



Sulfur Components In LPG Fractions by GC-SCD

UOP Method 791-16

Scope

This method is for determining trace amounts of sulfur species in liquefied petroleum gases (LPG) streams using a gas chromatograph equipped with a sulfur chemiluminescence detector (GC-SCD). Individual components are determined quantitatively from 0.1 to approximately 200 mass ppm sulfur. Higher concentrations of sulfur may be measured by modifying the instrument conditions to accommodate the increase in signal.

Reference

ASTM Practice D 1265, "Sampling Liquefied Petroleum (LP) Gases (Manual Method),"

ASTM Practice D 5287, "Automatic Sampling of Gaseous Fuels,"

ASTM Method D6667-14, "Standard Test Method for Determination of Total Volatile Sulfur in Gaseous Hydrocarbons and Liquefied Petroleum Gases by Ultraviolet Fluorescence"

ASTM Method D6849-13, "Standard Practice for Storage and Use of Liquefied Petroleum Gas (LPG) in Sample Cylinders for LPG Test Methods"

UOP Method 516, "Sampling of Gasolines, Distillate Fuels and C3-C4 Fractions"

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

Outline of Method

A reproducible sample volume is introduced into a gas chromatograph equipped with a fused silica capillary column internally coated with methyl silicon, sulfur chemiluminescence detector (SCD) and control and quantitation software. The SCD is sulfur specific and responds to all sulfur compounds on an equimolar basis. The mass-ppm sulfur concentration of each sulfur component in an LPG sample is calculated using the gas chromatographic external standard method of quantitation. The total sulfur is then verified via ASTM method D6667.

Apparatus

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

Chromatographic column, 40 m x 0.32 mm ID fused silica capillary, Agilent J&W DB-Sulfur SCD, G3903-63002

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. SAFETY DATA SHEETS (SDS) OR EXPERIMENTAL SAFETY DATA SHEETS (ESDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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Clamp, for ring stand and sample cylinders. minimum opening 38.1-mm, VWR International, Cat. No. C6088-12

Clamp holder, for ring stand and clamp, VWR International, Cat. No. C6088-2

Cylinder, for sample collection – Sulfinert coated, DOT 3E 1800, 500 mL capacity, Restek Cat. No. 24133, Equip with two sulfinert valves, Restek Cat No. 21400, and 6900 kPa gauge (1000 psi)

Gas chromatograph, temperature programmable, built for capillary column chromatography utilizing a split injection system having a deactivated glass injection port insert and equipped with a sulfur chemiluminescence detector (Agilent Model 8355 or equivalent) that will give a minimum peak height response of 10 times the background noise for 0.1 mass-ppm of a sulfur peak when run under recommended conditions

Regulator, air, two-stage, high purity, Matheson Trigas, Model 3810A-590

Regulator, hydrogen, two-stage, high purity, Matheson Trigas, Model 3810A-350

Ring stand, with rectangular base, 140- × 229-mm with 610-mm rod, VWR International, Cat. No. 470104-060

Tubing, Sulfinert® Treated, 1.59-mm (1/16-inch) OD, 0.030 mm ID, 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 psig), Thomas Scientific, Cat. No. 9567K20

Valve, injection, 2.0- μ L internal sample volume injector, stainless steel, UWP series, with 1.59-mm (1/16-inch) fittings, manual with standoff, Valco Instruments, Cat. No. 2CI4UWE2

Valve, metering, 3.175-mm (1/8-inch), straight, stainless steel, Swagelok, Cat. No. SS-ORS2-V

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

Blend, LPG, calibration, certified standard, sulfur species in known concentrations in isobutane, size No. 3 treated aluminum cylinder, with eductor tube, pressurized with an inert gas to 1437 kPa gauge (210 psig), Matheson Gas Products (required for analysis of LPG streams). The calibration blend life is certified for 12 months by Matheson Gas Products.. The blend must be monitored regularly and replaced when changes in concentration or species present are noted.

Gas Purifier, hydrogen, to remove oxygen and moisture from carrier gas, VICI Metronics, Cat. No. P200-1

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

Hydrogen, zero-gas, 99.95% minimum purity

Procedure

The analyst is expected to be familiar with general laboratory practices, the technique of gas chromatography, and the equipment being used. Dispose of all 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 Liquified 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. Analysis must be performed as soon as possible after sampling to minimize sulfur adsorption on cylinder walls, and to minimize reactions that produce changes in the composition of sulfur compounds in the cylinder. Cylinders must be lined with a Sulfinert coating to further prevent sulfur adsorption onto the cylinder walls.

Chromatographic Technique

1. Install a gas purifier between the carrier gas source and the carrier gas inlet on the gas chromatograph
 - Column life is significantly reduced if the gas purifier is not used
2. Install the fused silica capillary column in the gas chromatograph according to the manufacturers specifications.
3. Install the injection valve in the carrier gas line just ahead of the injection port and connect the valve ports according to the manufacturer's instructions (Figure 1).
4. Establish the recommended operating conditions as given in Table 1.
 - Other conditions may be used provided they produce the required sensitivity and chromatographic separations equivalent to those shown in the Typical Chromatogram .

Table 1
Recommended Operating Conditions

Carrier gas	hydrogen
Column Flow (constant flow)	1 mL/min
Split flow	50 mL/min
Injection port temperature	250 °C
Column temperature program	
Initial temperature	40 °C
Initial time	3 min
Programming rate 1	15 °C/min
Intermediate final temperature	150 °C
Intermediate time	0 min
Programming rate 2	20 °C/min
Final temperature	250 °C
Final time	10 min
SCD Detector	*
Sample size	2.0 μL (repeatable for LPG)

*The sulfur chemiluminescence detector is setup and operated according to the manufacturer's instructions.

5. Program the column oven to 250 °C and maintain this temperature until a stable baseline has been obtained at the required sensitivity.
6. Cool the column oven 40 °C.

Calibration of Apparatus

Quantitative results are based on the injection of a repeatable volume of a sample and a calibration blend (external standard). A response factor is then used to relate the peak area obtained for the primary standard blend to the peak areas of all sulfur compounds in the LPG sample. The sulfur chemiluminescence detector responds to all sulfur compounds on an equimolar basis.

1. Connect the valve on the eductor tube of the LPG calibration blend. Figure 2 shows common LPG sample cylinders
2. Analyze the blend in triplicate as described under Analysis of LPG Samples, Steps 6 through 13. Two of the injections should take place before the analytical samples, the third after. Take the mean of the response factors calculated from these three runs.
 - The peak area from each of the three runs should not deviate from the average by more than 10% of the value. If greater deviations occur, make certain that there are no problems with the equipment and then make further runs until the required repeatability is obtained on two consecutive runs.
3. Determine a response factor to be used for all sulfur species to 3 decimal places using Equation 1:

$$Q = \frac{L}{K} \quad (1)$$

where:

K = average peak area for the sum of the sulfur compounds in the blend

L = concentration of the sum of the sulfur, as sulfur, in the blend, mass-ppm

Q = response factor for sulfur species, mass-ppm/area count

Analysis of LPG Samples

1. Connect about 5-10 cm of FEP Teflon tubing to the outlet port of the injection valve as shown in Figure 1.
 - This will form a "sight glass" to ensure that no air bubbles are in the injection port
 - Tubing internal volume and length must be minimized.
2. Connect the metering valve to the exit end of the tygon tubing
3. Connect Tygon tubing to the exit end of the metering valve to vent
4. Pressurize the LPG vessel containing the sample to approximately 1723 kPa gauge (250 psig) with nitrogen.
 - Other inert gases such as He may be used.
5. Mount the cylinder in a vertical position so that the non-outage tube end is facing downwards and connect the bottom valve to the sample injector valve inlet tubing (Figure 2)
 - The connecting tubing between the cylinder and injector valve should be as short as possible.
 - Sulfinert tubing should be used for connecting the valve to the LPG sample.
 - For self standing cylinders containing an eductor tube, connect the eductor tube outlet to the injector valve inlet tubing.
6. Place the injection valve in the fill position.
7. Ensure that the metering valve is closed.
8. Open fully the bottom valve of the vessel containing the sample.
 - On upright cylinders with eductor tubes, open the eductor tube valve.

9. Partially open the metering valve to permit LPG to flow through the sampling system and observe the sight glass to verify there are no entrained bubbles.
10. Stop the sample flow by closing the metering valve.
11. Immediately switch the injection valve to the inject position and start the recorder, integrator and column temperature programming sequence.
 - The injection valve should remain in the inject position for the entire analysis.
12. Close the LPG cylinder valve and immediately open the metering valve to vent the sampling system.
13. Identify the components of interest by comparing the resultant chromatogram to the Typical Chromatogram (see Figure 3).

Calculations

Calculate the concentration of each sulfur species, as sulfur, in the LPG sample to the nearest 0.1 mass-ppm below 10 mass-ppm or to the nearest mass-ppm above 10 mass-ppm using the following formula:

$$V = GQ \quad (2)$$

where:

- G** = peak area of the specific sulfur species in the sample
- Q** = previously defined, Eq. 1, mass-ppm/area count
- V** = concentration of sulfur compound as sulfur, mass-ppm S

To calculate the total sulfur concentration of the analytical sample use equation 3:

$$T = \sum V \quad (3)$$

where:

- T** = total concentration of sulfur in sample, mass-ppm S
- V** = previously defined, Eq. 2

After the total sulfur is calculated by GC, a total sulfur value must be obtained by D6667 or equivalent method. The total sulfur values must match within 10% relative of each other. If greater deviations occur reanalyze the sample. If problems persist, initiate troubleshooting procedures as per manufacturers directions.

Precision

Precision statements were determined on the Agilent Model 355 SCD detector using UOP Method 999, "Precision Statements in UOP Methods." It is expected that equivalent or newer SCD detectors will have similar precision, but has not been tested.

Repeatability

Based on two tests performed by each of two analysts on each of two different days (8 tests), the within-laboratory estimated standard deviations (esd) were calculated for components at specific concentrations and are listed in Table 2. Two tests performed in one laboratory by different analysts on different days should not differ by more than the allowable differences in Table 2 at the concentrations listed (95% probability).

Table 2
Repeatability and Site Precision, mg/kg (mass-ppm)

<u>Sample</u>	<u>Component</u>	<u>Mean S</u> <u>Concentration</u>	<u>Repeatability</u>		<u>Site Precision</u>	
			<u>Within</u> <u>Day esd</u>	<u>Allowable</u> <u>Difference</u>	<u>Within</u> <u>Lab esd</u>	<u>Allowable</u> <u>Difference</u>
Sample A	Methyl Mercaptan	192	2.5	10	3.0	12
	Thiophene	64	0.3	1	0.4	2
	Total	980	3.6	14	3.8	15
Sample B	Carbon Disulfide	5.7	0.29	1.1	0.30	1.2
	N-butyl Mercaptan	1.4	0.07	0.3	0.09	0.4
	Total	25	0.9	3	1.2	5

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 1.0 hour. The labor requirement is 0.6 hour.

Suggested Suppliers

Agilent Technologies, 5301 Stevens Creek Blvd, Santa Clara, CA 95051, www.agilent.com (877-424-4536)

Matheson Trigas, 166 Keystone Dr. Montgomeryville, PA 18936, www.mathesongas.com (800-416-2505)

Restek, 110 Benner Circle, Bellefonte, PA 16823 www.restek.com (1-814-353-1300)

Swagelok, 1117 Blackhawk Road, Rock Island, IL 61201, www.swagelok.com (309-787-6800)

Valco Instruments Co., 8300 Waterbury, Huston, TX 77055, www.vici.com (800-367-8424)

VWR International, 800 East Fabyan Parkway, Batavia, IL 60510 www.vwr.com (800-932-5000)

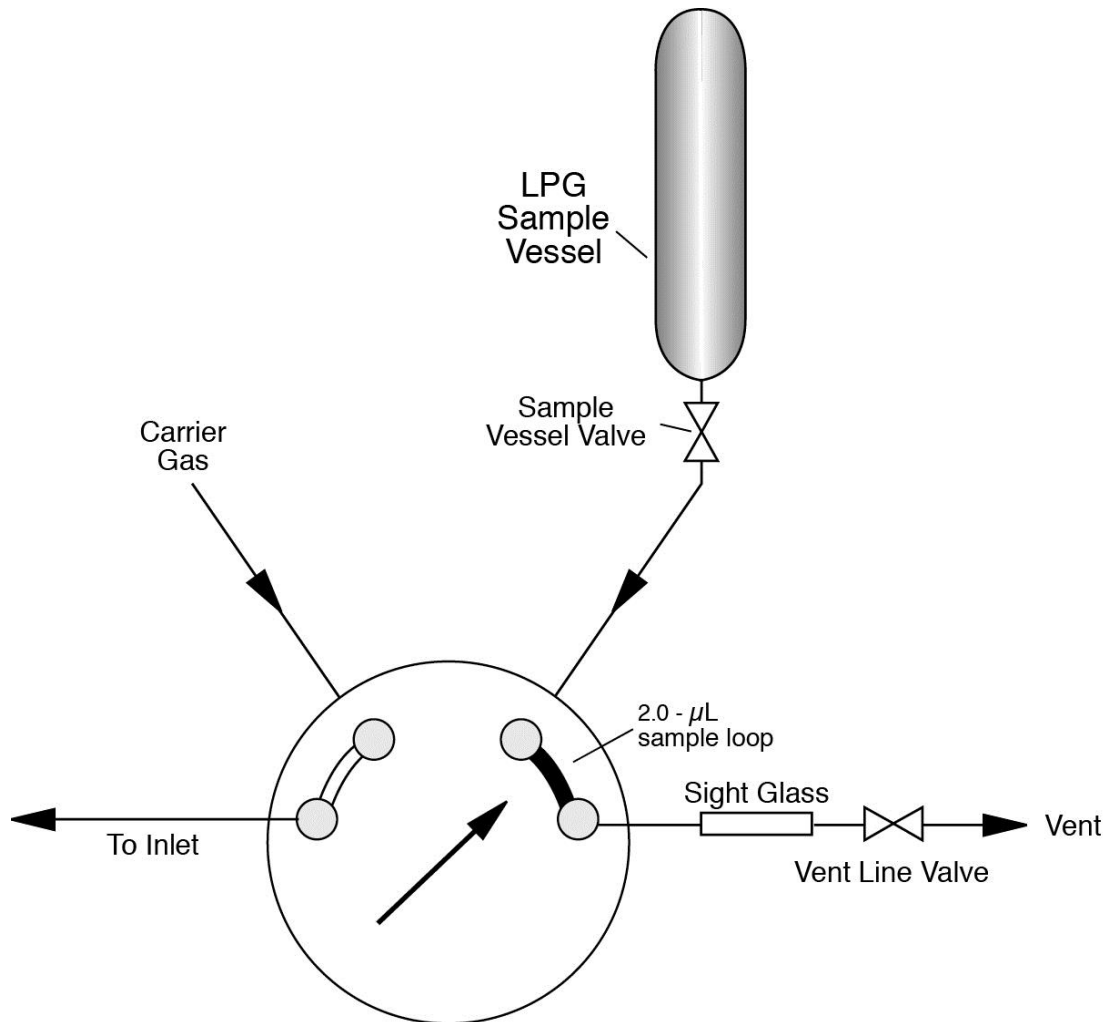


Figure 1
4 Port Valve Load position

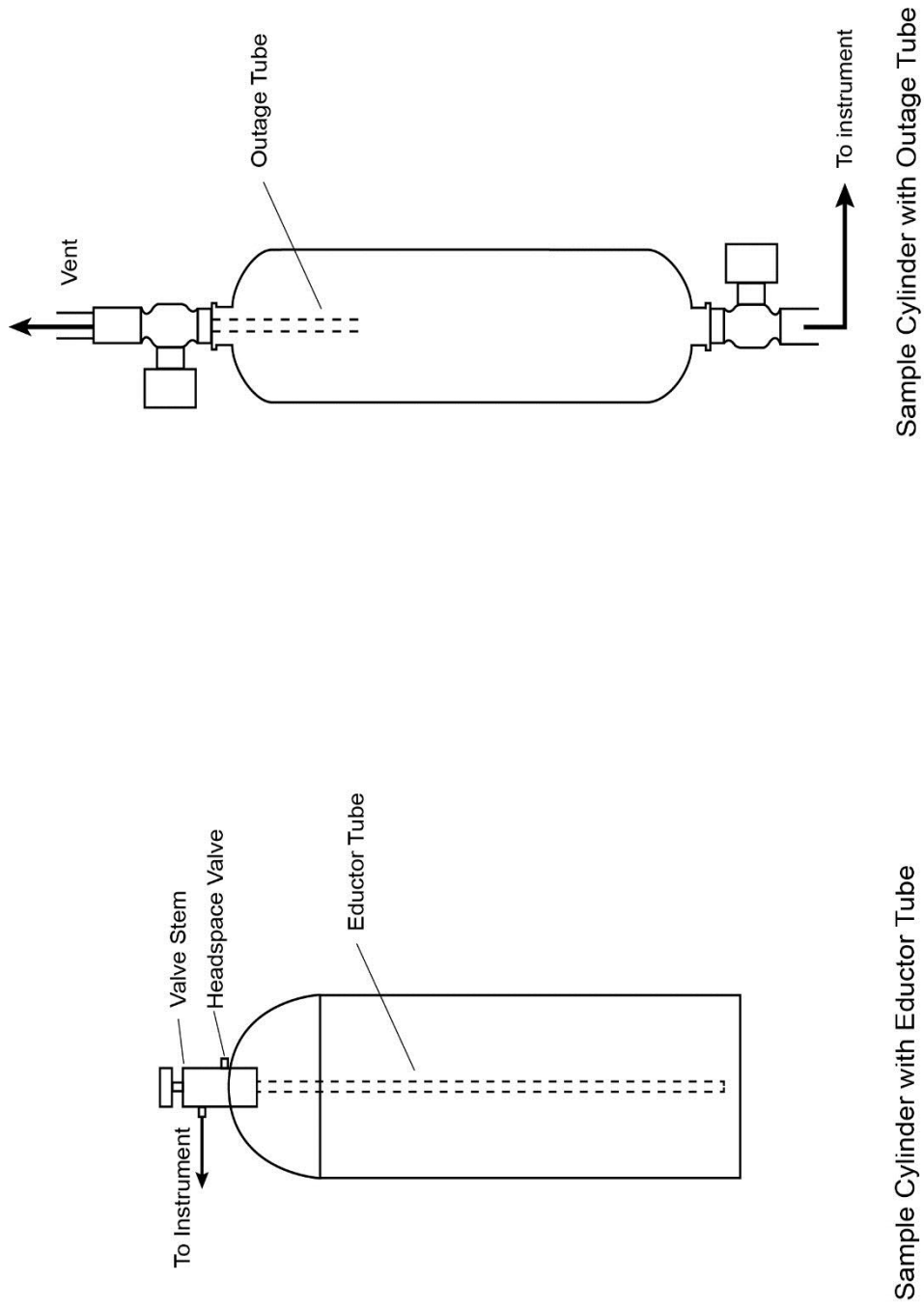


Figure 2
Common Sample Cylinder Diagrams

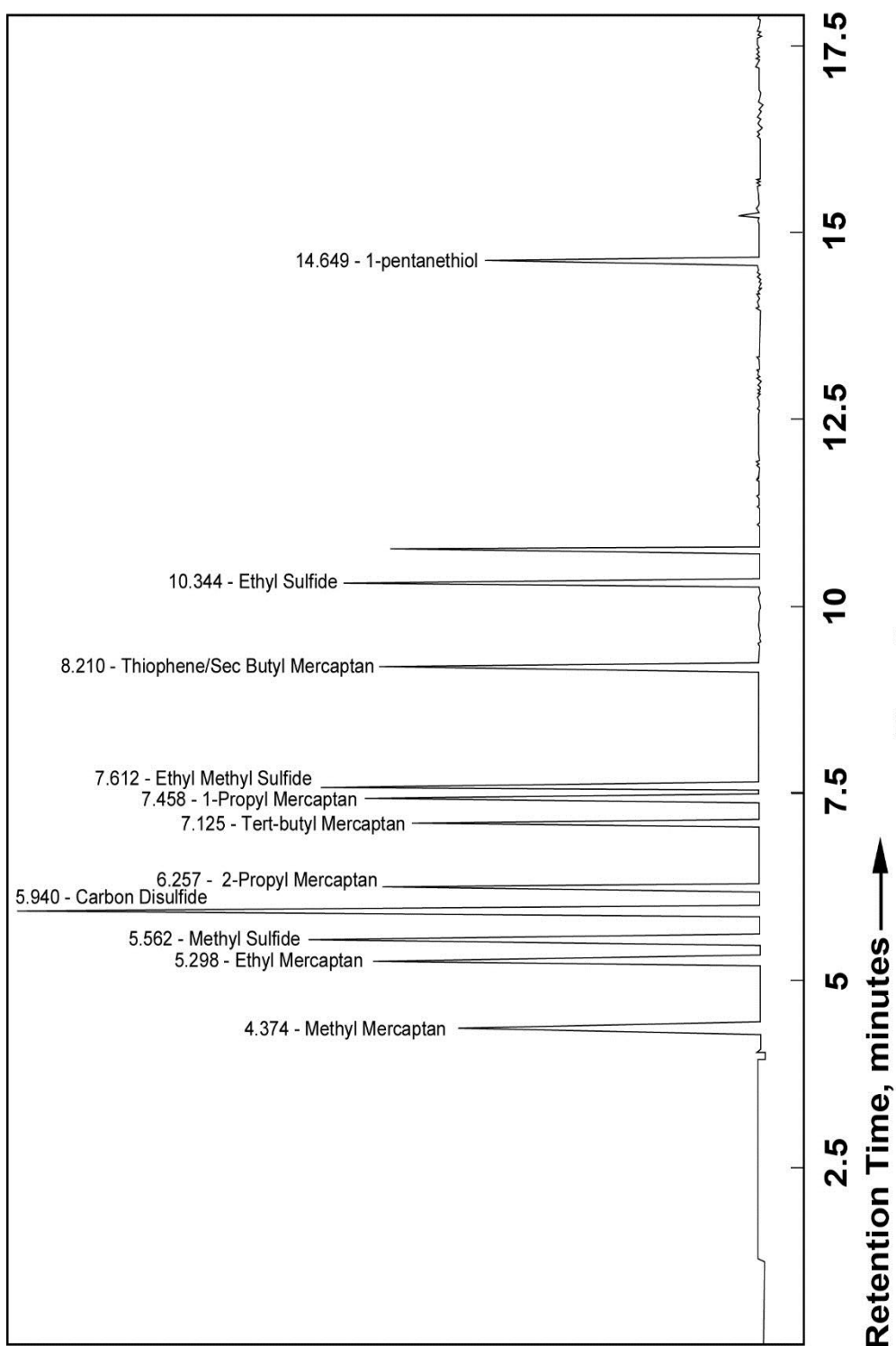


Figure 3
Typical Chromatogram