



Determination of Trace Methyl Mercaptan, Ethyl Mercaptan, and Isopropyl Disulfide in Polymer Grade Ethylene & Propylene by Gas Chromatography Mass Spectrometry

UOP Method 1021-19

Scope

This method is for determining trace methyl mercaptan, ethyl mercaptan, and isopropyl disulfide in high purity polymer grade ethylene and propylene gas or liquid using a gas chromatograph equipped with a mass spectrometer run in selected ion monitoring mode. The specific instrument is preconfigured and is capable of determining typical impurities in polymer grade ethylene or propylene, however this method only outlines the procedure for determining methyl mercaptan, ethyl mercaptan, and isopropyl disulfide. Methyl and ethyl mercaptan elute on the propylene tail but are readily extracted by unique ions. The lower limit of quantitation for methyl and ethyl mercaptan are 0.04 mol-(or mass-) ppm and 0.02 mol- (or mass-) ppm for isopropyl disulfide.

References

ASTM Practice D1265, "Standard Practice Sampling Liquefied Petroleum (LP) Gases (Manual methods)," www.astm.org

ASTM Practice D5287, "Automatic Sampling of Gaseous Fuels," 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

Wasson ECE Instrumentation, *Application 460-SP* instrument manual

Wasson ECE Instrumentation, *Dynamic Blender* instrument manual

Outline of Method

The method requires the use of a dedicated gas chromatographic mass spectrometer system that is configured for automated analysis which is capable, via valving and an on-board vaporizer, of determining impurities in polymer-grade ethylene or propylene gas or liquid. For the trace mercaptan and sulfide analysis, a reproducible sample volume is injected into a gas chromatograph (GC) that is equipped with a polar fused silica capillary column (Figure 1, column 2), a mass spectrometer detector, and control and quantitation software. The concentrations of methyl mercaptan, ethyl mercaptan and isopropyl disulfide are determined by a multi-point external standard calibration curve

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for each component that represents the area of each selected ion versus its concentration, analyzed under identical conditions and injection volumes.

Significance and Use

High purity ethylene and propylene are used as feedstocks for production of polyethylene and polypropylene, respectively. The quality of the monomer is critical to successful polymerization. The presence of trace amounts of certain impurities can have detrimental effects on the catalyst and product yields. This test method is suitable for setting specifications, for use as an internal quality control tool, and for use in development or research work.

Apparatus

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

Analyzer Wasson-ECE Instrumentation Application 460-SP “GC/MS Analysis of Impurities in Polymer-grade Propylene”, 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. Pre-configured systems are available from Wasson-ECE for determining only mercaptans, the application specified can determine other impurities. The Wasson-ECE analyzer includes:

Chromatographic column, 60 meters, PLOT, part# 60 m 2358, Wasson-ECE Instrumentation

Chromatographic column, 60 meters, polar, part# 60 m 2318, Wasson-ECE Instrumentation

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 is required. Agilent Technologies, Model 7890.

Mass Spectrometer Detector, capable of selected ion monitoring and equipped with inert EI source, performance turbo pump, ion gauge controller kit and data system. Agilent Technologies, Model 5977B.

On-board Vaporizer, converts LPG to the gas phase prior to injection, Wasson-ECE Instrumentation

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

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

Dynamic Blender with mass flow controller, model DB302, Wasson-ECE Instrumentation

Flowmeter, Mass/VLM, Agilent Technologies, Model ADM 2000.

Leak detector, gas, Fisher Scientific, Cat. No. 03-251-702

Tubing, Sulfinert, .030-in ID x 1/16-in OD, Restek, Cat. No. 29230

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

Regulator, helium, two-stage, high purity, delivery pressure range 30 to 700 kPa (4 to 100 psi), Matheson Tri-Gas, Model 3122-580, Cat. No. SEQ3122A580, 2 required

Regulator, nitrogen, two-stage, high purity, delivery pressure range 30 to 700 kPa (4 to 100 psi),

Matheson Tri-Gas, Model 3122-580, Cat. No. SEQ3122A580

Regulator, 3 component mercaptan/disulfide blend, two-stage, high purity, delivery pressure range 30 to 1700 kPa (0 to 250 psi), Matheson Tri-Gas, Regulator must conform with cylinder valve

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

Reagents and Materials

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

Calibration blend, Gas, quantitative, containing methyl mercaptan, ethyl mercaptan, and isopropyl disulfide at the 10 mol-ppm level in helium, local supply.

Gas purifier, for carrier gases, to remove moisture, VICI Mat/Sen, Cat. Nos. P100-1(helium), P300-1(nitrogen), local supply.

Helium, UHP, 99.9995% minimum purity, total hydrocarbons less than 0.5 ppm as methane, local supply.

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

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of gas chromatography, mass spectrometry 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, "Sampling Liquefied Petroleum (LP) Gases (Manual Method)," ASTM Practice D 5287, "Automatic Sampling of Gaseous Fuels," UOP Method 516, "Sampling and Handling of Gasolines, Distillate Fuels, and C₃-C₄ Fractions," 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.
3. When a major change is made to the system, such as the power to the GCMS is interrupted, the GCMS needs to be tuned in accordance with the manufacturer's instructions. A new calibration curve should then be established.

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 Total Ion Chromatogram as shown in Figure 2.

Table 1
Recommended Operating Conditions

Carrier gas	helium
Mode	constant flow
Flow rate	1.5 mL/min
Head pressure	8.2 psig @ 40°C
Linear velocity	31.4 cm/sec @ 40°C
Split flow	15 mL/min
Injection port temperature	200°C
On-board Vaporizer temperature	80°C
Column temperature program	
Initial temperature	40°C
Initial time	6 min
Programming rate	15°C/min
Final temperature	150°C
Final time	3 min
Detector	
Ion Source	EI
Source temperature	230°C
Quad temperature	150°C
Transfer line temperature	280°C
Fixed Electron energy	70 eV
Acquisition Type	SIM
Sample size	1.0 mL, repeatable

Gas Samples and Blends

1. Choose and load appropriate method for gas sample analysis, ensuring valve 1 is in the on position to bypass the on-board vaporizer, see Figure 1.
2. Connect the 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 analysis.
 - If connecting the dynamic blender to the system, significantly more time (about 60 seconds) should be used to purge the inlet due to the decreased flow rate.
 - The stop flow technique is described however constant flow while injecting can also be used, especially when using the dynamic blender. The technique which provides the best precision between multiple injections should be used.
3. Identify methyl mercaptan, ethyl mercaptan, and isopropyl disulfide by matching retention time and their target ion as listed in Table 2. Record the area of each target ion from the extracted ion chromatogram.
 - A typical total ion chromatogram is shown in Figure 2 for reference.
 - Retention times of components may be influenced by the amount of propylene or diluent in the calibration blend or sample.

4. Repeat steps 1 and 2 for each sample until the peak areas from each run do not deviate by more than 10%.

Liquid Petroleum Gas (LPG Stream Samples)

1. 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 3 for diagram of common LPG cylinders.
2. Pressurize the LPG cylinder containing the sample (or blend) to approximately 1400 to 2068 kPa gauge (200 to 300 psig) with nitrogen or helium.
3. 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.
4. Choose and load appropriate method for LPG sample analysis, ensuring valve 1 is in the off position and the vaporizer is in line with the inlet of the system. Refer to Figure 1.
5. Ensure that the back-pressure restrictor valve is closed.
6. Fully open the bottom valve or eductor valve of the sample cylinder.
7. Partially open the back-pressure restrictor to permit LPG flow through the sampling system.
8. 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.
9. Stop the sample flow by closing the back-pressure restrictor valve.
10. With the back-pressure restrictor valve closed monitor the gas vent bubbler and wait 1 minute to ensure vaporized sample has flushed the sample loop.
11. Stop the flow, allow 5 to 10 seconds for the pressure to equilibrate, and start the analysis, the integrator and the column temperature programming sequence.
12. Close the LPG cylinder valve and open the back-pressure valve to vent the sampling system.
13. Identify methyl mercaptan, ethyl mercaptan, and isopropyl disulfide by matching retention time and their target ion as listed in Table 2. Record the area of each target ion from the extracted ion chromatogram.
 - A typical total ion chromatogram is shown in Figure 2 for reference.

- Retention times of components may be influenced by the amount of propylene or diluent in the calibration blend or sample.

14. Repeat steps 4 through 13 for each sample until the peak areas from each run do not deviate by more than 10%. Typically, 3-5 times when instrument is run daily.

Calibration

A calibration curve is required to relate the detector response of ion 47 for methyl mercaptan, ion 62 for ethyl mercaptan, and ion 108 for isopropyl disulfide to mol-ppm. Each calibration curve is generated by the analysis of gas calibration blends as described under Chromatographic Technique in triplicate and plotting the average area of each selected ion versus its concentration. Three or more component concentration levels are required to generate the plot. The different calibration levels can be obtained using the specified gas standard and the Wasson dynamic blender. See Appendix for the steps needed to use the blender.

- The calibration blend concentrations should bracket the expected concentration of the samples to be analyzed and not have a range of more than 2 orders of magnitude. Determine experimentally how long the calibration curve is valid, typically more than 2 months for the instrument specified if no major change were made to the system.
- A linear regression model should be used for the calibration curves, with the intercept not forced through zero. The R-squared (R^2) for the regression should be ≥ 0.99 .
- The peak areas from each of the triplicate blend runs should not deviate from the average by more than 10% (relative). 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. It is typical that after the instrument has been idle for a while, even just overnight, the first several injections are not repeatable.
- Confirm the stability of the chromatographic system by analyzing a reference sample or blend each day when samples are analyzed. If the results differ by more than 10% from the average of previous analyses, a problem has developed with the chromatographic system that needs to be resolved or possibly a new calibration curve is needed before samples can be analyzed.

Table 2

<u>Component</u>	<u>Target Ion Retention Times</u>		
	<u>Target Ion</u> <u>(m/z)</u>	<u>Typical Retention</u> <u>Time (minutes)</u>	<u>Molecular</u> <u>Weight (g/mol)</u>
Methyl Mercaptan	47	5.22	48.11
Ethyl Mercaptan	62	5.94	62.13
Isopropyl Disulfide	108	15.14	150.298

Note: Target ions are the molecular ion that are chosen to obtain high sensitivity and selectivity.

Calculations

Utilize the chromatographic software and apply a linear calibration model or calculate the absolute mol-ppm concentration of each component to the nearest 0.05 mol-ppm as shown in Equation 1.

$$\text{Component, mol-ppm} = A * X + B \quad (1)$$

where:

- A** = the slope of the multipoint calibration curve for the component, previously generated
- X** = target ion peak area of component
- B** = y intercept of the multipoint calibration curve for the component, previously generated,

If the calculated mol-ppm is less than or equal to 0 then the sample is either beyond the scope of the method or the calibration curve is not valid.

When mass-ppm concentrations are required, as in the case of analyzing a LPG, the conversion can

be made using Equation 2.

$$\text{Component, mass-ppm} = \frac{C * D}{42.08} \quad (2)$$

where:

C = component concentration in sample, mol-ppm

D = molecular weight of component, g/mole

42.08 = molecular weight of propylene, g/mole

Precision

Precision statements were determined on one gas and one LPG samples using UOP Method 999, "Precision Statements in UOP Methods."

Repeatability and Site Precision

A nested design was carried out for *various* trace mercaptan components with two analysts performed on a Wasson ECE Instrumentation configured GC. Each analyst carried out two tests on two separate days for components in a gas sample for a total of 8 analyses. 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. 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 Table 3 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 Table 3 with 95% confidence.

Table 3
Gas Sample
Repeatability and Intermediate Precision, mol-ppm

Component	Mean	Repeatability		Site Precision	
		<u>Within Day esd</u>	<u>Allowable Difference</u>	<u>Within Lab esd</u>	<u>Allowable Difference</u>
Methyl Mercaptan	0.697	0.0080	0.031	0.0232	0.141
Ethyl Mercaptan	0.497	0.0072	0.028	0.0355	0.216
Isopropyl Disulfide	9.069	0.0615	0.242	0.0702	0.276

The data in Table 3 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 is 0.3 hours. The labor requirement is 1.0 hour.

Suggested Suppliers

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

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

Praxair, 39 Old Ridgebury Rd. Danbury, CT 06810, USA (203-837-2213) www.praxair.com

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

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

Thomas Scientific, 1654 High Hill Road, Swedesboro, NJ 08085, U.S.A. (800.345.2100)
www.thomassci.com

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

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

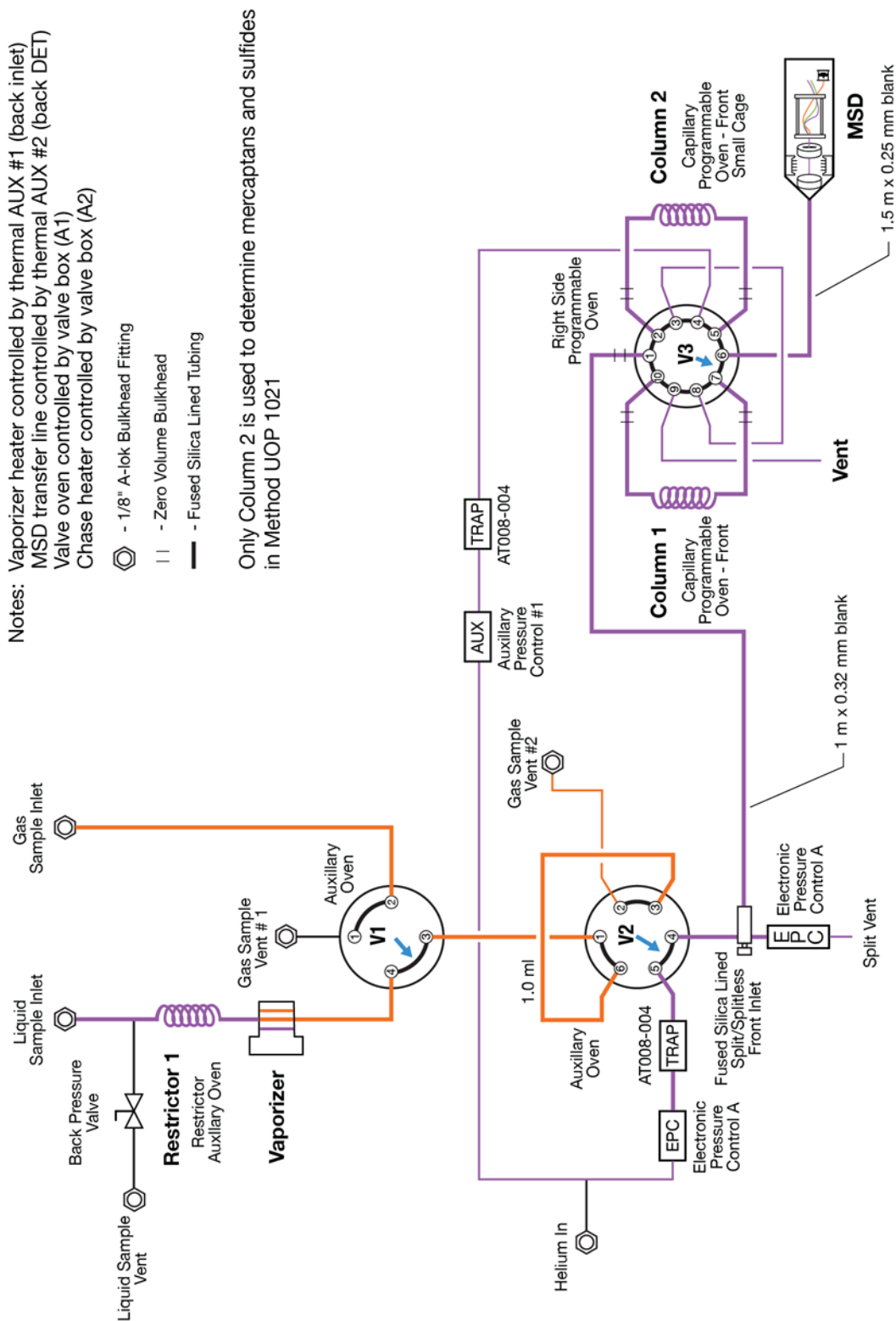
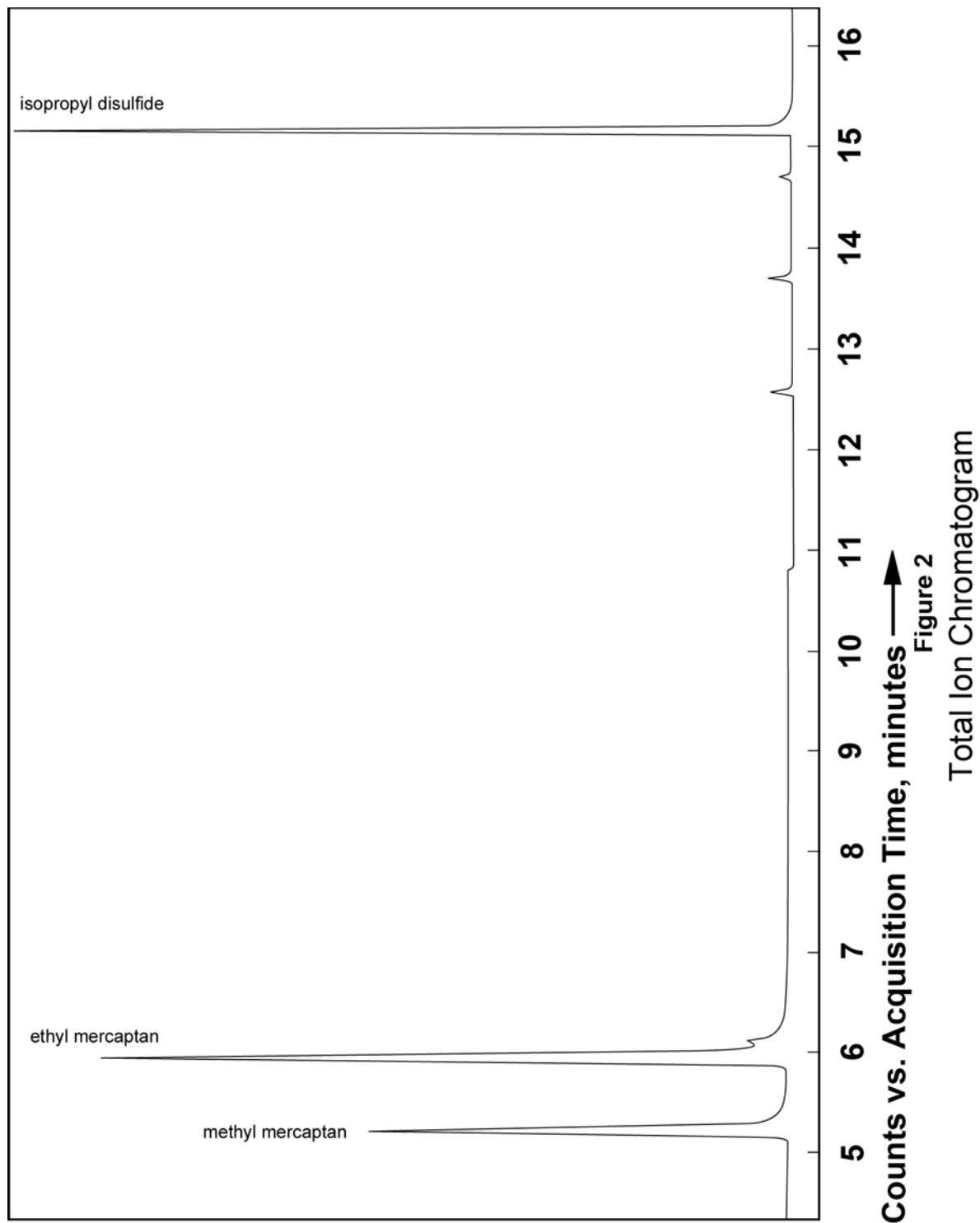


Figure 1
Valve Diagram



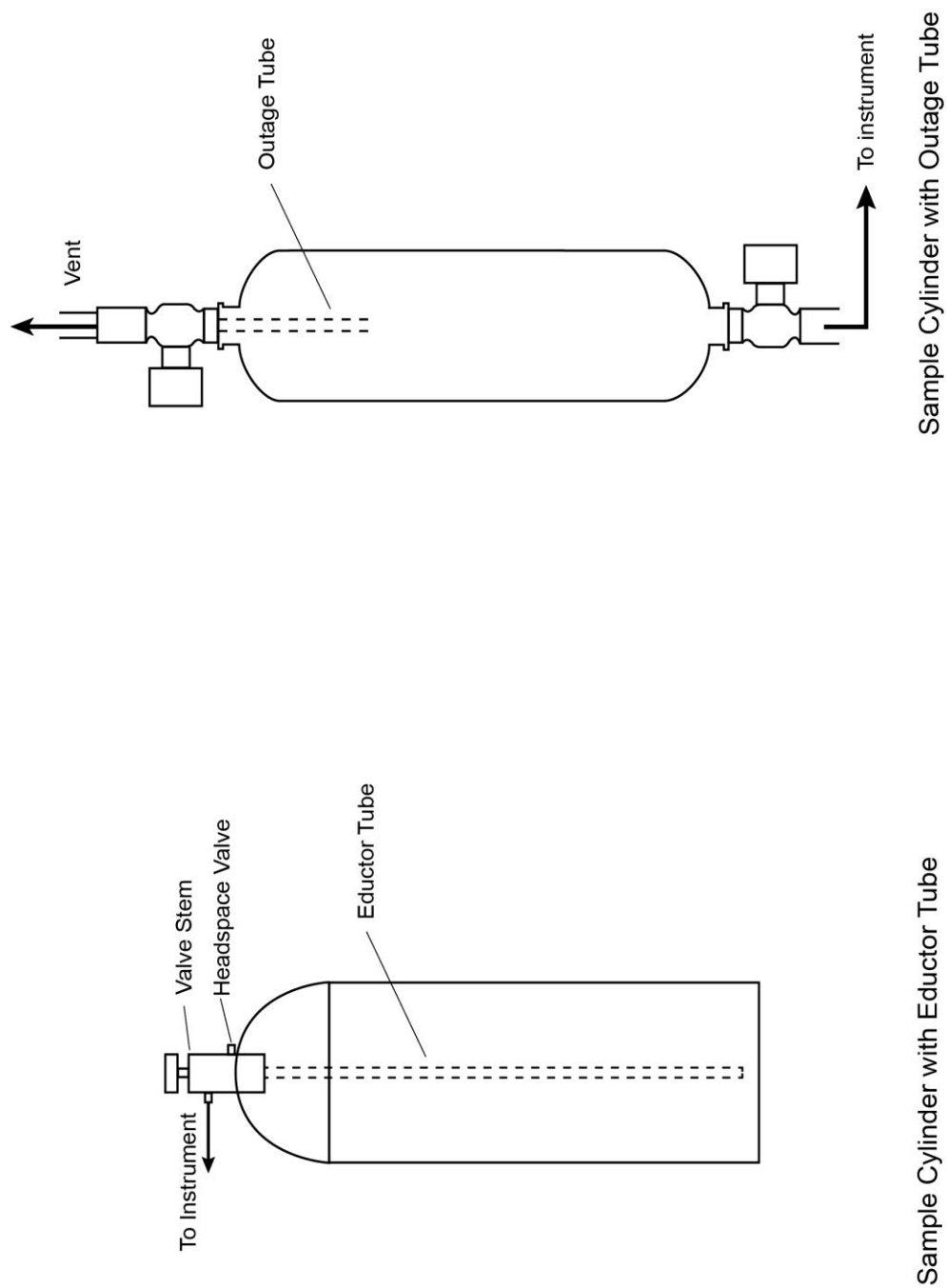


Figure 3
Common LPG Sample Cylinders

Appendix

Developing Calibration Curve with Wasson ECE Dynamic Blender

Scope

The Appendix describes how to use the dynamic blender from Wasson ECE to dilute a purchased gas blend to lower concentrations for establishing a calibration curve. It also describes how to perform the required calculations for determining the concentration of each component in the dilution.

Procedure

1. Follow instrument site prep and installation documentation for dynamic blender.
 - If instrument and blender are purchased from Wasson ECE the blender will be installed at the time of instrument installation.
2. Set temperature on bridge heater of blender to 70°C.
3. Connect regulated blend cylinder to 'gas sample inlet' of the dynamic blender using Sulfinert lined tubing.
4. Connect a flow meter to the end of the dynamic blender transfer line.
 - Ensure that there is a sufficient seal between the transfer line ferrule and the flow meter tube so that there are no leaks and an accurate reading can be made.
5. Open the cylinder valve and adjust the pressure using the cylinder regulator so that the flow meter reads between 1 and 1.5 mL/minute.
 - Due to the frit restrictor strength, regulated pressure of standard may need to be set to approximately 60 psig to get sufficient flow through the blender.
 - Regulated pressure of the standard or helium diluent may not exceed 100 psig when connected to the dynamic blender.
6. Allow flow to equilibrate.
 - If any adjustments to the pressure on the cylinder are made, sufficient time needs to be permitted for the flow to equilibrate.
 - Decreasing the pressure on the regulator will require a significant amount of time for the flow to equilibrate due to frit restrictor in dynamic blender.
7. Take reading from the flow meter. (F in the equation A-1 below)
8. Adjust helium flow on the dynamic blender to achieve desired concentration.
 - Consult Wasson dynamic blender instrument manual for specifics on how to operate equipment.
9. Record total flow of helium carrier gas and sample through the dynamic blender using the flow meter (E in the equation A-1 below).
10. Remove the transfer line from the flow meter and attach to the inlet of the Wasson instrument.
11. Follow procedure outlined in Chromatographic Technique, Gas samples and proceed with injection.

Calculations

Calculate the concentration of each component in the standard after blending, using equation A-1.

$$\text{Component in standard, mol-ppm} = \frac{\mathbf{F} * \mathbf{G}}{\mathbf{E}} \quad (\text{A-1})$$

where:

F = flow of the calibration blend passing through the blender (helium free flow), mL/min

G = certified concentration of component in standard, mol-ppm

E = total flow, calibration blend plus helium, mL/min