



Propane

Method number: PV2077

Target concentration: 1000 ppm (1800 mg/m³) OSHA TWA PEL

Procedure: Samples are collected by drawing a known volume of air through two Carbosieve S-III tubes in series. Samples are desorbed with carbon disulfide and analyzed by gas chromatography with a flame ionization detector.

Air volume and sampling rate studied: 50 minutes at 0.1 L/min (5 L)

Status of method: Partially validated method. This method has been only partially evaluated and is presented for information and trial use.

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Mary E. Eide

Solvents Branch
OSHA Salt Lake Technical Center
Salt Lake City UT-84115

1 General Discussion

1.1 Background

1.1.1 History of procedure

Propane has been monitored by combustible gas meter (Ref. 5.1). An attempt to collect propane in a gasbag showed a loss of propane from the gasbag atmosphere with time. The gasbag was stored at room temperature for 6 days, and showed an average 30.8% recovery. A solid sorbent tube would be convenient for the industrial hygienist, and allow for quantitation with confirmation. Two Carbosieve S-III tubes in series showed good desorption, retention and storage.

1.1.2 Potential workplace exposure (Ref. 5.2)

Propane is used as a household and industrial fuel. Propane is used in organic synthesis, the manufacture of ethylene, as an extractant solvent, refrigerant, gas enricher, an aerosol propellant, and in mixtures for bubble chambers.

1.1.3 Toxic Effects (This section is for information purposes and should not be taken as the basis for OSHA policy.) (Ref. 5.2)

Large quantities of propane in air can be an asphyxiant.

1.1.4 Physical properties (Ref. 5.2):

CAS:	74-98-6
IMIS:	2150
RTECS:	65285 (TX2275000)
DOT:	UN 1075; UN 1978
Molecular formula:	C ₃ H ₈
Molecular weight:	44.09
Freezing point:	- 188 °C
Boiling point:	- 42 °C
Explosive limits:	2.37-9.5% by volume
Flash point:	- 105 °C (- 156 °F)
Autoignition point:	467 °C (842 °F)
Odor:	odorless when pure
Color:	colorless gas
Synonyms:	dimethylmethane; propyl hydride

Structure:



1.2 Limit defining parameters

1.2.1 The detection limit of the analytical procedure is 4.7 µg/mL propane. This is the smallest amount that could be detected under the operating conditions used in this study.

1.2.2 The overall detection limit is 0.52 ppm based on a 5-liter air volume. All amounts in this study will be based on a 5-liter air volume.

1.3 Advantages

1.3.1 The sampling procedure is convenient.

- 1.3.2 The analytical method is reproducible and sensitive.
- 1.3.3 Reanalysis of samples is possible.
- 1.3.4 It may be possible to analyze other compounds at the same time.
- 1.3.5 Interferences may be avoided by proper selection of column and GC parameters.

1.4 Disadvantages

It is important to use two tubes in series. Both sections of the front tube are used to collect the propane efficiently near the PEL, and the second tube is used to monitor for breakthrough.

2 Sampling procedure

2.1 Apparatus

- 2.1.1 A calibrated personal sampling pump, the flow of which can be determined within $\pm 5\%$ at the recommended flow with the sample tubes in line.
- 2.1.2 Carbosieve S-III tubes, lot 728-39, containing 130-mg adsorbing section with a 65-mg backup section separated by silane treated glass wool, with a silane treated glass wool plug before the adsorbing section and after the backup section. The ends are flame sealed and the glass tube containing the adsorbent is 7-cm x 6-mm o.d. and 4-mm i.d., Supelco tubes (ORBO-91) or equivalent.

2.2 Sampling technique

- 2.2.1 The ends of the Carbosieve S-III tube are opened immediately before sampling.
- 2.2.2 Connect two Carbosieve S-III tubes in series and connect the second tube to the sampling pump with flexible tubing.
- 2.2.3 Tubes should be placed in a vertical position to minimize channeling, with the smaller sections towards the pump.
- 2.2.4 Air being sampled should not pass through any hose or tubing before entering the first adsorbent tube.
- 2.2.5 Separate and seal the Carbosieve S-III tubes with plastic caps immediately after sampling. Seal each sample lengthwise with Form OSHA-21 seal.
- 2.2.6 With each batch of samples, submit at least one blank tube from the same lot used for samples. This tube should be subjected to exactly the same handling as the samples (break ends, seal, & transport) except that no air is drawn through it.
- 2.2.7 Transport the samples (and corresponding paperwork) to the lab for analysis.
- 2.2.8 Bults, if submitted for analysis, must be shipped in a separate container from the samples.

2.3 Desorption efficiency

Six tubes were vapor spiked at each loading of 0.793 mg (88.0 ppm), 1.59 mg (176 ppm), 3.97 mg (440 ppm), 7.96 mg (883 ppm), and 15.92 mg (1770 ppm) propane. They were allowed to equilibrate overnight at room temperature. They were opened; each section placed into a

separate 2-mL vial, desorbed with 1 mL of the desorbing solution, for 30 minutes with occasional shaking, and then analyzed by GC-FID. The overall average was 105% (Table 2.3).

There seems to be some adsorption of the carbon disulfide onto the Carbosieve S-III, concentrating the solutions, resulting in desorption greater than 100%. A phase equilibrium study showed the same adsorption of carbon disulfide. A solution of 15.9 mg/mL propane in carbon disulfide was prepared. Three phase equilibrium samples were prepared by adding 1 mL of this solution to 130 mg of Carbosieve S-III, allowed to equilibrate for 30 minutes with occasional shaking, and analyzed, then comparing it to the original solution. The average recovery was 111%.

Table 2.3
Desorption Efficiency

Tube #	% Recovered				
	0.793 mg	1.59 mg	3.97 mg	7.96 mg	15.9 mg
1	93.9	102	108	108	113
2	92.5	102	103	110	110
3	lost	108	103	107	111
4	93.6	104	109	107	111
5	95.0	106	110	111	106
6	97.3	106	104	111	109
average	94.5	105	106	109	110

overall average 105%
standard deviation ± 6.57

2.4 Retention efficiency

Six tubes were vapor spiked with 15.9 mg (1770 ppm) propane, and allowed to equilibrate overnight. Breakthrough was measured by placing two Carbosieve S-III tubes in series, then three tubes had either 5 or 10 liters of humid air (91% RH) pulled through them. They were opened, desorbed, and analyzed by GC-FID. There was little or no propane found on the backup portions of the second tubes when 5 liters were drawn (Table 2.4). The retention efficiency averaged 102%.

Table 2.4
Retention Efficiency

liters drawn	% recovered			total
	front tube	'A'	second tube 'B'	
5	85.3	17.9	0.0	103
5	86.9	15.2	0.3	102
5	82.8	16.8	0.0	99.6
10	61.0	33.4	6.1	101
10	67.4	30.4	4.9	103
10	60.3	34.4	7.8	103

average = 102%

2.5 Storage

Carbosieve S-III tubes were spiked with 7.93 mg (883 ppm) propane and stored at room temperature until opened and analyzed. The recoveries averaged 98.1% for the 15 days stored (Table 2.5). The recoveries in Table 2.5 were desorption corrected.

Table 2.5
Storage Study

Day	% Recovered
7	96.0
7	97.9
7	97.0
15	96.5
15	97.1
15	104
average	98.1%

2.6 Precision

The precision was calculated using the area counts from six injections of each standard at concentrations of 0.793, 3.97, 7.93, and 15.9 mg/mL propane in carbon disulfide with 1 µL/mL p-cymene internal standard. The pooled coefficient of variation was 0.0154 (Table 2.6).

Table 2.6
Precision Study

Injection Number	0.793 mg/mL	3.97 mg/mL	7.93 mg/mL	15.9 mg/mL
1	34251	156694	284556	582670
2	32798	157806	283500	574057
3	33030	155915	283818	591181
4	34753	155876	291500	590488
5	33462	158726	290040	585300
6	34554	156619	290674	578308
average	33808	156939	287348	583667
Standard Deviation -	824	1121	3758	6749
CV -	0.0244	0.000714	0.0131	0.0116

pooled CV = 0.0154

Where:

$$CV \text{ (Coefficient of Variation)} = \frac{(\text{standard deviation})}{(\text{average})}$$

$$\text{Pooled CV} = \sqrt{\frac{A1(CV1)^2 + A2(CV2)^2 + A3(CV3)^2 + A4(CV4)^2}{A1 + A2 + A3 + A4}}$$

A1, A2, A3, A4 = number of injections at each level
CV1, CV2, CV3, CV4 = Coefficient of variation at each level

2.7 Air volume and sampling rate studied

2.7.1 The air volume studied is 5 liters.

2.7.2 The sampling rate studied is 0.1 liters per minute.

2.8 Interferences

Suspected interferences should be listed on sample data sheets.

2.9 Safety precautions

2.9.1 Sampling equipment should be placed on an employee in a manner that does not interfere with work performance or safety.

2.9.2 Safety glasses should be worn at all times.

2.9.3 Follow all safety practices that apply to the workplace being sampled.

3 Analytical method

3.1 Apparatus

3.1.1 Gas chromatograph equipped with a flame ionization detector. A Hewlett-Packard 5890 gas chromatograph was used in this study.

3.1.2 GC column capable of separating the analyte and an internal standard from any interference. The column used in this study was a 60-m x 0.32 mm (1.0 μ m d_i DB-5) capillary column.

3.1.3 An electronic integrator or some other suitable method of measuring peak areas.

3.1.4 Two milliliter vials with PTFE-lined caps.

3.1.5 A 1- μ L syringe or other convenient size for sample injection.

3.1.6 A 1000- μ L gas-tight syringe for standard preparation.

3.1.7 Pipettes for dispensing the desorbing solution. The Glenco 1-mL dispenser was used in this method.

3.1.8 Volumetric flasks, 5-mL, and other convenient sizes for preparing standards.

3.2 Reagents

3.2.1 Purified GC grade nitrogen, hydrogen, and air.

3.2.2 Propane gas, Reagent grade.

3.2.3 Carbon disulfide, Reagent grade.

3.2.4 p-Cymene, Reagent grade.

3.2.5 The desorbing solution is prepared by adding 250 μ L p-cymene to 1 liter of carbon disulfide to obtain a concentration of 0.25 μ L/mL p-cymene in carbon disulfide. The p-cymene is used as the internal standard.

3.3 Sample preparation

3.3.1 Sample tubes are opened and the front and back section of each tube are placed in separate 2-mL vials.

- 3.3.2 Each section is desorbed with 1 mL of the desorbing solution.
- 3.3.3 The vials are sealed immediately and allowed to desorb for 30 minutes with occasional shaking.

3.4 Standard preparation

- 3.4.1 Standards are prepared by diluting a known quantity of propane with the desorbing solution. A standard of 1000 µL/mL propane in the desorbing solution at 664 mmHg and 23 °C would be 1.59 mg/mL. This was calculated as follows:

$$\mu\text{g} / \text{mL} = \frac{(\mu\text{L gas})(\text{pressure})(298\text{ }^\circ\text{K})(\mu\text{mole})(\text{MW gas})}{(\text{mL desorbing solution})(760\text{ mm})(273\text{ }^\circ\text{K} + \text{temp. }^\circ\text{C})(24.46)(\mu\text{mole})}$$

Where:

µL gas = volume of gas added to standard (1000 µL)
 Pressure = atmospheric when standard was made (664 mmHg)
 760 mm = 1 atmosphere pressure
 Temp °C = room temperature when standard was made (23 °C)
 24.46 = Molar volume (liters/mole) of standard at 25 °C and 760 mmHg
 MW = molecular weight of gas (44.09 g/mole)

$$\text{ppm} = \frac{(\mu\text{g} / \text{mL})(\text{DV})(24.46)}{(\text{L})(\text{DE})(\text{MW})}$$

Where:

µg/mL = concentration of analyte in sample
 24.46 = Molar volume (liters/mole) at 25 °C and 760 mmHg
 MW = Molecular weight (g/mole)
 DV = Desorption volume, mL
 5 L = Air volume, L
 DE = Desorption efficiency, decimal

- 3.4.2 At least two separate standards should be made. A separate larger standard should be prepared to check the linearity of the response for propane.

3.5 Analysis

- 3.5.1 Gas chromatograph conditions.

<u>Flow rates</u>	<u>(mL/min)</u>	<u>Temperature</u>	<u>(°C)</u>
Nitrogen (makeup):	24	Injector:	180
Hydrogen (carrier):	1	Detector:	220
Air:	240	Column:	150
Hydrogen (detector):	30		
<u>Injection size:</u>	1 µL		
<u>Elution time:</u>	4.486 min.		

Chromatogram:

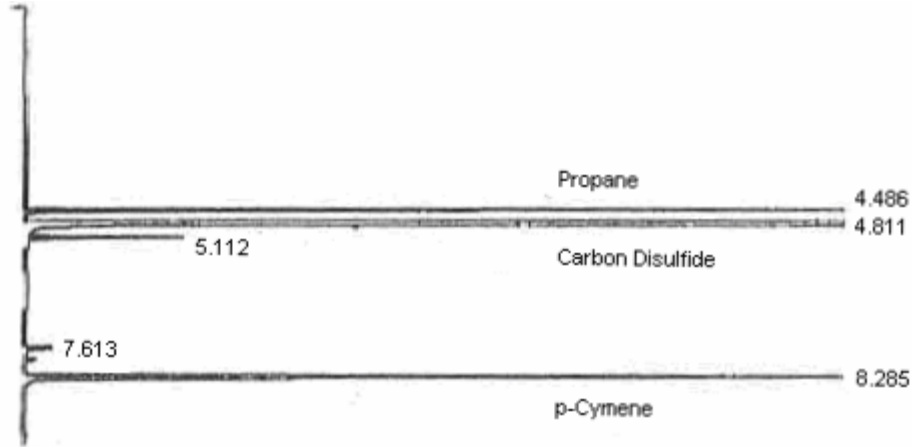


Figure 1. A standard of 1.59 mg/mL propane in carbon disulfide with 0.25 μ L/mL p-cymene internal standard.

3.5.2 Peak areas are measured by an integrator or other suitable means.

3.6 Interferences (analytical)

3.6.1 Any compound having the general retention time of the analyte or the internal standard used is interference. Possible interferences should be listed on the sample data sheet. GC parameters should be adjusted, if necessary, so these interferences will pose no problems.

3.6.2 Retention time data on a single column is not considered proof of chemical identity. Samples over the target concentration should be confirmed by GC/Mass Spec or other suitable means.

3.7 Calculations

3.7.1 A curve with area counts versus concentration is calculated from the calibration standards.

3.7.2 The area counts for the samples are plotted on the calibration curve to obtain the concentration of propane in solution.

3.7.3 To calculate the concentration of analyte in the air sample the following formulas are used:

$$\text{mass of analyte, } \mu\text{g} = \frac{(\mu\text{g} / \text{mL})(\text{desorption volume, mL})}{(\text{desorption efficiency, decimal})}$$

$$\text{moles of analyte} = \frac{(\text{mass of analyte, } \mu\text{g})(1\text{g})}{(\text{molecular weight})(10^6 \mu\text{g})}$$

$$\text{volume of analyte} = (\text{moles of analyte})(\text{molar volume})$$

$$ppm = \frac{(volume\ of\ analyte)(10^6)^*}{(air\ volume,\ L)}$$

* All units must cancel.

3.7.4 The above equations can be consolidated to form the following formula. To calculate the ppm of analyte in the sample based on a 5-liter air sample:

$$ppm = \frac{(\mu g / mL)(DV)(24.46)}{(L)(DE)(MW)}$$

Where:

$\mu g/mL$ = concentration of analyte in sample
 24.46 = Molar volume (liters/mole) at 25 °C and 760 mmHg
 MW = Molecular weight (g/mole)
 DV = Desorption volume, mL
 5 L = Air volume, L
 DE = Desorption efficiency, decimal

3.7.5 This calculation is done for each section of the sampling tube and the results added together.

3.8 Safety precautions

3.8.1 All handling of solvents should be done in a hood.

3.8.2 Avoid skin contact with all solvents.

3.8.3 Wear safety glasses at all times.

4 Recommendations for further study

Collection studies from a dynamic atmosphere need to be performed. Another desorbing solvent needs to be found that will not adsorb to the sampling media.

5 References

- 5.1 "NIOSH Manual of Analytical Methods", U.S. Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Second Edition, Vol. 2, Method S-87.
- 5.2 Sax, N., Lewis, R., "Hawley's Condensed Chemical Dictionary," Eleventh Edition, Van Nostrand Reinhold Co., New York, 1987, p. 969.