASTM Practice D4307, "Standard Practice for Preparation of Liquid Blends for Use as Analytical Standards," www.astm.org
- ASTM Practice D5287, "Standard Practice for Automatic Sampling of Gaseous Fuels," www.astm.org

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Nonconfidential UOP Methods are available from ASTM International, 100 Barr Harbor Drive, P.O. Box C700, West Conshohocken, PA 19428-2959, USA. The UOP Methods may be obtained through the ASTM website, www.astm.org, or by contacting Customer Service at service@astm.org, 610.832.9555 FAX, or 610.832.9585 PHONE.

ASTM Method D7423, "Standard Test Method for Determination of Oxygenates in C2, C3, C4, and C5 Hydrocarbon Matrices by Gas Chromatography and Flame Ionization Detection," www.astm.org

UOP Method 373, "Composition of C2 Through C5 Hydrocarbon Mixtures by Gas Chromatography," www.astm.org

UOP Method 516, "Sampling and Handling of Gasolines, Distillate Fuels, and C3-C4 Fractions," www.astm.org

UOP Method 999, "Precision Statements in UOP Methods," www.astm.org

Scanlon, J. T., and D. E. Willis. "Calculation of Flame Ionization Detector Relative Response Factors Using the Effective Carbon Number Concept." *Journal of Chromatographic Science* 23.8 (1985): 333-40. Web.

Outline of Method

The method requires the use of a dedicated pre-configured gas chromatograph equipped with an auxiliary oven that is configured for automated analysis and is capable, via valving, of determining trace oxygenates in refinery gas streams, C₄ liquefied petroleum gas (LPG), light isomerate and naphtha. A reproducible volume of sample is injected into a specially configured gas chromatograph (GC) that is equipped with two megabore capillary columns operating at different temperatures. The first column, a non-polar column, fractionates interfering sample components from the system. The second column, a selective Lowox column, separates and analyzes oxygenates. The non-polar column operates isothermally inside an auxiliary oven, and the Lowox column resides in the main GC oven. Initially, the columns are connected in series, and after the elution of components of interest from the non-polar column, the non-polar column is backflushed. The Lowox column is maintained in foreflush and temperature programmed, eluting compounds to a flame ionization detector (FID). Two sample injections (fractionations) may be required.

1. Valve 2 Fractionation A time is used to determine all oxygenates other than dimethyl ether.
2. Valve 2 Fractionation B time is used to determine only dimethyl ether.

Quantitative results are obtained by the external standard method of quantitation wherein the peak areas for the components of interest are compared to peak areas of a calibration standard. Effective carbon number (ECN) is used to calculate the relative response factors of the oxygenated components based on the response factor of the reference material. See Table 2 for a list of compounds and composites. Using pure compounds to calibrate each component can result in better accuracy.

Apparatus

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers or newer models may be used. Pre-configured instruments are available.

Analyzer, Wasson ECE Instrumentation, Application No. UOP960. See Figure 1 for Analyzer configuration. Other vendors also supply similar systems. Confirm with the selected vendor that the required separations are provided for the specific sample types to be analyzed. The Wasson-ECE analyzer includes:

Chromatographic column, 10 m x 530 µm ID x 10 µm Lowox, Agilent, Cat. No. CP8587

Fractionation column, 30 m x 530 µm ID x 5 µm MXT-1, Restek, Cat. No. 70179

Fused silica tubing, 2 m x 0.32 mm ID, deactivated, Agilent, Cat. No. CP803210

Gas chromatograph, capable of multiple temperature ramping, built for capillary column chromatography utilizing a split injection system with electronic pressure control (EPC), having a glass injection port insert. Three channels of additional electronic pressure control are required. Agilent Technologies, Model 7890.

Sample injector, syringe or injector capable of injecting a 4- μ L repeatable volume of sample. An automatic injection system is recommended, Agilent Technologies Model 7693A.

Balance, readability 0.1-mg

Clamp, for ring stand and sample cylinders, Fisher Scientific Cat. No. 02-217-000

Clamp holder, for ring stand and clamp, Fisher Scientific Cat. No. 02-217-005

Chromatographic Data System, for computerized instrument control of data acquisition and data reduction, ChemStation, Agilent Technologies.

Electronic leak detector, Agilent gas leak detector, Agilent, Cat. No. G3388B

Fittings, CGA, for LPG blend cylinder, CGA No. 510, Matheson Tri-Gas

Regulator, air, two-stage, high purity, Matheson Tri-Gas, Cat. No. SEQ3122A590

Regulator, hydrogen, two-stage, high purity, Matheson Tri-Gas, Cat. No. SEQ3122A350

Regulator, dimethyl ether blend, two-stage, high purity, Matheson Tri-Gas, Cat. No. SEQ3810A350

Regulator, nitrogen, two-stage, high purity, Matheson Tri-Gas, Cat. No. SEQ3122A580

Regulator, nitrogen, single stage, high purity, high pressure delivery to pressurize LPG sample and blend cylinders, Matheson Tri-Gas, Cat. No. SEQ3538A580

Ring stand, with rectangular base, 140- x 229- mm with 610- mm rod, Fisher Scientific, Cat. No. 14-679Q

Syringe, 10- μ L, for qualitative mixture preparation, Hamilton 701NF, Restek, Cat. No. 20167

Tubing, Sulfinert, .030-in ID x 1/16-in OD, Cat# 29230, Restek

Tubing, translucent, FEP Teflon, 3.2-mm (1/8-inch) OD, 1.6-mm (1/16-inch) ID, 3450 kPa (500 psi), Thomas Scientific, Cat. No. 9567K20

Reagents and Materials

References to catalog numbers and suppliers are included as a convenience to the method user. Other suppliers may be used.

Air, zero-gas, total hydrocarbons less than 2 ppm as methane

Blend, gas, quantitative, certified standard, containing 100 mol-ppm of dimethyl ether in research grade propane, Matheson Tri-Gas.

Blend, LPG, quantitative, certified standard, containing 10 mass-ppm of 2-butanone in research grade isobutane, contained in an aluminum Ultra-Line cylinder with a stainless-steel valve, Matheson Tri-Gas. A 250-psig nitrogen head pressure should be maintained on the LPG blend.

Cyclohexane, anhydrous, 99.5+%, Sigma-Aldrich, Cat. No. 227048. The anhydrous cyclohexane is kept under a nitrogen blanket between uses to prevent contamination.

Cyclopentanol, 99%, Sigma-Aldrich, Cat. No. C112208

Gas purifier, hydrogen carrier gas purifier, VICI Metronics, Cat. No. P200-1

Gas purifier, air (for detectors), VICI Metronics, Cat. No. P400-1

Gas purifier, nitrogen, for detector makeup gas, VICI Metronics, Cat. No. P300-1

Hydrogen, zero-gas, 99.99% minimum purity, total hydrocarbons less than 0.5 ppm as methane

Inlet liner, Siltek Deactivated, 5.2 mm ID Straight Inlet Liner for Agilent GCs equipped with split/splitless inlets, Restek, Cat. No. 21700

Methyl ethyl ketone (2-Butanone), 99.5%, Sigma-Aldrich, Cat. No. 270695

Nitrogen, zero-gas, 99.99% minimum purity, total hydrocarbons less than 0.5 ppm as methane

Oxygenated hydrocarbons, Sigma-Aldrich, see Table 2 for Catalog Numbers

Pipet bulb, 1-mL, Fisher Scientific, Cat. No. 03-448-25

Pipet, Pasteur, disposable, 146-mm, Fisher Scientific, Cat. No. 13-678-20A

Vials, glass, 20-mL, with caps, Fisher Scientific, Cat. No. 03-337-14

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of gas chromatography and the equipment being used. Dispose of used reagents, materials, and samples in an environmentally safe manner according to local regulations.

Sampling

Obtain the sample by following the procedures described in ASTM Practice D 1265, ASTM Practice D 5287, UOP Method 516, or other reliable technique.

Chromatographic Technique

1. Follow the instrument site preparation checklist provided by the manufacturer and arrange for installation by the manufacturer's service engineer to establish recommended operating conditions as listed in Table 1.
 - The Wasson-ECE analyzer comes with on-site installation and training by a Wasson-ECE engineer in the continental U.S., inquire with Wasson-ECE for other locations.
2. Install the gas purifier in the supply line between the carrier gas source and the carrier gas inlets on the gas chromatograph.
 - Column life is significantly reduced if the gas purifier is not used. Replace the gas purifier at intervals determined by good laboratory practice. An indicating oxygen trap may be placed downstream of the gas purifier. When the indicator shows one-half used, replace both the gas purifier and the indicating trap.
 - CAUTION: Hydrogen gas leakage into the confined volume of the column oven can cause a violent explosion. It is, therefore, mandatory to check for leaks each time a connection is made and periodically thereafter.
3. Install the Siltek metal inlet liner into the front injection port according to the instrument manufacturer instructions.
 - The Siltek liner has equivalent inertness to glass sleeves but, has greater total volume, allowing the large injections of LPG and volatile liquids will not exceed the vapor volume of the injection port.
 - Initially, the injection port should be maintained at 250°C for 24 hours to condition the Siltek injection port liner.

Operating Conditions

It is recommended to use the manufacturer operating conditions for this analysis to produce the required sensitivity and chromatographic separations equivalent to those shown in the Chromatogram in Figures 2, 3 & 4.

Table 1
Recommended Operating Conditions

Carrier gas	hydrogen
Front Inlet	
Temperature	250°C isothermal
Column head pressure @ 50°C	26.2 kPa gauge (3.76 psig)
Equivalent flow	18.6 mL/min
Flow mode	constant flow
Pressure pulse	53.8 kPa gauge (7.8 psig)
Pulse time	0.25 min
Split ratio	1.0
Split flow	7.8 mL/min
Auxiliary EPC	
Pressure	1.278 psi
Equivalent flow	9.8 mL/min
Flow mode	constant flow
Auxiliary 1 temperature (Wasson ECE valve box)	150°C isothermal
Auxiliary 2 temperature (bridge heater)	150°C isothermal
Main oven temperature programming	
Initial temperature	50°C
Initial time	0 min
Programming rate	10°C/min
Final temperature	250°C
Final time	0 min
Front Detector	FID
Temperature	275°C
Hydrogen flow rate*	25 mL/min
Air flow rate*	400 mL/min
Makeup nitrogen flow rate*	25 mL/min
Constant makeup mode	
Back Detector (if installed)	FID
Temperature	275°C
Hydrogen flow rate*	30 mL/min
Air flow rate*	400 mL/min
Makeup nitrogen flow rate*	25 mL/min
Constant makeup mode	
Run Table	
Valve 2 “on” at	A time for all oxygenates
Valve 2 “off” at	B time for dimethyl ether
	19.5 min
For Gas samples add:	
Valve 3 “on” at	0.01 min
Valve 3 “off” at	0.75 min
For LPG samples add:	
Valve 1 “on” at	0.01 min

Valve 1 “off” at

0.75 min

Sample size**Liquids****4.0 µL (syringe)****Gas****0.5 mL (gas valve)****LPG****2.0 µL (LPG valve)*****Consult the manufacturer’s instrument manual for suggested flow rates****Fractionation Time Determination**

1. Choose and load the appropriate method for liquid sample analysis with Valve 2 in the “off” position.
2. Set up a run table on the GC with Valve 2 “on” at 5.00 minutes and Valve 2 “off” at 19.5 minutes.
3. Prepare a blend as described in ASTM D4307-17 to contain approximately 100 mass-ppm of cyclopentanol.
 - This is used to set Valve 2 Fractionation A time
 - Cyclopentanol is not the highest boiling oxygenate determined but it is the latest eluting from the boiling point column. Setting the backflush time based on cyclopentanol ensures sufficient time for components listed in Table 2 to elute from the column.
4. Inject 4 µL of the cyclopentanol blend and start the GC and chromatographic data system.
5. Reduce the Valve 2 “on” time by 0.05-minute increments until the cyclopentanol peak area begins to decrease. Record the “on” time before the peak area decreases as the cut time for Fractionation A.
6. Next, to determine the Fractionation B time, choose and load the appropriate method for gas sample analysis with Valve 3 configured and Valve 2 in the “off” position.
7. Set up a run table on the GC with Valve 2 “on” at Fractionation A time and Valve 2 “off” at 19.5 minutes.
8. Connect the dimethyl ether calibration blend cylinder to the sample inlet with Sulfinert tubing and purge the system with the gas to be analyzed for 20 seconds. Stop the flow, allow 5 to 10 seconds for the pressure to equilibrate, and start the analysis.
9. Continue to reduce the Valve 2 “on” time obtained in step 5 until the area for the dimethyl ether peak does not decrease. Record the “on” time before the peak area decreases as the cut time for Fractionation B.
 - Typical Fractionation A times are less than 5 minutes while typical Fractionation B times are less than 2.5 minutes. Repeat steps 1-8 periodically and any time the fractionation column is changed.

Calibration Blends - LPG samples

A blend containing approximately 10 mass-ppm of 2-butanone in high-purity isobutane is required for calibration. Run the calibration blend in triplicate daily when samples are analyzed as described under *Chromatographic Technique*.

- The calibration standard is run to determine system response for 2-butanone. Calibrations are done in triplicate on any day samples are run.
- Peak areas from each of the triplicate runs should not deviate from the average by more than 5% of the value. If greater deviations occur, make certain that there are no problems with the equipment, then make additional runs until the required repeatability is obtained on three consecutive runs.

Calibration Blends - Gas samples

A blend containing approximately 100 mol-ppm of dimethyl ether in high-purity propane is required for calibration. Run the calibration blend in triplicate daily when samples are analyzed as described under *Chromatographic Technique*.

- The calibration standard is run to determine system response for dimethyl ether. Calibrations are done in triplicate on any day samples are run.
- Peak areas from each of the triplicate runs should not deviate from the average by more than 5% of the value. If greater deviations occur, make certain that there are no problems with the equipment, and then make additional runs until the required repeatability is obtained on three consecutive runs.

Calibration Blends - Liquid Samples

Prepare a calibration blend as described in ASTM Method D4307, "Preparation of Liquid Blends for Use as Analytical Standards," to contain approximately 50 mass-ppm of 2-butanone in cyclohexane. Run the calibration blend in triplicate daily when samples are analyzed as described under *Chromatographic Technique*. The lifetime of this calibration blend is estimated at one week.

- The calibration standard is run to determine system response for 2-butanone. Calibrations are done in triplicate on any day samples are run.
- Peak areas from each of the triplicate runs should not deviate from the average by more than 5% of the value. If greater deviations occur, make certain that there are no problems with the equipment, then make additional runs until the required repeatability is obtained on three consecutive runs.

Sample Analysis

Use the Fractionation A time for the Valve 2 "on" time to determine all oxygenates except dimethyl ether and use the Fractionation B time for the Valve 2 "on" time to determine only dimethyl ether. When running a gas or LPG sample or blend insure the appropriate method is loaded with either Valve 1 for gases or Valve 3 for LPGs configured. For LPG, follow Steps 8 through 18. For gas samples, proceed to Step 19 and 21. For liquid injection by autosampler, start at Step 22.

1. Using Fractionation A time for Valve 2, inject 4 μ L of pure cyclohexane and start the GC and chromatographic data system.
2. Monitor the baseline for peaks in the oxygenate region of the chromatogram.
3. Make repeat injections of the cyclohexane until few or no peaks are detected in the oxygenate region of the chromatogram.
4. Prepare a qualitative blend at approximately 50 mass-ppm of each oxygenate of interest in cyclohexane.
 - This mixture is used to determine retention times of the oxygenates
5. Inject 4 μ L of qualitative blend and start the GC and chromatographic data system.
 - Qualitative blend should be run periodically to ensure oxygenate retention times.
6. Run the appropriate calibration blend. For LPGs, use the 10 mass-ppm 2-butanone LPG blend, for gases use the 100 mol-ppm dimethyl ether gas blend, for liquids use the 50 mass-ppm 2-butanone liquid blend.
7. For LPG, follow Steps 8 through 18. For gas samples, proceed to Step 19 and 21. For liquid injection by autosampler, proceed to Step 22.

LPG Samples

8. Place the LPG sample cylinder in a vertical position in a hood or well-vented area. If the cylinder has an outage tube, the outage tube must be at the top. Briefly open the bottom valve to check

that no water or sediment is present in the LPG. If water or sediment is determined to be present, discontinue the analysis and obtain a clean sample.

- LPG samples are usually contained in a cylinder having valves on both ends or, in some cases, a cylinder where one of the valves is connected to an eductor tube. If the sample cylinder contains an eductor tube, invert the cylinder and briefly open the valve not connected to the eductor tube to check that no water or sediment is present. See Figure 5 for diagram of common LPG cylinders.
9. Pressurize the LPG cylinder containing the sample (or blend) to approximately 1400 to 2068 kPa gauge (200 to 300 psig) with nitrogen or helium.
 - Confirm that the sample container can handle the desired pressure prior to pressurizing.
 - Confirm that the cylinder is not liquid full by venting a small amount of the contents into a laboratory fume hood prior to pressurizing.
 10. Mount the cylinder securely on a ring stand in a vertical position. If the cylinder has an outage tube, the outage tube fitting must be at the top. Connect the bottom valve to the liquid sample inlet tubing.
 - If the cylinder is fitted with an eductor tube, connect the eductor tube outlet to the sample injection inlet tubing in such a manner that the eductor tube is sampling liquid LPG.
 - The connecting tubing between the cylinder and the liquid sample inlet must be as short as possible.
 11. Choose and load appropriate method for LPG sample analysis, ensuring valve 1 is in the off position. Refer to Figure 1.
 12. Ensure that the back-pressure restrictor valve is closed.
 13. Fully open the bottom valve or eductor valve of the sample cylinder.
 14. Partially open the back-pressure restrictor to permit LPG flow through the sampling system.
 15. Continue the flow until the flow emitting from the liquid sample vent is liquid and no bubbles are observed through translucent Teflon tubing.
 - CAUTION: Inspect the translucent tubing regularly. Replace at first signs of wear or kinking. Pressure rating on the translucent tubing must be rated higher than pressure on sample or blend cylinder.
 16. Stop the sample flow by closing the back-pressure restrictor valve and start the GC and chromatographic data system.
 17. Close the LPG cylinder valve and open the back-pressure valve to vent the sampling system.
 18. Repeat steps 8 through 17 for each LPG sample or blend, injecting identical volumes of each.

Gas Samples

19. Choose and load appropriate method for gas sample analysis, ensuring valve 3 is configured, see Figure 1.
20. Connect the gas sample cylinder or calibration blend cylinder to the sample inlet with Sulfinert tubing and purge the system with the gas to be analyzed for 20 seconds. Stop the flow, allow 5 to 10 seconds for the pressure to equilibrate, and start the GC and chromatographic data system.
21. Repeat steps 19 and 20 for each gas sample or blend, injecting identical volumes of each.

Liquid Samples

22. For liquid samples, inject, start the GC and chromatographic data system. Repeat for each liquid sample or blend, injecting identical volumes of each.

23. After the completion of each analysis, confirm the presence of oxygenated compounds, by first comparing the sample chromatogram to the cyclohexane chromatogram. Any peaks in the oxygenate region that are of the same intensity and common to the two chromatograms should not be calculated for sample result purposes, as they are likely to be artifacts and not oxygenates. Then compare the sample chromatogram to the chromatogram of the qualitative mixture to identify oxygenated compounds in the sample. Be sure that all peaks are properly integrated, small peaks are detected, and baseline noise is not integrated. Separate peaks that are not completely resolved from each other using a perpendicular drop to the baseline unless they are obviously on the tail of a much larger peak.
24. Obtain the density of liquid samples using ASTM Method D 4052. The relative density of LPG samples may be determined by ASTM Method D 1657 or by using the calculation in ASTM Method D 2163 after obtaining the composition using UOP Method 373, or ASTM Method D 2598.

Calculations

Calculate the response factor of the reference material, 2-butanone for liquid and LPG samples and dimethyl ether for gas samples, to four significant figures using Equation 1. Use the average peak area from triplicate blend runs.

$$F = \frac{A}{B} \quad (1)$$

where:

- A** = concentration of reference material in blend (mol-ppm for gas, mass-ppm for LPG and liquid)
- B** = average area of reference material peak
- F** = response factor for reference material

Calculate the amount of an individual component to the nearest 0.1 mol-ppm or mass-ppm below 100 mol-ppm or mass-ppm and to the nearest mol-ppm or mass-ppm above 100 mol-ppm or mass-ppm using Equation 2.

$$C = FGH \frac{J}{K} \quad (2)$$

where:

- C** = amount of component in sample (mol-ppm for gas, mass-ppm for LPG and liquid)
- F** = previously defined, Equation 1
- G** = peak area of sample component
- H** = component response relative to reference material as found in Table 2. If the components are a composite peak, use the highest listed response factor in the composite to calculate.
- J** = relative density of reference blend (for LPG and liquid samples only)
- K** = relative density of sample (for LPG and liquid samples only)

Table 2
Oxygenated Component Properties and Retention Times

<u>Component</u>	<u>Retention Time***, minutes</u>	<u>Aldrich Cat. No.</u>	<u>Purity</u>	<u>Response Relative to Dimethyl Ether (gas samples)</u>	<u>Response Relative to 2- Butanone (LPG & Liquid samples)</u>
Dimethyl ether*	5.34	295299	99+%	1	1.917
Ethyl methyl ether*	6.65	**	**	0.652	1.25
Diethyl ether*	7.65	346136	99%	0.536	1.028
Acetaldehyde*	7.9	110078	99%	0.956	1.833
Methyl formate*	8.59	291056	99%	1.303	2.498
<i>tert</i> -Butyl ethyl ether*	8.69	253898	99%	0.443	0.85
<i>tert</i> -Butyl methyl ether*	8.83	293210	99.80%	0.478	0.917
Isopropyl ether	8.92	296856	99%,	0.443	0.85
Propylene oxide	8.98	240397	99+%	0.598	1.146
<i>sec</i> -Butyl methyl ether	9.05	424463	99%	0.478	0.917
Propionaldehyde*	9.42	P51451	97%	0.598	1.146
Butyl methyl ether	9.5	235377	99%	0.478	0.917
<i>tert</i> -Amyl methyl ether	9.8	283096	97%	0.443	0.85
<i>n</i> -Propyl ether	9.92	111333	99+%	0.443	0.85
Butyl ethyl ether	10.24	268925	99%	0.443	0.85
Isobutyraldehyde	10.32	240788	99+%	0.522	1
Tetrahydrofuran	10.38	270385	99.50%	0.522	1
<i>n</i> -Butyraldehyde*	10.87	B103284	99%	0.522	1
Methyl acetate	10.95	296996	99.50%	0.956	1.833
Tetrahydropyran & Trimethylacetaldehyde (composite)	11.02	293105	99%	0.467	0.896
		T71501	97%	0.467	0.896
Methyl alcohol*	11.47	270474	99.90%	1.391	2.666
Acetone*	11.69	270725	99.90%	0.63	1.208
2-Methylbutyraldehyde	11.83	M33476	95%	0.467	0.896
Isovaleraldehyde & Cyclobutanone (composite)	12.11	146455	97%	0.467	0.896
		C96001	99%	0.507	0.972
Methyl propionate	12.2	109258	99%	0.637	1.222
<i>n</i> -Valeraldehyde*	12.4	110132	97%	0.467	0.896
2-Butanone*	12.83	270695	99.50%	0.522	1
Ethyl alcohol*	13.08	270741	Not denatured	0.667	1.278
2-Ethylbutyraldehyde	13.08	110094	92%	0.435	0.833
3,3-Dimethylbutyraldehyde	13.16	359904	95%	0.435	0.833
2-Methylvaleraldehyde	13.23	258563	98%	0.437	0.837

Methyl butyrate*	13.58	246093	99%	0.554	1.062
1,4-Dioxane	13.68	270539	99.90%	0.934	1.791
Hexanal*	13.74	115606	98%	0.434	0.832
3-Pentanone	13.82	127604	98%	0.467	0.896
3,3-Dimethyl-2-butanone	14.11	P45605	98%	0.435	0.833
2-Pentanone*	14.18	448516	99+%	0.467	0.896
2-Propanol &	14.29	270490	99.50%	0.56	1.074
1-Propanol &		293288	99.50%	0.504	0.967
Cyclopropyl methyl ketone* (composite)		C120006	99%	0.456	0.875
2-Methyl-3-pentanone	14.34	108707	97%	0.435	0.833
3-Methyl-2-pentanone	14.77	M67001	99%	0.435	0.833
Cyclopentanone	14.97	C112402	99+%	0.456	0.875
4-Methyl-2-pentanone &	15.13	293261	99.50%	0.435	0.833
3-Hexanone* (composite)		103020	98%	0.435	0.833
2-Methyl-1-propanol &	15.27	270466	99.50%	0.46	0.881
2-Butanol &		294810	99.50%	0.495	0.949
2-Methyl-2-propanol* (composite)		308250	99.50%	0.46	0.881
Cyclobutanol	15.42	156434	99.50%	0.481	0.923
2-Hexanone	15.58	103004	98%	0.435	0.833
1-Butanol*	15.72	270679	99.80%	0.46	0.881
3-Methyl-2-butanol &	15.96	110949	98%	0.45	0.863
Neopentyl alcohol (composite)		N7206	99%	0.425	0.815
3-Pentanol	16.12	P8025	98%	0.45	0.863
tert-Amyl alcohol*	16.19	240486	99+	0.403	0.773
2-Methyl-1-butanol*	16.54	133051	99+%	0.425	0.815
Cyclopentanol	16.54	C112208	99%	0.415	0.796
2-Pentanol*	16.6	P8017	98%	0.45	0.863
3-Methyl-1-butanol	16.89	309435	99+%	0.425	0.815
1-Pentanol*	16.95	138975	99+%	0.425	0.815

*Indicates commonly found oxygenates

** not available from Aldrich Chemical

*** retention times are provided as an example only

Precision

Precision statements were determined on two liquid samples, one LPG sample, and one gas sample using UOP Method 999.

Repeatability and Site Precision

A nested design was carried out for trace oxygenated hydrocarbons analysis with two analysts performed on a Wasson ECE Instrumentation configured GC. Each analyst carried out two tests on two separate days for each type of sample for a total of 24 tests. Using a stepwise analysis of variance procedure, the within-day and within-lab estimated standard deviations (esd) were calculated at the

concentration means listed in Tables 3 through 5. Two analyses performed in one laboratory by the same analyst on the same day should not differ by more than the repeatability allowable differences shown in Tables 3 through 5 with 95% confidence. Two analyses performed in one laboratory by different analysts on different days should not differ by more than the site precision allowable differences shown in Tables 3 through 5 with 95% confidence.

Table 3
LPG Sample
Repeatability and Intermediate Precision, mg/kg (mass-ppm)

<u>Component</u>	<u>Mean Concentration</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within Day esd</u>	<u>Allowable Difference</u>	<u>Within Lab esd</u>	<u>Allowable Difference</u>
Diethyl Ether	10.0	0.05	0.2	0.07	0.3
Methyl Formate	7.9	0.06	0.2	0.06	0.2
Ethyl t-Butyl Ether	10.3	0.07	0.3	0.09	0.3
Methyl t-Butyl Ether	10.3	0.07	0.3	0.09	0.3
Acetone	24.7	0.19	0.7	0.2	0.8
2-Butanone	10.2	0.08	0.3	0.08	0.3
Methyl Isobutyl Ketone	10.2	0.09	0.3	0.10	0.4

Table 4
Gas Sample
Repeatability and Intermediate Precision, mol-ppm

<u>Component</u>	<u>Mean Concentration</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within Day esd</u>	<u>Allowable Difference</u>	<u>Within Lab esd</u>	<u>Allowable Difference</u>
Methyl t-Butyl Ether	5.5	0.01	0.1	0.05	0.2
Methanol	2.0	0.08	0.3	0.09	0.3
Acetone	3.3	0.01	0.1	0.05	0.2
Ethanol	1.6	0.06	0.2	0.06	0.2
Isopropanol + n- Propanol	5.8	0.04	0.1	0.15	0.9
2-Butanol	2.8	0.05	0.2	0.07	0.3
n-Butanol	3.3	0.04	0.1	0.12	0.5

Table 5
Liquid Sample
Repeatability and Intermediate Precision, mg/kg (mass-ppm)

<u>Component</u>	<u>Mean Concentration</u>	<u>Repeatability</u>		<u>Site Precision</u>	
		<u>Within Day esd</u>	<u>Allowable Difference</u>	<u>Within Lab esd</u>	<u>Allowable Difference</u>
Methyl formate	29.5	0.36	1.4	0.60	2.4
n-Valeraldehyde	31.3	0.19	0.8	0.25	1.0
Ethanol	22.4	0.31	1.2	0.37	1.4
2-Pentanone	28.6	0.15	0.6	0.20	0.8

2-methyl-1-butanol	32.5	0.13	0.5	0.20	0.8
Acetone	32.0	0.30	1.2	1.28	7.8
2-Butanone	40.6	0.32	1.3	1.19	5.3
2-methyl-2-Propanol	42.6	0.31	1.2	0.63	2.8

The data in Tables 3 through 5 are a short-term estimate of repeatability. When the test is run routinely in the field, a control standard and chart should be used to develop better estimates of the long-term repeatability.

Reproducibility

There is insufficient data to calculate the reproducibility of the test at this time.

Time for Analysis

The elapsed time for one analysis including calibration is 2.5 hours. The labor requirement is 1.5 hours. For subsequent analyses, the elapsed time is 0.3 hour with the labor requirement of 0.3 hour.

Suggested Suppliers

Agilent Technologies, 2850 Centerville Rd., Wilmington, DE 19808-1610 (302-633-8000) www.agilent.com

Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15219-4785 (412-490-8300) www.fishersci.com

Matheson Tri-Gas, 166 Keystone Drive, Montgomeryville, PA 18936 (215-641-2700) www.mathesontrigas.com

Restek, 110 Benner Circle, Bellefonte, PA 16823 (814-353-1300) www.restek.com

Sigma-Aldrich, P.O. Box 14508, St. Louis, MO 63178 (800-325-3010) www.sigma-aldrich.com

Supelco, 595 North Harrison Road, Bellefonte, PA 16823 (814-359-3441) www.sigma-aldrich.com

Swagelok Company, 29500 Solon Rd., Solon, OH 44139 (440-248-4600) www.swagelok.com

VICI Metronics, 26295 Twelve Trees Poulso, Washington 98370 (360-697-9199) www.vici.com

VICI Valco Instruments, 7806 Bobbitt, Houston, TX 77255 (713-688-9345) www.vici.com

Wasson ECE, 101 Rome Ct., Fort Collins, CO 80524 (970-221-9179) www.wasson-ece.com

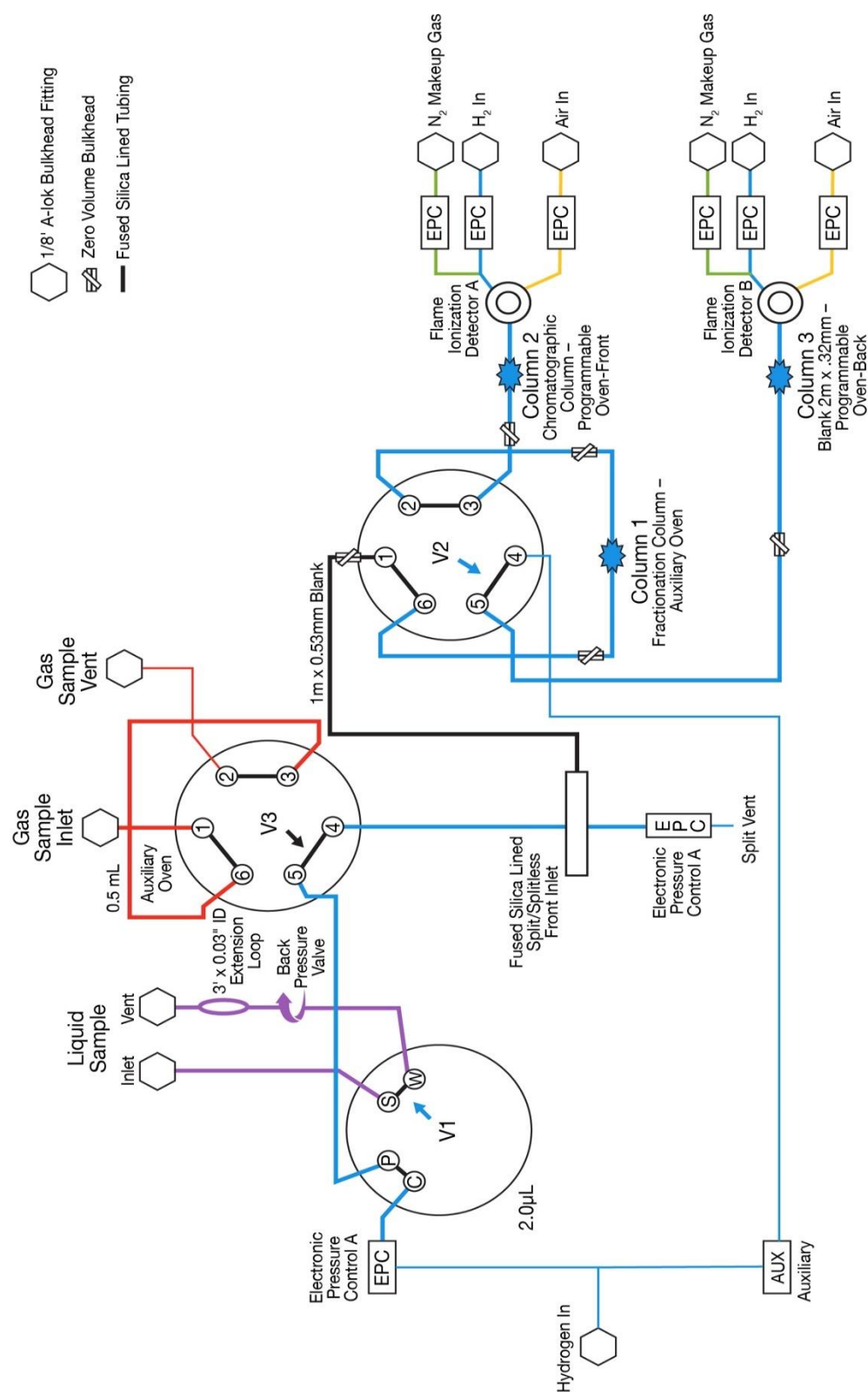


Figure 1
Wasson/Agilent GC Configuration

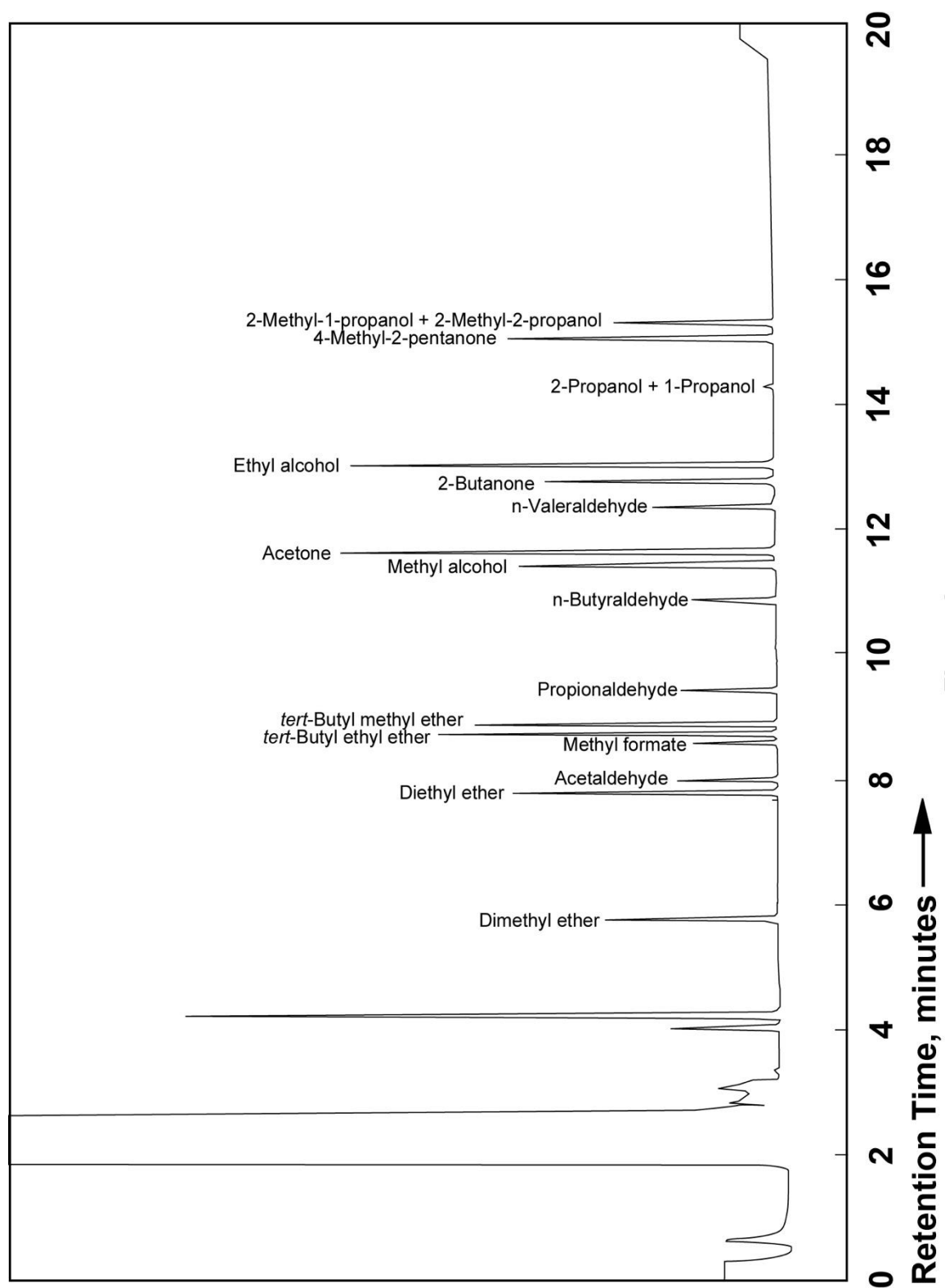


Figure 2
Chromatograms of LPG Reference Blends

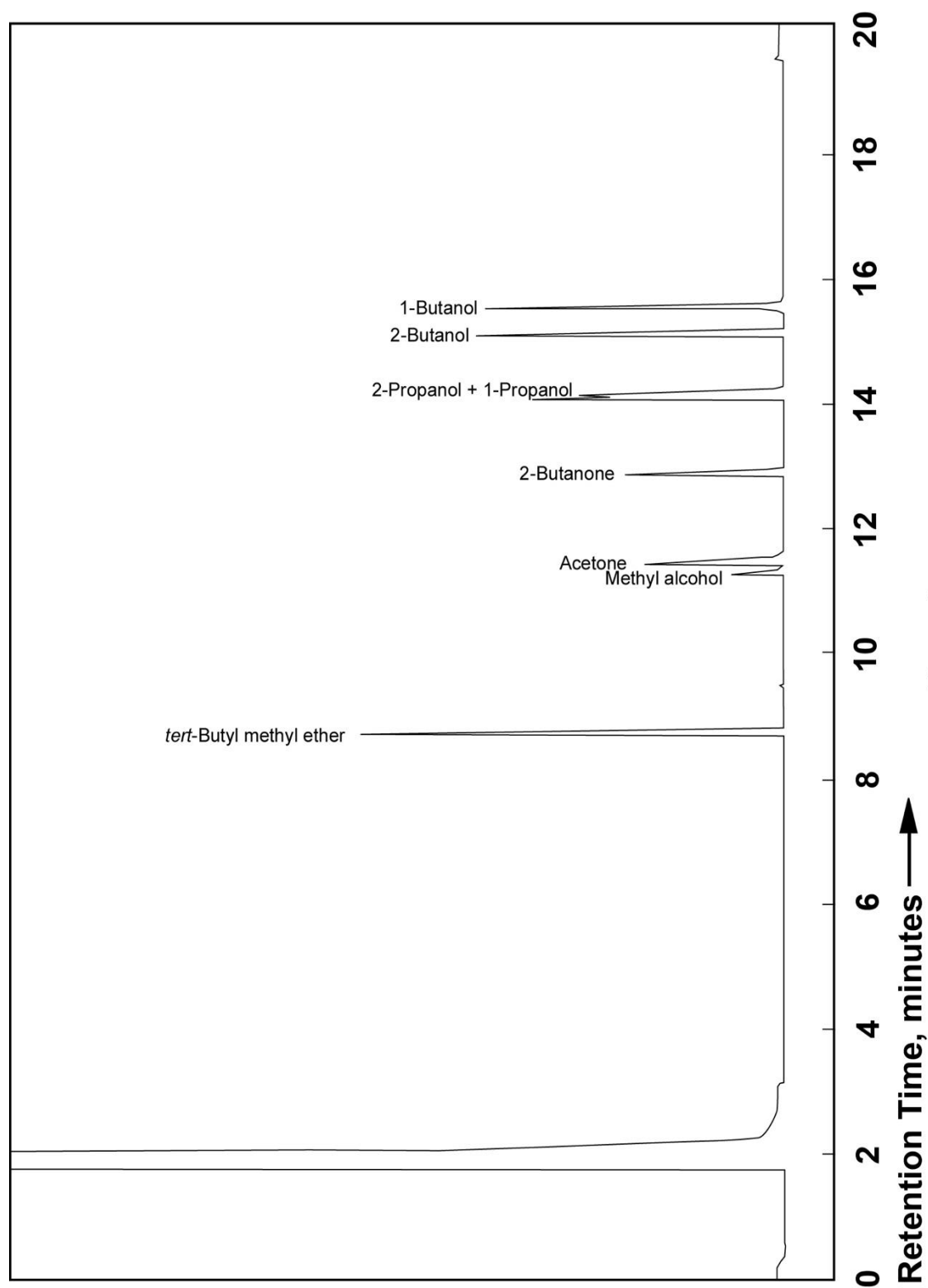


Figure 3
Chromatogram of Gas Blend

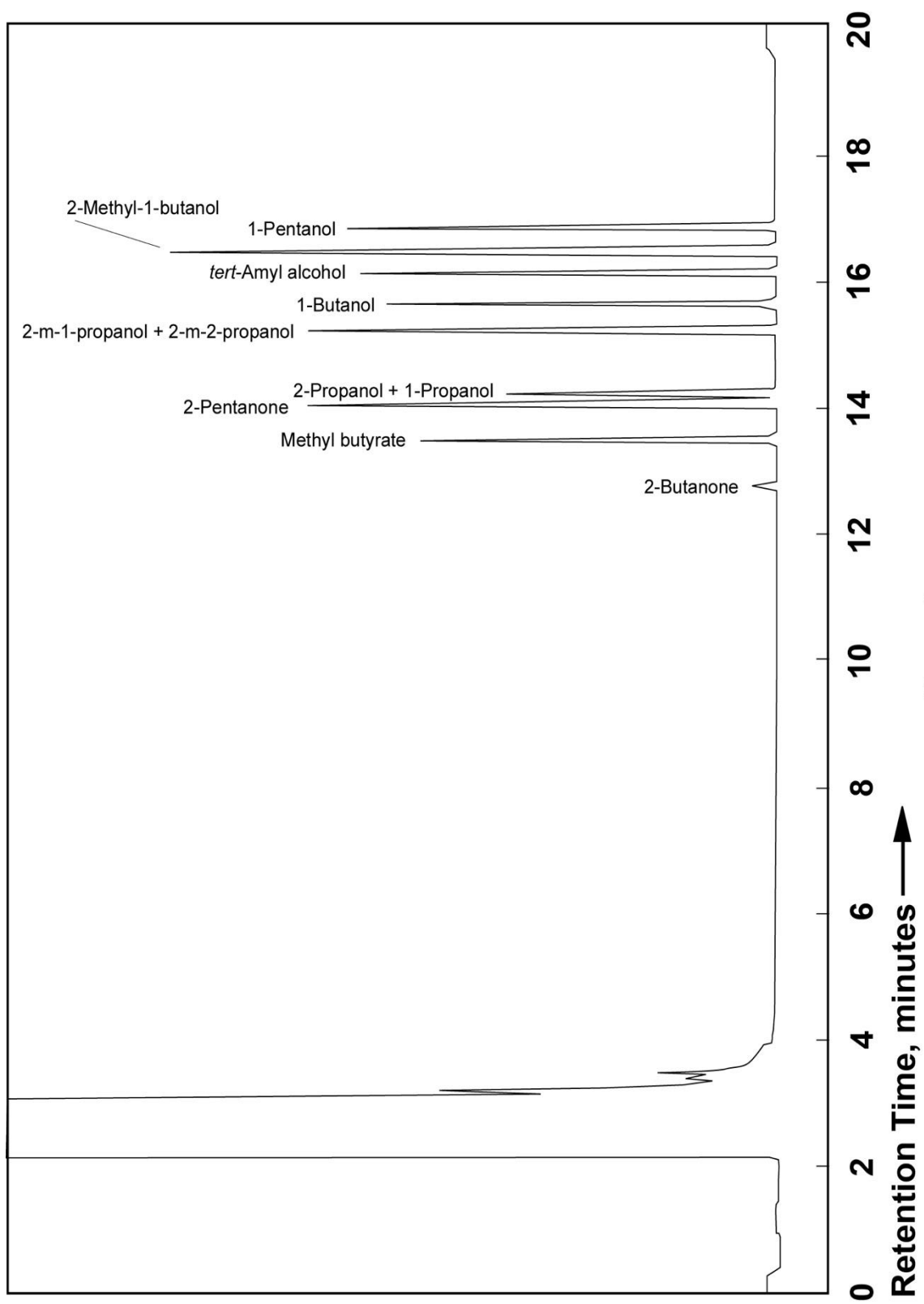


Figure 4
Chromatogram of Liquid Reference Sample

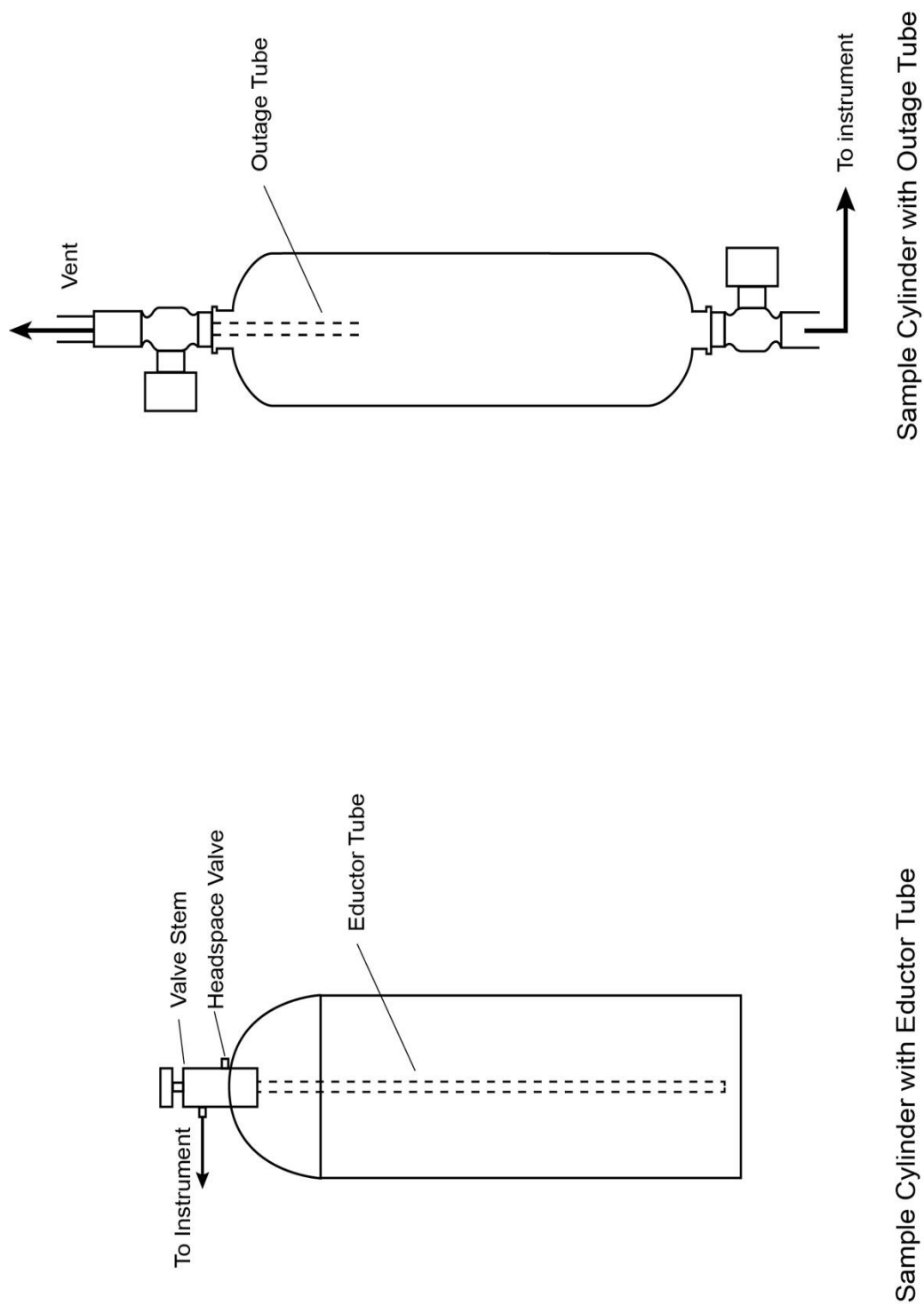


Figure 5
Common LPG Sample Cylinders