



## Standard Test Method for Trace Carbonyl Sulfide in Propylene by Gas Chromatography<sup>1</sup>

This standard is issued under the fixed designation D 5303; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

<sup>ε1</sup> NOTE—Warning notes were editorially moved into the standard text in March 2003.

### 1. Scope

1.1 This test method covers the determination of traces of carbonyl sulfide (COS) in propylene. It is applicable to COS concentrations from 0.5 to 4.0 mg/kg (parts per million by mass). See Note 1.

NOTE 1—The lower limit of this test method is believed to be below 0.1 mg/kg, depending on sample size and sensitivity of the instrumentation being used. However, the cooperative testing program was conducted in the 0.5 to 4.0 range due to limitations in preparing commercial test mixtures.

1.2 The values stated in SI units are to be regarded as the standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific precautionary statements are given in Section 8.

### 2. Referenced Documents

#### 2.1 ASTM Standards:

D 3609 Practice for Calibration Techniques using Permeation Tubes<sup>2</sup>

D 4468 Test Method for Total Sulfur in Gaseous Fuels by Hydrogenolysis and Rateometric Colorimetry<sup>3</sup>

E 840 Practice for Using Flame Photometric Detectors in Gas Chromatography<sup>4</sup>

### 3. Summary of Test Method

3.1 A procedure is given for removing a sample from the sample cylinder, separating COS from propylene, detecting

COS, calibrating the detector, quantitating COS content in the sample, and assaying the gas standard. General comments and recommended techniques are given.

3.2 A relatively large volume of sample is injected into a gas chromatograph having a single packed column, operated isothermally at 10 to 50°C, that separates COS from propylene. COS is detected with a flame photometric detector.

3.3 Calibration data, based on peak areas, are obtained using a known gas standard blend of COS in the range expected for the sample. The COS peak area in the sample is measured and the concentration of COS calculated.

3.4 The COS gas standard blend is assayed prior to use for calibration.

### 4. Significance and Use

4.1 In processes producing propylene, COS usually remains with the C<sub>3</sub> hydrocarbons and must be removed, since it affects product quality. COS acts as a poison to commercial polymerization catalysts, resulting in deactivation and costly process downtime.

4.2 Accurate gas chromatographic determination of trace COS in propylene involves unique analytical problems because of the chemical nature of COS and idiosyncracies of trace level analyses. These problems result from the reactive and absorptive nature of COS, the low concentration levels being measured, the type of detector needed, and the interferences from the propylene sample matrix. This test method addresses these analytical problems and ways to properly handle them to assure accurate and precise analyses.

4.3 This test method provides a basis for agreement between two laboratories when the determination of trace COS in propylene is important. The test method permits several calibration techniques. For best agreement between two labs, it is recommended that they use the same calibration technique.

### 5. Interferences

5.1 Hydrogen sulfide (H<sub>2</sub>S) or sulfur dioxide (SO<sub>2</sub>) can be present in the propylene and must be separated from COS. (See Note 2.)

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.D0.03 on Propylene.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 11.03.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 05.06.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 03.06.

NOTE 2—H<sub>2</sub>S and SO<sub>2</sub> are separated from COS with the Carbo-pack BHT 100 columns or with the Chromosil 300 column.

## 6. Apparatus

6.1 *Gas Chromatograph*—Any gas chromatograph (GC) equipped with a flame photometric detector/electrometer system (FPD), as described in 6.2, may be used. A GC/FPD equipped with an output signal linearizer is also permitted.

6.2 *Detector System*, flame photometric detector, either single or dual burner design. Noise level must be no more than one recorder chart division (see 6.5). The signal for COS must be at least twice the noise level at the 0.1 mg/kg level. A discussion of this detector is presented in Practice E 840. The electrometer used with the detector must have a sensitivity of 10<sup>-12</sup> A full scale on a 1 mV recorder to achieve optimum detectability at lowest levels.

6.3 *Column*—Any column that will effect the complete separation of COS from propylene and other compounds normally present in propylene concentrates, and that is sufficiently inert to preclude the loss of COS, may be used. Columns that meet these criteria, and that were used in the cooperative study for this test method, are listed in Table 1.

6.4 *Sample Inlet System*—Any gas sampling valve or gas tight syringe that will permit introduction of up to 5.0 mL to the column, and that will not cause any loss of COS, is suitable.

6.5 *Recorder*—Any strip chart recorder with a full scale range of 1 mV, a maximum full scale balance time of 2 s, and a minimum chart speed of 0.5 cm/s, may be used.

6.6 *Data Handling System*—Any commercially available GC integrator or GC computer system capable of accurately integrating the area (uVs) of the COS peak is satisfactory. Data systems that will linearize the logarithmic output of the FPD are also satisfactory.

6.7 *Sample Cylinders*, 300 mL capacity or larger, fluorocarbon lined stainless steel, Type DOT 3E, 12409 kPa (1800 psi) working pressure.

## 7. Reagents and Materials

7.1 *Air*, zero grade.

7.2 *Carbonyl sulfide (COS)*, lecture bottle, 97.5 % min. (**Warning**—Toxic! See Section 8, Hazards.)

7.3 *Gas Calibration Blends*, 1 to 10 mg/kg COS in either nitrogen, argon, propylene or a propylene/argon mixture. They can be obtained from any commercial supplier or prepared as shown in Appendix X1 or Test Method D 4468.

7.4 *Gas Sampling Syringe*, 0.1, 1.0, and 5.0 mL.

7.5 *Gas Sampling Valve and Sample Loops*, fluorocarbon or 316 stainless steel. See Footnote B of Table 1.

7.6 *Glass Vials*, 125 cm.

7.7 *Hydrogen*, pure grade, 99.9 %.

7.8 *Isooctane* (2,2,4-trimethylpentane), sulfur free, minimum purity 99 mol %. (**Warning**—Flammable! Health Hazard.)

7.9 *Nitrogen or helium*, 99.999 % min.

7.10 *TFE-fluorocarbon septa and aluminum seals for vials*.

## 8. Hazards

8.1 Carbonyl sulfide is toxic and narcotic in high concentrations, and upon decomposition can liberate hydrogen sulfide. Exposure to dangerous concentrations of COS is most likely when handling the pure component for preparation of standard blends for assaying the COS calibration gas standards.

## 9. Sampling

9.1 Supply samples to the laboratory in high pressure cylinders coated internally with TFE-fluorocarbon, or otherwise specially treated to reduce or eliminate loss of COS due to reaction with the cylinder walls.

9.2 The sample cylinder and contents should be at room temperature prior to sampling to the chromatograph. Test samples as soon as possible after receipt.

NOTE 3—Cooperative studies indicate that the measured value for COS will decrease with time.

9.3 Place the sample cylinder in a vertical position and use either of the following two techniques to obtain a vaporized sample from the container for introduction into the GC.

9.3.1 Connect the sample cylinder to the sampling valve on the chromatograph, using a minimum length of 316 ss tubing, so that sample is withdrawn from the bottom of the cylinder. Adjust the flow rate from the sample cylinder so that complete vaporization of the liquid occurs at the cylinder valve. A flow rate of 5 to 10 bubbles/s through a water bubbler placed at the sample vent is sufficient (see Note 4). Turn the sampling valve to the “flush” position and flush for approximately 15 s. Shut off the cylinder valve and allow the pressure to drop to atmospheric.

NOTE 4—If the flow rate is too fast, warming of the valve can be required to avoid freezing and to ensure complete vaporization of the sample.

9.3.2 Alternatively, obtain a sample with a gas tight syringe. A convenient way to do this is to use flexible plastic tubing to connect the bottom of the sample cylinder to the water bubbler and then to pierce the tubing with the syringe needle after flow is established.

TABLE 1 Suitable GC Columns and Temperatures<sup>A</sup>

Column Number	Size, m × mm	Tubing <sup>B</sup> Type	Packing and Oven Temperature, °C
1	0.9 × 3.78	SS	Porapak R, 80/100 Mesh; 47
2	1.4 × 3.78	TFE <sup>C</sup>	Carbopack BHT 100, 40/60 Mesh; 25,40 <sup>D</sup>
3	1.8 × 3.78	TFE	Carbopack BHT 100; 25,30 <sup>D</sup>
4	1.8 × 3.78	TFE	Porapak Q, AW, 50/80 Mesh (Above in Series); 74
5	2.4 × 3.78	SS	Carbopack BHT 100; 47
6	2.8 × 3.78	TFE	Carbopack BHT 100, 40/60 Mesh; 50
7	3.6 × 3.78	TFE	Carbopack BHT 100, 40/60 Mesh; 50
8	4.3 × 3.78	TFE	Chromosil 300; 50 <sup>E</sup>
9	6.1 × 3.78	TFE	Hayes Sep Q, 80/100 Mesh; 65

<sup>A</sup> These columns have been tested cooperatively and found suitable for use with this test method.

<sup>B</sup> 316 SS Tubing for columns or connection of sample cylinder to sampling system can be TFE lined internally to improve on system stability. This tubing is commercially available from chromatography vendors.

<sup>C</sup> TFE—Homopolymer of tetrafluoroethylene.

<sup>D</sup> Identical columns used by different labs at different temperatures.

<sup>E</sup> Propyne (methyl acetylene) can interfere with COS using this column.

## 10. Preparation of Apparatus

10.1 Install in the GC according to the manufacturer's instructions any of the columns that meet the criteria in 6.3. Set the instrument conditions as follows:

- 10.1.1 *Oven Temperature*, as determined by column used,
- 10.1.2 *Detector*, 100 to 200°C, and
- 10.1.3 *Injector*, 100 to 150°C.

## 11. Calibration

11.1 Three methods of calibration are permitted. These are the Standard Sample Method (see 11.2), the Permeation Tube Method (see 11.3) and Blend Preparation Techniques (see 11.4). Obtain a calibration standard according to one of these methods, which are described below. Then follow the procedure in 12.1-12.4 and the calculations described in 11.5.

11.2 *Standard Sample Method*—Purchase a certified commercial calibration sample of 10 mg/kg COS in propylene, or other suitable matrix gas such as nitrogen, argon, or a propylene/argon mixture. If an inert gas is chosen, the user must ensure that the column is actually effecting a separation of COS and propylene. Establish a calibration curve with the standard sample using either a gas syringe or different size sample loops. For example, assume the normal sample size for the analysis is 1.0 mL and the calibration range to be established is 0.5 to 5 mg/kg of COS. Establish a calibration curve by injecting the volumes of a 10 mg/kg standard sample shown in the first column of the table below. The equivalent concentration of COS in a 1.0 mL sample would be that shown in the second column:

Standard Sample	Equivalent Concentration, COS mg/kg
0.05	0.5
0.10	1.0
0.20	2.0
0.30	3.0
0.40	4.0
0.50	5.0

11.3 *Permeation Tube Method*—Refer to Practice D 3609 for directions on using permeation tubes.

11.4 *Blend Preparation Techniques*—Techniques for the preparation and assay verification of calibration blends in the laboratory are described in Appendix X1 and Appendix X2. Also, a technique using a moving piston graduated cylinder apparatus, that is described in the calibration section of Test Method D 4468, can be used. However, some laboratories have found that the preparation of such blends is far from easy, and successful efforts require considerable knowledge and experience.

11.5 *Quantitation*—The flame photometric detector responds logarithmically to the mass of the sulfur present in the flame. Some GC/FPD systems are programmed to linearize logarithmic data, and with such systems the output can be correlated directly with the COS concentration, using a single point calibration. Calculate a calibration factor,  $F$ , in accordance with (Eq 1) below:

$$F = C/A \quad (1)$$

where:

- $F$  = calibration factor,
- $C$  = concentration, mg/kg, of COS in this test method, and

$A$  = area (uVs) of the COS peak in this test method.

$F$  will be used in (Eq 2) in 13.1.1. However, if a linearizer is not used, or if the data system does not have a provision to handle logarithmic output, use the method in 11.5.1 or the alternate in 11.5.2, below:

11.5.1 Calculate the nanogram (ng) amounts of sulfur, as described in Appendix X3, for each injection of the standard, and plot the natural logarithm ( $ln$ ) of peak area versus the  $ln$  (ng) of sulfur, as illustrated in Table 2 and Fig. 1. The plot should be a straight line.

11.5.2 Alternatively, plot the concentration of COS in mg/kg versus the square root of the peak area. This plot should also be a straight line.

## 12. Procedure

12.1 Using either the gas sampling valve or a gas tight syringe, as described in 9.3, inject the sample into the gas chromatograph.

12.2 Record the response of the FPD on the strip chart recorder as the COS elutes from the column.

12.3 Alternatively, obtain the computer or integrator output of COS retention time and peak area.

12.4 Obtain duplicate chromatograms of the sample. Fig. 2 illustrates a typical analysis using a Carbo-pack BHT-100 column.

## 13. Calculation

13.1 Depending on the method of calibration used (see Section 11), determine the concentration of COS in the sample.

13.1.1 If the system provides a linearized output, determine COS concentration according to (Eq 2), below:

$$COS, \text{ mg/kg} = F \times S \quad (2)$$

where:

- $F$  = calibration factor from (Eq 1), and
- $S$  = area (uVs) of the COS peak from the sample.

13.1.2 If a calibration curve of  $ln$  peak area versus  $ln$  (ng) sulfur was used (see 11.5.1), then determine the concentration of COS as shown in Appendix X1.

TABLE 2 Example of COS Calibration Data<sup>A</sup>

NOTE—COS Standard (3.00 ng S/cm<sup>3</sup>).

Amount of Standard Injected (cm <sup>3</sup> )	Amount of Standard Injected (ng S)	$y^B$ (peak area units)
3.0	9.0	53
3.0	9.0	51
2.5	7.5	39
2.5	7.5	38
2.0	6.0	25
2.0	6.0	23
1.5	4.5	18
1.5	4.5	16
1.0	3.0	10
1.0	3.0	9
0.5	1.5	3
0.5	1.5	4

<sup>A</sup> Correlation coefficient of fit ( $r$ ) = 0.9952:  
 $m$  = slope (detector response factor) = 1.4920,  
 $y$  = peak area units,  
 $z$  = nanograms of sulfur as COS injected, and  
 $b$  = intercept = 1.8394.

<sup>B</sup> Calibration equation:  $y = bz^m$ .

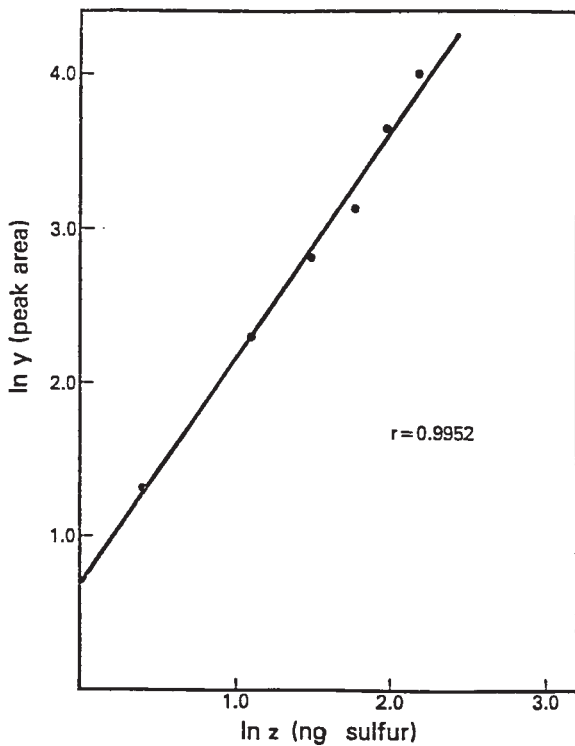
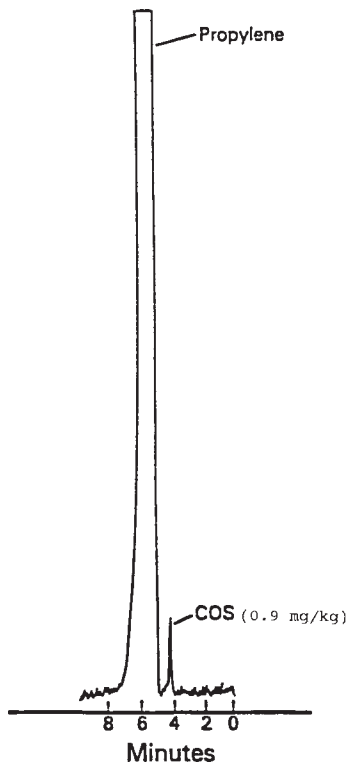


FIG. 1 COS Calibration Plot



NOTE—Carbopack BHT-100 column.

FIG. 2 Chromatogram of COS in Propylene

13.1.3 If a calibration curve of concentration versus log peak area was used (see 11.5.2), then determine the COS concentration as follows:

13.1.3.1 Calculate the log of the area of the COS peak of sample.

13.1.3.2 Take the COS concentration directly from the curve using the log value from 13.1.3.1.

NOTE 5—If a calibration method is used that gives results in  $\text{cm}^3/\text{m}^3$  (ppm by volume), such as that in Test Method D 4468, then results must be converted to mg/kg. Use the following formula to do this:

$$\text{COS, mg/kg} = B \times M1/M2 \quad (3)$$

where:

$B$  = COS,  $\text{cm}^3/\text{m}^3$ ,

$M1$  = mole weight, COS = 60.1, and

$M2$  = mole weight, propylene = 42.1.

#### 14. Precision and Bias

14.1 Precision—The precision of this test as determined by the statistical examination of interlaboratory test results is as follows:<sup>5</sup>

14.1.1 Repeatability—The difference between successive results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the long run, in the normal and correct operation of the test method exceed the following values only in one case in twenty (see table in 14.1.2):

$$\text{repeatability} = 0.15 X \quad (4)$$

where:

$X$  = the average of two results in mg/kg.

14.1.2 Reproducibility—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, exceed the following values only in one case in twenty (see table below):

$$\text{reproducibility} = 1.0 X \quad (5)$$

where:

$X$  = the average of two results in mg/kg.

Average Value mg/kg	Repeatability mg/kg	Reproducibility mg/kg
0.5	0.11	0.7
1.0	0.15	1.0
2.0	0.21	1.4
3.0	0.26	1.7
4.0	0.30	2.0

14.2 Bias—Since there is no acceptable reference material suitable for determining the bias for the procedure in this test method (D 5303) for measuring carbonyl sulfide, bias has not been determined.

#### 15. Keywords

15.1 carbonyl sulfide; flame photometric detector; gas chromatography; propylene

<sup>5</sup> Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR: D02-1298.

## APPENDIXES

### (Nonmandatory Information)

#### X1. PREPARATION OF A LIQUID ASSAY STANDARD

##### X1.1 Preparation Example:

X1.1.1 Pipet 100 mL isooctane ( $iC_8$ ) into the sample bottle and seal it with a septum and cap. Inject through the septum 0.5 mL COS. This standard contains 6.3 ng S/ $\mu$ L, as calculated below:

X1.1.2 Use the ideal gas law in the form  $P_1V_1/T_1 = P_2V_2/T_2$ . Assume ambient conditions: 30°C, 740 mm Hg. Weight of COS/ $iC_8$  solution = 69.2 g:

$$V_2 = \frac{P_1V_1T_2}{P_2T_1} = \frac{760 \text{ mmHg}}{740 \text{ mmHg}} \times \frac{22\,400 \text{ mL}}{\text{mol}} \times \frac{303 \text{ K}}{273 \text{ K}} = 25\,533 \text{ mL/mol} \quad (\text{X1.1})$$

$$\frac{60 \text{ g COS}}{\text{mol}} \times \frac{1 \text{ mol}}{25\,533 \text{ mL}} \times 0.5 \text{ mL COS}$$

$$= 1.175 \times 10^{-3} \text{ g COS} \\ = 0.63 \times 10^{-3} \text{ g S} \quad (\text{X1.2})$$

$$\frac{0.63 \times 10^{-3} \text{ g S}}{69.2 \text{ g}} = \frac{9.1 \times 10^{-6} \text{ g S}}{\text{g solution}} \quad (\text{X1.3})$$

$$\frac{9.1 \times 10^{-6} \text{ g S}}{\text{g solution}} \times \frac{0.6919 \times 10^{-3} \text{ g } iC_8}{\mu\text{L } iC_8} = \frac{6.30 \times 10^{-9} \text{ g S}}{\mu\text{L}} = 6.3 \text{ n S}/\mu\text{L} \quad (\text{X1.4})$$

X1.1.3 The sulfur concentration in the liquid standard may be cross-checked by microcoulometry, that determines total sulfur content.

#### X2. PREPARATION OF CALIBRATION GAS BLENDS

##### X2.1 Apparatus

- X2.1.1 *Bottles*, heavy wall, “soda pop” type, 980 mL.
- X2.1.2 *Crimp Caps*, drilled and fitted with a septum.
- X2.1.3 *Bottle Capper*.
- X2.1.4 *Manometer*.
- X2.1.5 *Magnetic Stirrer and Stirring Bars*.
- X2.1.6 *Gas Lock Syringe*.

##### X2.2 Reagents

- X2.2.1 *Carbonyl sulfide*.
- X2.2.2 *Hydrogen sulfide*.
- X2.2.3 *Propylene*, reagent grade.

##### X2.3 Procedure

X2.3.1 Cap a 980 mL bottle containing a stirring bar, and purge with propylene for 20 min at a rate of 500 mL/min.

X2.3.2 Pressurize to 10 psig with propylene.

X2.3.3 Place on stirrer, transfer (by use of gas lock syringe) 1 mL of neat COS. Allow to stir for 5 min.

X2.3.4 Prepare a second bottle in the same manner as in X2.3.1-X2.3.3, except that instead of COS a 1 mL portion of the first blend is added by means of a syringe. This yields a standard gas blend of 0.527 mg/kg.

X2.3.5 Blends of varying concentrations of COS in propylene can be made in the same manner, by varying the amount of the primary blend used in making the final calibration blend.

#### X3. CALCULATION FOR SULFUR CONTENT OF STANDARD

X3.1 *Sample Calculation*—For ng S/mL as COS: assume the calibration equation is as follows:

$$y = 1.8394 z \quad (\text{X3.1})$$

for range of  $y$  values 3 to 53 (refer to Table 2), and 5 mL of a propylene sample gives a COS peak area of 29 units. Therefore:

$$29 = 1.8394 z \quad (\text{X3.2})$$

where:

$$z = 6.35 \text{ ng S}/5 \text{ mL} = 1.27 \text{ ng S}/\text{mL of sample.}$$

X3.2 This corresponds to 1.44 mg/kg ( $w/w$ ) COS as calculated below:

*Basis:*

$$\text{pure propylene, mol wt.} = 42.1 \text{ g/mol} \quad (\text{X3.3})$$

$$\text{ambient condition: } 740 \text{ mm Hg, } 30^\circ \text{ C}$$

$$\text{sulfur analysis: } 1.27 \text{ ng S}/\text{mL} = 2.38 \text{ ng COS}/\text{mL}$$

$$\text{wanted: mass of } 1 \text{ mL propylene}$$

Use ideal gas law:

where:

$$PV = nRT = (\text{grams}/\text{MW}) \times RT$$

$$P = \text{pressure in atmospheres,}$$

$$V = \text{volume in mL,}$$

$$MW = \text{molecular weight of propylene in g/mol,}$$

$$R = \text{gas constant} = 82.05 \text{ mL atm}/^\circ \text{ K mol,}$$

$$T = \text{temperature in } ^\circ \text{ Kelvin} = 303, \text{ and}$$



$$\text{grams} = \frac{PV(MW)}{RT} : \quad (X3.4)$$

$$\text{mg/kg COS} = \frac{2.38 \times 10^{-9} \text{ g COS}}{1.65 \times 10^{-3} \text{ g}} = 1.44 \times 10^{-6} \times 10^6 = 1.44 \quad (X3.5)$$

$$= \frac{\frac{(740 \text{ mm Hg})}{760} (1 \text{ mL}) (42.1 \text{ g/mol})}{\frac{(82.05 \text{ mL atm})}{K \text{ mol}} (303 \text{ K})} = 1.65 \times 10^{-3} \text{ g} \quad (X3.4)$$

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