

SEMI C3.6-0701

SPECIFICATION FOR PHOSPHINE (PH₃) IN CYLINDERS, 99.98% QUALITY

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1 Description

1.1 Phosphine is a highly toxic, flammable, colorless gas with an odor of decaying fish. In high concentrations, it is pyrophoric. It is shipped as a liquid in cylinders under its own vapor pressure.

2 Specifications

QUALITY: 99.98%

Impurities	Maximum Acceptable Level (ppm)*
Arsine (AsH ₃)	10
Carbon dioxide (CO ₂)	10
Carbon Monoxide (CO)	1
Heavy Metals	**
Hydrogen (H ₂)	100
Nitrogen (N ₂)	50
Oxygen (O ₂) + Argon (Ar)	5
Particles	**
Hydrocarbons expressed as Methane (C ₁ -C ₂)	4
Water (H ₂ O) (v/v)	1
TOTAL LISTED IMPURITIES	181

* An analysis of significant figures has not been considered. The number of significant figures will be based on analytical accuracy and the precision of the provided procedure.

** To be determined between supplier and user.

3 Physical Constants (for information only)

	Metric Units	US Units
Molecular weight	33.997	33.997
Boiling point at 1 atm	-87.7°C	-125.9°F
Density of gas at 25°C (77°F) and 1 atm	1.402 kg/m ³	0.0875 lb/ft ³
Specific gravity of gas at 21.1°C (70°F) and 1 atm (air = 1)	1.146	1.146
Density of liquid at boiling point	744 kg/m ³	46.45 lb/ft ³

4 Analytical Procedures

4.1 Carbon Monoxide, Carbon Dioxide, and Hydrocarbons (expressed as methane) — This procedure is for the determination of carbon monoxide, carbon dioxide, and hydrocarbons in phosphine using a gas chromatograph with a methanizer and a flame ionization detector. (See Note 1 and Figure 1.)

4.1.1 Detection Limit — 0.1 ppm each impurity.

4.1.2 Instrument Parameters

4.1.2.1 Column — Porapak QS, 3.5 m (12 ft) by 3.2 mm (1/8 in) OD by 2.2 mm (0.085 in) ID ss or equivalent.

4.1.2.2 Carrier Flow — 35 mL/min helium.

4.1.2.3 Support Gases

Hydrogen: 30 mL/min added to the carrier gas between the column outlet and the methanizer inlet.

Air: 500 mL/min.

4.1.2.4 Temperatures:

Detector	110°C
Injector	40°C
Oven	40°C
Methanizer	370-400°C

4.1.2.5 Sample Volume — 3 mL.

4.1.3 Calibration Standards — 1-10 ppm each: carbon monoxide, carbon dioxide, methane, ethane*, ethylene*, and acetylene*, balance helium. *These components are for reference only.

4.1.4 Operating Procedure

4.1.4.1 Inject the calibration standard into the column using a gas sampling valve. Record retention times and peak areas. Order of elution is carbon monoxide, methane, carbon dioxide, acetylene, ethylene.

4.1.4.2 Inject the sample to be tested in the same manner as the calibration standard. Vent the phosphine after the ethylene peak. Record the retention times and peak areas.

4.1.4.3 Repeat 4.1.4.1.

4.1.4.4 Calculation of Concentrations

4.1.4.4.1 Carbon Monoxide and Carbon Dioxide — Compare the average peak areas for the calibration standard to those of the phosphine sample being tested. Calculate the concentration of each impurity, using the formula below. The results may not exceed the specification in Section 2 of this standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \text{Concentration of Standard} = \text{Concentration of Sample}$$

4.1.4.4.2 Total Hydrocarbons Expressed as Methane (C_1 - C_2) — Compare the peak area of methane in the calibration standard with the sum of the areas of the hydrocarbons detected in the phosphine sample. Calculate the concentration of total hydrocarbons using the formula below. The results may not exceed the specifications in Section 2 of this standard.

$$\frac{\frac{\text{Sum of areas for all Hydrocarbons detected}}{\text{Standard Peak Area for Methane}} \times \text{Concentration of Methane in Standard}}{\text{THC Concentration of Sample}}$$

4.2 Hydrogen, Nitrogen, and Oxygen + Argon, Arsine — This procedure is for the determination of hydrogen, nitrogen, oxygen + argon, and arsine in phosphine using a gas chromatograph with a discharge ionization detector. (See Note 2 and Figure 2.)

4.2.1 Detection Limits — 100 ppb (mol/mol) hydrogen, 100 ppb (mol/mol) oxygen + argon, 500 ppb (mol/mol) nitrogen, 5 ppm (mol/mol) arsine.

4.2.2 Instrument Parameters

4.2.2.1 Columns:

Column 1:	Porapak QS, 2.5 m (8 ft) by 3.2 mm (1/8 in) OD by 2.2 mm (0.085 in) ID ss or equivalent.
Column 2:	Molecular Sieve 5A, 3 m (10 ft) by 3.2 mm (1/8 in) OD by 2.2 mm (0.085 in) ID ss or equivalent.

4.2.2.2 Carrier Flow — 25 mL/min helium.

4.2.2.3 Temperatures

Detector	10°C
Injector	30°C
Oven	40°C

4.2.2.4 Sample Volume — 1 mL.

4.2.3 Calibration Standard — 5–50 ppm (mol/mol) nitrogen, 1–10 ppm (mol/mol) oxygen, 1–10 ppm (mol/mol) argon, 10–100 ppm (mol/mol) hydrogen, 5–10 ppm (mol/mol) arsine, balance helium.

4.2.4 Operating Procedure

4.2.4.1 Determination of the Switching Time — Inject the calibration sample in 4.2.3 above and note the time when the hydrogen peak appears through detector B. Switching valve 1 at that time will give an arsine peak through detector A and hydrogen, oxygen + argon, and nitrogen peaks through detector B.

4.2.4.2 Inject the calibration standard into the column using the same gas valve. Switch at the time determined in 4.2.4.1 and record retention times and peak areas. Order of elution is hydrogen, oxygen + argon, and nitrogen on detector B. Order of elution is phosphine and arsine on detector A.

4.2.4.3 Inject the sample being tested in same manner as the calibration standard. Record the retention times and peak areas.

4.2.4.4 Repeat 4.2.4.2.

4.2.4.5 Compare the average peak areas of the calibration standard to those of the phosphine sample being tested. Calculate the concentration of each impurity, using the formula below. The results may not exceed the specifications in Section 2 of this standard.

$$\frac{\text{Sample Peak Area}}{\text{Standard Peak Area}} \times \text{Concentration of Standard} = \text{Concentration of Sample}$$

4.3 Water — This procedure is for the determination of moisture in phosphine using continuous flow electrolysis of water in a phosphorous pentoxide (P_2O_5) cell, modified as per the manufacturer's recommendation, for use with phosphine.

4.3.1 Detection Limit — 0.5 ppm (vol/vol).

4.3.2 Instrument Parameters

4.3.2.1 Flow Requirements — Set the sample flow rate and pressure in accordance with manufacturer's instructions.

4.3.3 Calibration Standards — Construct a calibration curve which contains at least three points covering the range of interest. Verify the standards employed independently on a condensation dew point/frost point hygrometer. Standards are prepared in nitrogen.

4.3.4 Operating Procedure

4.3.4.1 Obtain representative sample of gas to analyze and direct to unit as with the standards.

4.3.4.2 Determine the moisture content in sample gas by comparing the indicated concentration with the calibration curve constructed in 4.3.4.1. The result may not exceed the specification in Section 2 of this standard.