CODE OF PRACTICE
PHOSPHINE

AIGA 051/20

(Revision of AIGA 051/08)

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As part of a program of harmonization of industry standards, the Asia Industrial Gases Association (AIGA) has published this publication AIGA 051, *Code of Practice Phosphine,* jointly produced by members of the International Harmonization Council and originally published by AIGA jointly with Japan Industrial and Medical Gasses Association (JIMGA) as T-S/37, *Code of Practice Phosphine.*

This publication is intended as an international harmonized publication for the worldwide use and application by all members of the International Harmonization Council whose members include the Asia Industrial Gases Association (AIGA), Compressed Gas Association (CGA), European Industrial Gases Association (EIGA), and Japan Industrial and Medical Gases Association (JIMGA). Each Regional association's technical content is identical, except for regional regulatory requirements and minor changes in formatting and spelling.

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1 Introduction

Phosphine is a toxic, colorless gas with an odor of decaying fish or more commonly like that of welding grade acetylene. It is shipped as a liquefied compressed gas under its own vapor pressure of 516 psi (3558 kPa). It is also supplied in a gaseous state, diluted with other gases under pressure. It is flammable, pyrophoric, and highly toxic.

The issue of the safe handling of phosphine is a very important and relevant topic to the compressed gas industry as well as the user community of this specialty gas.

Phosphine is used as a doping agent for silicon-based solid state electronic devices. It is thermally diffused into the silicon layer using furnaces or by an ion implantation system (n-type dopant). It is also used to manufacture compound semiconductors such as light-emitting diodes (LEDs) by reaction with a metal organic such as trimethyl gallium forming a gallium phosphide layer. Phosphine is also used in the semiconductor industry to grow a capping layer. Phosphine can be inadvertently generated in mining and manufacturing processes involving phosphorous compounds and paints and herbicides containing phosphorous compounds. Phosphine is also used as a fumigant for grain.

Phosphine can be safely handled if equipment is properly designed and maintained and employees are trained. As a minimum, all personnel shall have access to the phosphine safety data sheet (SDS) and training in the use of the SDS and other reference material.

NOTE—In this publication, phosphine is understood to be in the gaseous phase unless otherwise stated.

2 Scope and purpose

2.1 Scope

This publication is intended for the suppliers, distributors, and users of phosphine and its handling equipment. This publication includes guidance for design of equipment, selection of cylinders and valves, handling controls, and safety practices. Guidelines on the operational steps associated with the use of phosphine and phosphine mixtures as well as fire protection, gas detection, ventilation, and related safeguards are also included. The manufacture, purification, and analysis of phosphine are beyond the scope of this publication, although the general guidance given is also relevant to these processes.

2.2 Purpose

This publication was written to address the high toxicity and flammability of phosphine where the consequences of improper handling of phosphine could cause injury, death, and/or facility damage. This publication provides a description of the potential hazards involved in handling phosphine and the guidelines to follow to minimize risk potential.

3 Definitions

For the purpose of this publication, the following definitions apply.

3.1 Publication terminology

3.1.1 Shall

Indicates that the procedure is mandatory. It is used wherever the criterion for conformance to specific recommendations allows no deviation.

3.1.2 Should

Indicates that a procedure is recommended.

3.1.3 May

Indicates that the procedure is optional.

3.1.4 Will

Is used only to indicate the future, not a degree of requirement.

3.1.5 Can

Indicates a possibility or ability.

3.2 Technical definitions

3.2.1 Absolute pressure

Based on a zero reference point, the perfect vacuum. Measured from this reference, the standard atmospheric pressure at sea level is 101.325 kPa, abs (14.696 psia); however, local atmospheric pressure can deviate from this standard value because of weather conditions and the elevation above or below sea level.

3.2.2 Apparatus

Accessory equipment such as valves, pressure relief devices (PRDs), regulators, non-return valves (check valves) used with compressed gas.

3.2.3 Gas

Gas or gas under pressure as defined in United Nations (UN) *Recommendations on the Transport of Dangerous Goods, Model Regulations* and in *Globally Harmonized System of Classification and Labelling of Chemicals* (GHS) [1, 2].

A gas is a substance that (a) at 50 °C has a vapor pressure greater than 300 kPa; or (b) is completely gaseous at 20 °C at a standard pressure of 101.3 kPa [1, 2].

3.2.4 Containers

Vessels of various shapes, sizes, and materials of constructions such as cylinders, portable tanks, or stationary tanks, and of designs meeting the specifications of the American Society of Mechanical Engineers (ASME), Transport Canada (TC), United States Department of Transportation (DOT), *European Agreement Concerning the International Carriage of Dangerous Goods by Road* (ADR), Japanese Industrial Standard (JIS), or national authorities and are filled with compressed gases [3].

3.2.5 Critical temperature

Temperature above which a pure gas cannot be liquefied, regardless of the degree of compression.

3.2.6 Cylinder

Transportable pressure receptacle having a water capacity that does not exceed 150 L that can be filled with a gas under pressure.

3.2.7 Filling ratio

Ratio of the mass of liquefied gas introduced in a container to the mass of water at 15 °C (59 °F) that would fill the same container fitted ready for use.

NOTE—Also known as fill density, filling factor, maximum fill degree, or maximum fill pressure.

3.2.8 Flammable gas

Gas in which either a mixture of 13% or less (by volume) with air ignitable at 0.101 MPa, abs (14.696 psia) or a flammable range with air of at least 12% regardless of the lower limit. These limits shall be determined at 0.101 MPa, abs (14.696 psia) pressure and at a temperature of 20 °C (68 °F).

3.2.9 Gas supplier

Business that produces, fills, and/or distributes compressed gases and compressed gas containers.

3.2.10 Handling

Moving, connecting, or disconnecting a gas container under normal conditions.

3.2.11 Hazard

Any condition that could cause injury to personnel or property.

3.2.12 Highly toxic

Gases that have an LC_{50} in air less than or equal to 200 ppm for a 1 hour exposure, which corresponds to gases classified as Acute Toxicity Category 1 according to UN GHS [2]. Refer to 3.2.15.

NOTE—In this publication, parts per million (ppm) means parts per million by volume (ppmv).

3.2.13 Hot zone

Area immediately around the chemical spill and the surrounding region that could be in serious danger from physical hazards such as fire, explosion, or chemical exposure.

NOTE—Generally, only firefighters and the emergency response team who are members of a specialized hazardous material (HAZMAT) team will enter the hot zone.

3.2.14 Inert gas

Gas that is not toxic, doesn't support human breathing, and reacts scarcely or not at all with other substances.

3.2.15 Lethal concentration 50 (LC_{50})

Concentration of a substance in air, exposure to which for a specified length of time is expected to cause the death of 50% of the entire defined experimental population.

NOTE—Usually measured as ppm or mg/m^3.

3.2.16 Lower flammability limit (LFL)

Lower limit of flammability (point at which a flame just starts to propagate) of a gas or vapor at ordinary ambient temperatures and pressure expressed in percent of the gas or vapor in air by volume. The LFL will vary with temperature and pressure.

NOTE—Also referred to as lower explosive limit (LEL).

3.2.17 National standards, guidelines, regulations

Technical standards set by the regulatory authorities of the country in which the equipment/facility is used, with respect to design, construction, testing, and use. Where available and applicable, these standards shall be followed.

3.2.18 Oxidizer

Gas or gas mixture that is able, at atmospheric pressure, to support the combustion more than a reference oxidizer consisting of 23.5% oxygen in nitrogen (for example, gaseous oxygen, nitrous oxide, or fluorine).

3.2.19 Pressure

Force per unit of area exerted by a gas to its surroundings. The term megapascal (MPa) is the standard term for pressures used in this publication. 1 MPa = 1000 kPa = 20,885.4 psf = 145 psi = 10 bar.

3.2.20 Pressure relief device

Pressure and/or temperature activated device that may be used to prevent the pressure from rising above a predetermined maximum and thereby prevent equipment or container failure due to overpressurization.

3.2.21 Pyrophoric gas

Flammable gas that ignites spontaneously in air at a temperature of 54 °C (129 °F) or less.

3.2.22 Safety data sheet (SDS)

Written or printed information concerning a hazardous material (properties, precautions, etc.) following national regulations.

3.2.23 Test pressure

Pressure at which the container is hydraulically or pneumatically tested and is the pressure that shall not be exceeded under any foreseeable normal operating conditions (for example, during filling).

3.2.24 Toxic gas

Compressed gas that has a LC_{50} in air of less than or equal to 5000 ppm but greater than 200 ppm for a 1-hour exposure, which includes gases classified as Acute Toxicity Category 2 and 3 according to UN GHS [2].

3.2.25 Threshold limit value–Time weighted average (TLV®–TWA)

Concentration to which a person may be exposed, 8 hours a day, 40 hours a week, without harm [4].

3.2.26 Upper flammability limit (UFL)

Upper limit of flammability (point at which a flame can still nominally propagate) of a gas or vapor at ordinary ambient temperatures and pressure expressed in percent of the gas or vapor in air by volume. The UFL will vary with temperature and pressure.

NOTE—Also referred to as upper explosive limit (UEL).

3.2.27 Valve outlet caps and plugs

Removable attachments that usually form a gas-tight seal on valve outlets provided by the gas supplier with certain gases.

NOTE—Some caps are designed only for valve thread protection and are not gas-tight.

3.2.28 Valve protection cap

Rigid removable cover provided for container valve protection during handling, transportation, and storage.

4 Gas properties

4.1 General

Phosphine is a metal hydride gas with the chemical formula PH_3. It is highly toxic with an established LC_{50} 1 hour of 20 ppm and LC_{50} 4 hour of 10 ppm. In addition to its toxicity, it is also flammable and explosive in air, and can autoignite at ambient temperatures. It is not considered to be corrosive in the dry gaseous state. It is slightly soluble in water and soluble in most organic solvents. It possesses an odor of decaying fish and welding grade acetylene [2].

Table 1 shows properties of phosphine.

Figure 1 and Figure 2 show a vapor pressure curve for phosphine.

4.2 Physical properties

Avoid sources of ignition, sparks, and flames due to the flammable properties of phosphine. Avoid contact with air as phosphine is pyrophoric and can form explosive mixtures in concentrations of 1.6% or greater in air. Phosphine poses a severe fire hazard and an explosion risk. Phosphine is stable at room temperature and begins to decompose at approximately 375 °C (707 °F) with complete decomposition at approximately 593 °C (1100 °F) [5].

4.3 Chemical properties

Phosphine is incompatible with oxidizing materials, members of the halogen family, and acids. Phosphine is a strong reducing agent and reacts vigorously with oxidizers such as potassium permanganate, sodium hypochlorite, oxygen, ozone, chlorine, fluorine, and nitric oxide. Phosphine can have some reaction with water and the alkali metal family.

Phosphine is not known to polymerize.

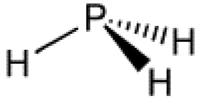
4.4 Health properties

Refer to 5.2.

4.5 Pyrophoric and flammability properties

Refer to 5.1.

Table 1—Properties of phosphine

Property	SI units	U.S. units	Reference
Synonyms	hydrogen phosphide, phosphorous hydride, phosphorated hydrogen		
Chemical formula	PH_3		
CAS number	7803-51-2		
UN number	UN 2199		
Physical state	Gas		
Color	Colorless		
Odor	decaying fish; welding grade acetylene		
Molecular weight	33.998		
Boiling point at 1atm	–87.74 °C	–125.93 °F	[6]
Melting point at 1 atm	–133.78 °C	–208.8 °F	[6]
Decomposition temperature range	375 °C to 593 °C	707 °F to 1100 °F	[5]
Critical temperature	51.6 °C	124.88 °F	[5]
Critical pressure	6.536 MPa, abs	947.97 psia	[5]
Critical volume	113.32 cm^3/mol	6.915 in^3/mol	[6]
Critical density	0.3 g/cm^3	18.7 lb/ft^3	[6]
Critical compressibility factor	0.274		[6]
Density of liquid at 25 °C at 3.46 MPa	0.491 g/cm^3	30.65 lb/ft^3	[6]
Density of gas at 21.1 °C at 101325 Pa	1.408 kg/m^3	0.0879 lb/ft^3	[6]
Specific gravity of gas at 25 °C and 1 atm (air =1)	1.184		
Vapor pressure at 21.1 °C (70 °F)	3558 kPa	516 psi	[7, 8]
Latent heat of vaporization at 25 °C (77 °F)	204.7 kJ/kg	88 Btu/lb	
Solubility in water at 25 °C and 101325 Pa	269.7 ppm (wt)		[6]
pH	Not applicable		
Volatility	Not applicable		
Odor threshold (varies with impurities)	0.03 ppm to 3 ppm		[9, 10]
Evaporation rate	Not applicable		
Flash point	Not applicable		
Lower flammability limit (LFL)	1.6, 1.8%		[11, 12 ,13]
Upper flammability limit (UFL)	98%		[14, 15]
Autoignition temperature	37.8 °C	100 °F	[5, 15, 16]
Molecular shape	trigonal pyramidal		
Dipole moment	0.58 D		[17, 18]
Standard enthalpy of formation at 25 °C, $\Delta_f H^0_{gas}$	+5.4 kJ/mol		[19, 20]
Structure			

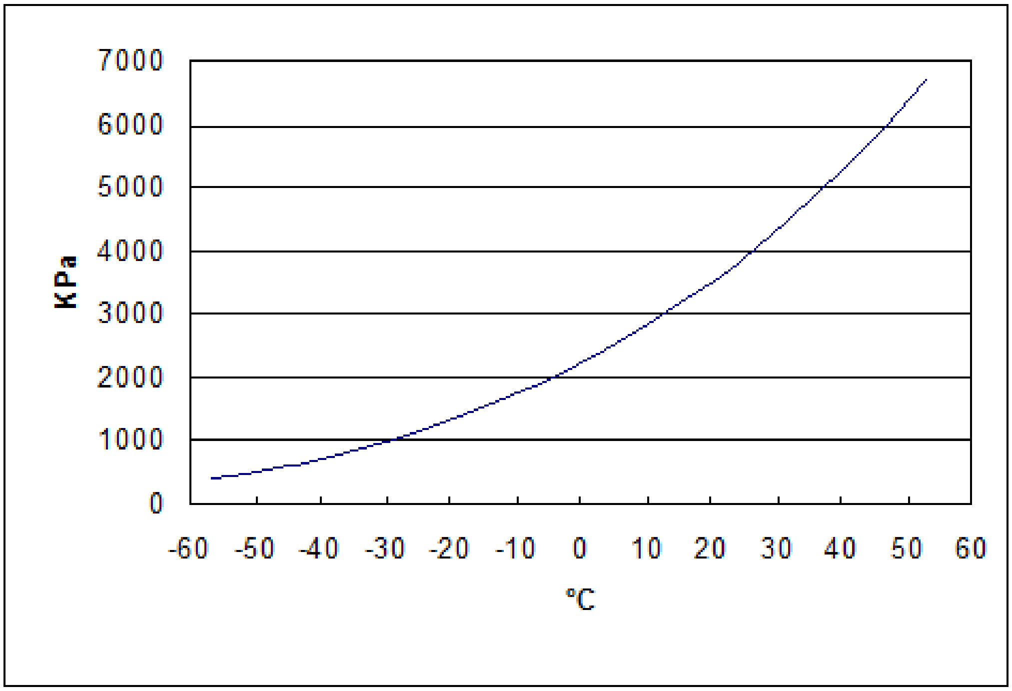


Figure 1—Phosphine vapor pressure curve (SI Units)

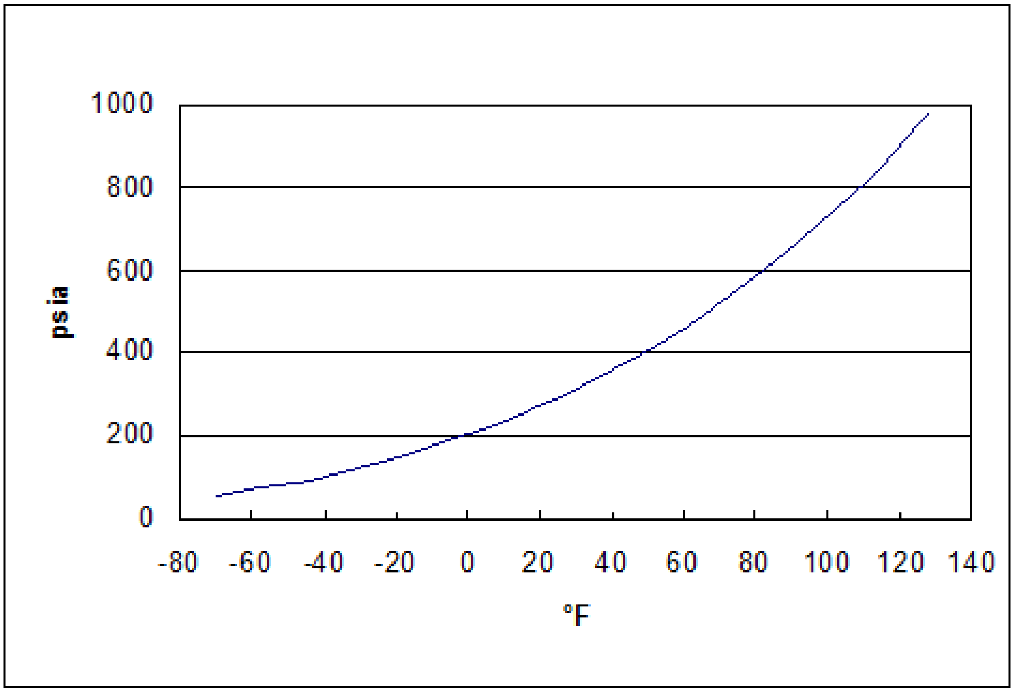


Figure 2—Phosphine vapor pressure curve (U.S. Units)

4.6 Environmental properties

With controls, phosphine releases can be minimized and pose no threat to human life and the environment.

Phosphine released into the atmosphere reacts principally with the hydroxyl ion (OH^-) radical to form hydroxy phosphide ion (OHP^-). The eventual products will be water and phosphorus oxyacids. Phosphine is also removed from air by soils and oxidized to orthophosphate. Many countries have regulations with measurable action to be taken if a release occurs. The users of phosphine shall review application regulations.

- Phosphine is considered a hazardous air pollutant (HAP). It is known or suspected to cause serious health effects and/or adverse environmental effects;
- Phosphine users should employ a variety of tools to prevent direct pollutant discharges into waterways, municipal wastewater treatment facilities, or allow polluted runoff;
- Emergency response programs are established and at times mandated to eliminate any danger to the public and the environment posed by hazardous substance releases. To help fulfill this mission, local governments can require that the person or organization responsible for phosphine use notify the government when the amount on-site reaches a predetermined limit;
- Guidance documents should be obtained from the local government agency to offer direction in following regulations and control emissions; and
- Risks to human health and the environment vary considerably depending upon the type and extent of exposure. Phosphine users are strongly encouraged to characterize risk on the basis of locally measured or predicted exposure scenarios.

Risk assessment values or other media quality standards may be used in countries to evaluate the health risks posed by exposures to toxic chemicals. These values are typically specified as concentration limits that shall not be exceeded to avoid health risks. These published values can be compared directly to information about the concentration of a chemical in the environment to identify potential health hazards. If a chemical concentration exceeds a relevant media quality standard, action to reduce environmental contamination or exposure is warranted.

5 Gas major hazards

5.1 Fire and explosion hazards [21, 22, 23, 24, 25]

Phosphine is flammable and explosive in air and can autoignite at ambient temperatures.

The lower flammability limit (LFL) is reported to be 1.6% to 1.8% by volume in air [11, 12, 13]. The upper flammable limit (UFL) is 98% [14, 15]. When phosphine burns, it produces a dense white cloud of phosphorus pentoxide (P_2O_5) fumes. These fumes are a severe respiratory tract irritant due to the rapid formation of orthophosphoric acid (H_3PO_4) on contact with moisture (water) in human lungs.

Therefore, personnel shall wear protective clothing and self-contained breathing apparatus (SCBA) when fighting phosphine fires. Only trained personnel should respond to phosphine fires.

As in the case of a fire of any flammable gas, the flow should be stopped if it is safe and practical to do so. Normally, this can be accomplished by shutting off the cylinder valve if safe to do so.

Flammable gases shall not be used near open flames, sources of heat, or adjacent to oxidizers and non-explosion proof electrical systems. Transportation, storage, and use of phosphine should be in well- ventilated areas.

In order for a phosphine ignition to occur, two conditions need to occur simultaneously:

- concentration of phosphine is within its flammable limits; and
- sufficient air or an alternate oxidizing source is present.

Since phosphine is a pyrophoric gas, no source of ignition is required.

Phosphine can begin to slowly decompose into its elements of phosphine and hydrogen at temperatures of 375 °C (707 °F) [5].

The presence of impurities, particularly diphosphine (PH_2-PH_2), often causes phosphine to ignite spontaneously at room temperature and can form explosive mixtures with air as low as 1.6% [11]. However, it should be noted that phosphine can diffuse into the atmosphere without autoignition when a fume hood, cabinet, or other ventilated area exhaust velocity is high.

If the flow of phosphine cannot be stopped, let it burn until the fire stops naturally, keeping adjacent cylinders and equipment cool. If a phosphine fire is extinguished and the flow of phosphine is not stopped, a hazardous combustible mixture can continue to form. It is possible that the mixture can then be auto-ignited even under low oxygen concentration and any unburned phosphine can ignite violently, explode, cause more damage, and restart the fire. Measures shall be taken to protect persons from cylinder rupture in the case of cylinder failure or piping failure.

Although a phosphine fire shall not be extinguished until the flow of phosphine is stopped, water sprays should be used to extinguish any secondary fire and to prevent the spread of fires. The phosphine containing equipment can be kept cool by water sprays to decrease the rate of phosphine release or to prevent further damage. This is best done at a distance. A controlled water spray can help knock down and minimize the dispersion of phosphine and phosphine by-products in the gas cloud. Water used in firefighting can become contaminated when in contact with the oxidized phosphine by-products (phosphorus oxides and/or oxyacids), so there should be measures in place to contain and possibly treat such contaminated water.

Remote controlled water spray equipment is preferable to the use of hoses in cooling equipment and to reduce the spread of fire. Should the use of hoses become necessary, operating personnel should remain behind protective structures, upwind of the fire, and wear protective clothing and SCBA.

Firefighting or other emergency personnel should communicate and cooperate with personnel who are familiar with the physical and toxicological properties of phosphine. They should also communicate and cooperate with personnel who are familiar with materials in the area of the emergency. Unexpected conditions may require special actions.

If a cylinder of phosphine or supply piping system is ruptured so that quantities of phosphine are released and ignited, hazardous conditions can exist:

- Flame effects—The major concern is that the flames can impinge on surrounding valves and piping thus weakening these structures potentially leading to failure. Fire balls or jet fires can be present. Wind velocity and direction can change the shape of the fire ball or jet to an elliptical shape and push it further downwind of the release;
- Radiation effects—The major concern is that radiation effects from the fire can result in the excessive heating of adjacent equipment and process lines; and
- Reaction by-products—Oxidation of phosphine yields water and phosphorus oxides and oxyacids.

A thorough process hazard analysis (PHA) with identified sufficient safeguards shall be in place to minimize the risk of a potential incident.

5.2 Toxicology

5.2.1 Phosphine exposure

Phosphine is highly toxic to the human respiratory system and organs. Phosphine has an odor of decaying fish or welding grade acetylene. The odor of phosphine depends on the impurities it contains and the environment into which it is released.

The main hazard to humans is the possibility of unrecognized occupational exposure to phosphine causing acute poisoning. Neither smell nor sensory irritation can be relied upon for warning of toxic concentrations, especially in the presence of other fumes, gases, or vapors. Approximately 20% to 50% of persons can detect the odor threshold value of 0.03 ppm to 3 ppm [9, 10].

The predominant pathological feature in acute fatal cases is pulmonary edema. Severe non-lethal cases complain of pain and tightness in the chest. Neurological abnormalities include headache, vertigo, tremors, and unsteady gait, and can progress to convulsions, coma, and death; they can mimic alcoholic intoxication. Gastrointestinal symptoms include loss of appetite, thirst, nausea, vomiting, diarrhea, epigastric pain, and jaundice. Other effects described include thrombocytopenic purpura and hypotension.

The primary route of entry for phosphine is inhalation. Phosphine can be corrosive to the respiratory tract and primarily attacks the cardiovascular and respiratory systems causing central nervous system (CNS) depression, peripheral vascular collapse, cardiac arrest and failure, and pulmonary edema.

There have been no long-term studies on the effects of phosphine on animals or man and there are no data relating to mutagenicity, teratogenicity, or carcinogenicity [26].

Symptoms are rapid in onset and characterized by:

- headache;
- dizziness;
- weakness;
- apathy;
- nausea;
- vomiting;
- cough;
- dyspnea;
- decrease in blood pressure;
- change in pulse rate;
- diarrhea;
- tremors and convulsions;
- intense thirst;
- tightness in the chest;
- restlessness;
- hemoglobinuria;
- paralysis; and
- coma [26].

Table 2 shows regulatory exposure limits for phosphine.

5.2.2 Medical treatment for phosphine exposure

Detailed prehospital and hospital management practices for treatment of phosphine exposures can be found in *Medical Management Guidelines for Acute Chemical Exposures* [27].

Key points from these guidelines for phosphine include:

- There is no antidote for phosphine poisoning. Treatment consists of support of respiratory and cardiovascular functions; and
- Victims exposed only to phosphine gas do not need decontamination before medical treatment as they pose no serious risks of secondary contamination to personnel outside the hot zone.

Table 2—Regulatory exposure limits for phosphine

CAS Number: 7803-51-2	**Value**	**Reference**
LC_{50} rat 1 hour [27]	20 ppm	[28]
U.S. OSHA Permissible Exposure Limit (PEL) Time-Weighted Average (TWA) for General Industry [28, 29]	0.3 ppm (0.4 mg/m^3)	[29, 30]
Threshold Limit Value–Time Weighted Average (TLV®–TWA) [3]	0.3 ppm (0.42 mg/m^3)	[4]
Threshold Limit Value–Short Term Exposure Limit (TLV®–STEL) [3]	1 ppm (1.4 mg/m^3)	[4]
Recommended Exposure Limit (REL) TWA [28, 29]	0.3 ppm (0.4 mg/m^3)	[29, 30]
Recommended Exposure Limit (REL) STEL [28, 29]	1 ppm (1 mg/m^3)	[29, 30]
NIOSH Immediately Dangerous to Life or Health (IDLH) Concentration [29]	50 ppm	[31]
Acute Exposure Guideline Levels (AEGLs) [30] AEGL-1 (30 minutes) AEGL-2 (30 minutes) AEGL-3 (30 minutes)	 NR ppm 4.0 ppm 7.2 ppm	[32]

NOTES

1 NR: Not recommended due to insufficient data

2 PEL TWA: expressed as a time-weighted average is the concentration of a substance to which most workers can be exposed without adverse effects averaged over a normal 8 hours workday or a 40-hour workweek.

3 TLV TWA: expressed as a time-weighted average is the concentration of a substance to which most workers can be exposed without adverse effects.

4 TLV STEL: a 15 minute TWA exposure that should not be exceeded at any time during a work day.

5 REL TWA: expressed as a time-weighted average is a recommended exposure limit for an 8 or 10-hour time-weighted average exposure and/or ceiling.

6 REL STEL: a 15 minute TWA exposure that should not be exceeded at any time during a workday.

7 IDLH: to ensure that a worker can escape from an exposure condition that is likely to cause death or immediate or delayed permanent adverse health effects or prevent escape from the environment.

8 AEGL-1 is the airborne concentration (expressed as ppm or mg/m^3) of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic nonsensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.

AEGL-2 is the airborne concentration (expressed as ppm or mg/m^3) of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects or an impaired ability to escape.

AEGL-3 is the airborne concentration (expressed as ppm or mg/m^3) of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening adverse health effects or death.

9 For occupational exposure limits (OELs) for European countries, refer to EIGA's SDS 100 for phosphine at www.eiga.eu.

6 Gas handling equipment—general considerations

The equipment used to handle phosphine shall be designed, constructed, and tested in accordance with the regulatory requirements of the country in which the equipment is operated. The equipment shall be designed to withstand the maximum pressure and temperature at which it is to be operated. Special piping and pressure vessel code requirements can apply due to the highly toxic nature of phosphine (for example, ASME Class M material). See Section 8 for gas cylinder filling and packaging requirements. A PHA shall be performed and documented on all phosphine systems. As phosphine is a highly toxic, flammable, and pyrophoric gas, consideration should be given to the following issues when designing systems to handle phosphine:

- materials of construction;
- compatibility of sealing compounds;
- system pressures and overpressure protection;
- valve types and filter types;
- tubing;
- purification materials;
- system leak tests and purge;
- system temperature control;
- use of electrical control and use of electrically classified equipment;
- monitoring system;
- abatement system;
- system vent; and
- regulators.

6.1 Materials of construction

Selection of metals and nonmetals shall be made taking into account the compatibility guide in Table 3. It is extremely important that all gas control equipment be compatible with the gas being passed through it. The use of a device that is not compatible with the service gas can damage the unit and cause a leak that could result in property damage or personal injury. If a material is not listed and is required to be used in phosphine service and is thought to be compatible, it should be first tested to confirm compatibility before use under defined temperature, pressure, and flow conditions.

The Table 3 material compatibility guide is prepared for use with dry phosphine at a normal operating temperature of 21.1 °C (70 °F). Information can vary if different operating conditions exist.

Table 3—Material compatibility guide [33]

Materials of construction																			
Metals									**Plastics**						**Elastomers**				
Steel	303 SS	304 SS	316 SS	Monel®	Aluminum	Brass	Zinc	Copper	Kynar®	PCTFE	Polycarbonate	PVC	Teflon®	Tefzel®	Buna-N	Kalrez®	Neoprene®	Polyurethane	Viton®
S	S	S	S	S	S	S	U	S	S	S	?	S	S	S	S	S	S	S	S

S = Satisfactory U = Unsatisfactory ? = Unknown or limited data

NOTES

1 Nickel gaskets are acceptable as a diameter index safety system (DISS)/vacuum coupling radiation (VCR) gasket but discoloration of the surface can result.

2 If used, some plastics and elastomers absorb phosphine.

3 While ISO 11114-1, *Gas cylinders—Compatibility of cylinder and valve materials with gas contents—Part 1: Metallic materials* addresses concern for hydrogen embrittlement, and while it is also acknowledged that the UN Model Regulations P200 Packaging Instruction requires an “H” stamp for steel cylinders charged with phosphine, there is no conclusive proof that phosphine is an embrittling gas [34, 1].

6.2 Compatibility of sealing compounds

Consideration should be given to the compatibility of lubricants, seals, greases, and sealing compounds that come in contact with phosphine under normal or upset conditions. Refer to vendor supplied data.

6.3 System pressures and overpressure protection

Due to the hazardous nature of phosphine, a conservative engineering and design approach shall be applied to the system whether for pure phosphine or phosphine mixtures.

System pressures can be high due to the vapor pressure of phosphine at 21.1 °C (70 °F), which is 3558 kPa, abs (516 psia). The correct use of pressure reduction equipment is essential to control system pressure (refer to 10.2). Design should address conditions where system pressure can be subjected to subatmospheric conditions and draw in air or other gas stream contamination that is used in the system. Precautions shall be taken to ensure that phosphine gas does not condense and liquefy in process areas not intended for liquid.

Gaseous mixtures of phosphine are routinely packaged at pressures less than or equal than the rated cylinder working pressure. Gas panels typically use a gas regulator to reduce the cylinder pressure to the operating condition. Ensure that all components in the system are rated for these pressures.

Where system design pressures can be exceeded due to any component failure or operator error, overpressure protection shall be provided. Overpressure protection may involve pressure relief devices (PRDs) and/or instrumented systems depending on local code requirements.

Piping system safety relief valve outlets shall link to a properly designed abatement system or safe location (where permitted).

All discharges from process emergency venting such as PRDs, etc., that do not go to an abatement system shall be:

- piped to the outside of buildings;
- discharged to a safe area well away from personnel; and
- confirmed acceptable by use of dispersion analysis.

Refer to Section 11.

6.4 Valve types and filter types

Metal diaphragm valves and bellows valves provide a better leak tightness as compared to packed valves. The use of nonmetal material for diaphragms or bellows is not recommended due to the permeation potential of phosphine through the nonmetal. Ball valves, butterfly valves, gate valves, needle valves, or packed valves are not recommended for use in phosphine service due to a higher leak potential either through or around the valve seat, seals, or the valve body.

Mesh filters made of stainless steel work well as do those made of polytetrafluoroethylene (PTFE). Sintered metal filters are also recommended. Phosphine has been shown to decompose to phosphorous and hydrogen on the surface of nickel filter media. The decomposition rate was found to be low at ambient temperatures. However, it is recommended that nickel filters not be used in low phosphine concentration applications (for example, less than 1000 ppm). Over time a solid film growth of nickel phosphides on filter membrane surfaces can increase the pressure drop across a filter and degrade filter performance.

The use of restrictive flow orifices (RFOs) has been a routine practice since the mid-1980s. For example, the restrictor has a small diameter of 0.152 mm (0.006 in), 0.254 mm (0.010 in), and 0.3 mm (0.012 in), and is of stainless steel materials of construction. While early designs had a filter element capable of capturing particles that were greater than two microns, the use of such filters is not currently part of RFOs in service today. The RFO threads into the valve outlet. In the event of a shearing of a process line or a valve being accidentally opened, the RFO significantly reduces the amount of gas that could be released and that would need to be environmentally treated. Some jurisdictions and insurance companies require the use of RFOs.

Also during the 1980s, air actuated valves began to be used. They allowed for remote opening and closing of the cylinder valve, and afforded an extra measure of safety both at the filling as well as at the point of use.

6.5 Tubing

Some national bodies or insurance companies require the use of coaxial tubing when the tubing is outside of an exhausted enclosure. Welded or metal face seal connections are the preferred connection methods due to their leak integrity. The use of mechanical fittings should be limited.

6.6 Purity

Phosphine in the electronic industries is offered at high purity by the supplier. Purities offered range from low 99.995% to 99.9999+%. Point of use purification can be used to remove additional contaminants.

A system purge shall be completed before the use or removal of the purifier.

6.7 System leak tests and purge

After system installation or maintenance, the system shall be leak checked and purged with an inert gas before commissioning with phosphine or phosphine mixtures.

Connections that are routinely remade in the process (for example, cylinder pigtail or other connections) shall be leak checked at a pressure equal to or greater than the source pressure.

The best purge systems are those that are automated. The number of purge cycles is a function of the inert purge pressure available, the use of vacuum, the size of the tubing/piping system to be purged, and the desired final dilution value. Common purge gases are nitrogen and helium. Hydrogen is also used as a purge gas. Typical gas delivery systems shall be purged to a safe level of phosphine. The use of manual purge control has a higher potential for operator error and requires clear operator instructions if used.

6.8 System temperature control

Systems using phosphine can operate at varying temperatures depending on the application. Some systems can require an external heat source for the cylinder and process lines to maintain product flow. Cylinders and process lines shall not exceed 50 °C (122 °F). In addition, directly heating cylinders using resistance heaters is not recommended. Indirect heating or the use of approved, electrically classified heating blankets and line heaters is preferred.

When working with any compressed liquefied gas, product condensing in process lines is a possibility, especially when product flows to a relatively cooler area of the system. Use the vapor pressure versus temperature relationship such as the one shown in Figure 1 and Figure 2 to avoid condensation of the product in the process lines at any given pressure and temperature.

6.9 Use of electrical control and use of electrically classified equipment

Since phosphine is flammable and pyrophoric, electrical systems shall meet the requirements of the local regulations covering flammable classifications.

These classifications are for generic volatile flammable liquids or flammable gases that if mixed with air can burn or explode. In such cases, liquids, vapors, or gases are normally confined within closed containers or closed systems from which they can escape only in case of accidental rupture or breakdown. It should be noted that ignitable concentrations of gases or vapors of flammable gas, flammable liquid-produced vapor, or combustible liquid-produced vapor mixed with air are normally prevented by having forced mechanical ventilation that is under negative pressure. This could become hazardous through the failure or abnormal operation of the ventilating equipment.

NOTE—Outdoor phosphine installations in the United States generally do not require electrical classification.

6.10 Monitoring system

6.10.1 Gas monitoring

There is a need to ensure personnel as well as process equipment are protected by phosphine detection systems that are accurate, efficient, and easy to use and maintain.

Persons exposed to hazardous levels could be unaware of its presence. The manifestation of symptoms can be delayed and appear after several hours. A gas monitoring system continuously monitors primary locations for phosphine including, but not limited to, the following areas:

- storage;
- operator areas;
- gas cabinets;
- laboratories;
- fume hoods;
- process rooms; and
- abatement system exhaust.

The gas monitoring system shall have a backup source of power.

Refer to 7.1 for information on life safety control.

Detection methods vary, as do their sensitivity to phosphine as well as cross-sensitivity to other gases. It is desirable to have a system capable of networking existing systems from various manufacturers, and the ability to accommodate ongoing expansion. Typical detector types suitable for phosphine are:

- photo-absorption;
- photo-ionization;
- electrochemical;
- colorimetric tape;
- thermal conductivity; and
- catalytic bead.

A gas detection system with a sensing interval not exceeding 5 minutes can be required in certain jurisdictions.

6.10.2 Fire and smoke monitoring

When phosphine burns, it produces a dense white cloud of phosphorus pentoxide (P_2O_5) fumes. These fumes are a severe respiratory tract irritant due to the rapid formation of orthophosphoric acid (H_3PO_4) on contact with moisture (water) in human lungs.

Since phosphine is flammable and capable of autoignition (pyrophoric at higher concentrations), monitoring for a flame is appropriate. However, the initial hazard is the high toxicity of the gas at low ppm levels. This toxicity concern occurs well below the LFL of phosphine. Thus, it is recommended that gas monitoring should be directed to ppm emissions in addition to flame monitoring. For higher concentration concerns, a monitoring system capable of detecting a flame is recommended.

Flame detectors suitable for phosphine service shall be located to detect fire in potential phosphine leak areas. Whenever flame detection occurs, immediate shutdown of the process is required. This is best achieved with automatic valves controlled with nitrogen instead of air. An alarm should be transmitted so responsible parties can act on the condition.

The use of ultraviolet/infrared (UV/IR) flame detectors is suitable for phosphine service. Other detectors can offer comparable detection depending on detector location and action required. Temperature rise indicators can also be suitable for indoor use. Such systems work best in heating, ventilation, and air conditioning (HVAC) controlled environments.

Refer to 7.1 for additional gas monitoring considerations.

6.10.2.1 Indoor systems

Flame detectors used indoors shall be located in the room or within gas cabinets depending on cylinder storage requirements and use. Potential leak zones include:

- cylinder valves (cylinder interface, PRDs, and outlet connections);
- process equipment (reactor, vacuum pump, purification systems);
- process and purge panels; and
- exhaust ducts.

Gas cabinets or fume hoods shall be equipped with automatic sprinkler systems. The sprinkler head(s) should be positioned to keep the cylinder(s) and related gas panel system cool, but not meant to extinguish a fire in the cabinet or hood. There are generally specific requirements on water flow rate and duration of water spray that shall be followed. These are national code specific.

6.10.2.2 Outdoor systems

Flame detectors used outdoors should be compatible with the environment. They should be field tested to avoid false alarms due to sunlight, arc welding, artificial lighting, or other stray sources that can inadvertently activate the detector.

During a fire phosphine systems and cylinders should be cooled rather than extinguished since the continued leakage of phosphine could result in a latent explosion of accumulated phosphine.

A manual or automatic (where required) deluge water spray system is suitable for outdoor system control.

Systems shall be designed and installed in accordance with national regulations to ensure compliance. There are generally specific requirements on water flow rate and duration of water spray that shall be followed. Protection of nearby structures should be considered.

6.11 Abatement system

Refer to Section 11.

6.12 System vent

All vents in the system shall be directed to an abatement system. These include vacuum pump exhaust, system vent, and vacuum venturi exhaust.

7 Process and operation

7.1 Life safety control (gas detection and alarm systems)

Procedures shall be in place to control worker exposure to phosphine and its by-products. Compliance with these procedures can prevent adverse effects of exposure in the workplace through air exposure or through skin exposure. Specific compliance activity can be prescribed by national regulations. The following items should be considered part of a life safety control program.

7.1.1 Monitoring

- Environmental workplace air/land monitoring—Occupational exposure shall be controlled so that no worker is exposed to concentrations greater than allowed either as gas or solid inorganic compound;
- Monitor calibration/inspection—Routine inspection of monitoring equipment to verify performance and reliability;
- Monitor operation/performance of abatement systems—Routine inspection of abatement equipment to verify performance and reliability; and
- Leak detection devices shall be installed to trigger emergency response actions in compliance with regulations of the authorities having jurisdiction (AHJ).

7.1.2 Life safety system

- Periodic review of HVAC air balance through building, fume hoods, gas cabinets, and abatement systems—With time, air flows/exhausts can change and required capture velocities could be less than required levels. Ventilation dampers should be locked in place to prevent the altering of required ventilation between air balances;
- Alarm testing and inspection—Routine testing and inspection of alarm systems to verify performance and reliability;
- Since phosphine is a flammable and pyrophoric gas, firefighting systems shall be considered and follow regulations of the AHJ;
- Gas scrubbing or ventilation systems should be installed to handle gas leaks. National regulations may require gas scrubbing or ventilation to handle gas leaks; and
- Gas storage and process areas should be designed with more than one exit.

7.1.3 Management

- Work clothing management—Daily change outs, a place for contaminated clothing, a separate locker room from manufacturing environment;
- Workers who are required to wear respiratory protection shall be medically evaluated and fit tested to confirm worker ability and clearance for use. Workers shall also be trained and certified in the use of personal protective equipment (PPE);
- Training and emergency response—Training should be conducted on the emergency response to situations that involve the possible release or exposure to phosphine and by-products;
- General awareness training—Personnel involved in the manufacturing, processing, maintenance, handling, storage, and/or transportation shall be trained on the exposure effects (signs, symptoms, medical attention) of phosphine and by-products using the SDS and other safety information related to the environment and to personnel. Additional training can be required by local jurisdictions that include personnel safety, preventive maintenance, and environmental management programs;

- Record keeping programs—A program should be documented explaining what to record, when to record, how often to record, place of record storage, and length of time for records to be stored before disposal;
- Labeling of products/containers—With complete name and applicable hazards as required by regulations;
- Clear, documented work practices/procedures—Control of equipment, process clean-up, waste disposal, and operations control; and
- Emergency action plan—response and evacuation protocols for site alarms, releases, and abatement of loss of contaminant.

7.2 Operational procedures and personnel

Clearly defined written work instructions are required to ensure safe handling and processing of phosphine. The work instruction should describe in sufficient detail the information needed on how to perform a specific task. These work instructions shall be written in a clear and simple language and shall exist in any viewable form. Instructions shall be under version control and the latest versions of the work instructions should be readily available to the operator should questions arise.

Operators shall be notified and trained when procedures are changed. A risk assessment shall be carried out on all operations involving phosphine. Any changes to these procedures or process equipment shall be reviewed under management of change (MOC) practices.

Components and materials that can be used on phosphine systems shall be clearly identified and carefully stored and handled to ensure that they do not become contaminated. It is recommended that cylinder valve outlet connections gaskets are only handled while wearing approved gloves. This can avoid the risk of:

- contamination of the gaskets by the natural oils found on the skin; and
- contamination of the operator from residue phosphine by-products found on the used gasket.

All personnel involved in handling of phosphine and the operations of phosphine systems shall be trained. This training shall include the importance of cleanliness and the need for exclusive use of specified materials and components on phosphine systems.

Personnel who operate gas systems shall have a good understanding of the properties, fire and explosion hazards, and toxicity of phosphine. They should also be trained to take action in the event of an emergency. Wherever possible, preventive measures shall be considered to protect operators (for example, gas cabinets, fume hoods, PPE, remote controlled valves, and barrier walls).

7.3 Ventilation

Ventilation is required for storage areas, gas cabinets, fume hoods, and areas where phosphine is processed, stored, or handled. Where multiple exhaust ducts feed into a common system, measures shall be taken to ensure reverse flow is not possible.

7.3.1 Direct venting into exhaust systems

Phosphine should not be directly vented into exhaust ventilation systems as fire or explosion can occur due to autoignition of the phosphine itself, from the ignition of other flammables, or from chemical side reactions that could be present in the exhaust system.

Pure phosphine or mixtures greater than the LFL shall be diluted with an inert gas before venting to reduce the risk of fire or explosion.

7.3.2 Dedicated process vent

Phosphine discharged from process panels (or other processes) to an exhaust system should be dedicated to phosphine service.

Vent lines should be constantly purged with inert gas to prevent air (or other backflow of gases) from entering into the vent system.

The venting system should be designed to minimize pressure drop.

Purge systems should be dedicated and isolated systems to curtail the potential backflow of phosphine.

7.3.3 Common guidelines

Regulations vary by country and should be verified, but the following are common guidelines.

7.3.3.1 Necessity of ventilation for phosphine

- During normal operations, do not vent toxic and flammable gases to the atmosphere except through a properly designed abatement system (see 6.12); and
- Mechanical ventilation shall be used to exchange air where phosphine is processed or handled to quickly exhaust any fugitive phosphine emissions.

7.3.3.2 Types of ventilation

- Indoor storage and use areas and storage buildings for compressed gases and cryogenic fluids shall be provided with mechanical exhaust ventilation;
- For indoor storage, forced ventilation is required and shall follow applicable regulations;
- Gas rooms shall be provided with an exhaust ventilation system; and
- Where outdoor storage is allowed, forced ventilation is generally not required.

7.3.3.3 Consideration for ventilation design

- The gas cabinet or exhausted enclosure shall be provided with an exhaust ventilation system designed to operate at a negative pressure relative to the surrounding areas:
  - The velocity at the face of access ports or windows, with the access port or window open, shall be adequate to protect the user from fugitive emissions. In the United Kingdom, a minimum velocity of 1 m/s (3 ft/s) across the face of the small valve manipulation opening is recommended for normal operating conditions and
  - The number of air exchanges per hour (inside the gas cabinet or exhausted enclosure) may be regulated by local authorities;
- The mechanical ventilation rate shall be adequate. In the United States, the rate of not less than 0.3 $m^3/min/m^2$ (1 $ft^3/min/ft^2$) of floor area over the area of storage or use is required;
- The exhaust system shall take into account the density of the potential gases released and leak points:
  - For gases that are heavier than air, like phosphine, exhaust should be taken near the floor
  - Some phosphine mixtures (helium, hydrogen) are lighter than air, exhaust should be taken near the ceiling and
  - The location of both the exhaust and inlet air openings shall be designed to provide air movement across all portions of the floor or room to prevent the accumulation of vapors;
- Exhaust ventilation should not be recirculated within the room or building if the cylinders, containers, or tanks stored are capable of releasing hazardous gases like phosphine;
- Water sprinkler systems should be installed and properly sized for gas cabinets, fume hoods, and areas where phosphine is being processed or stored;

- Equipment used to contain or capture phosphine shall be noncombustible;
- Equipment used, like air handling fans, shall be non-sparking by design and construction;
- Ventilation systems shall discharge at an adequate distance from intakes of air-handling systems, air conditioning equipment, air compressors, and building openings such as windows and doorways;
- Storage and use of compressed gases should be located at an adequate distance from air intakes;
- In some local jurisdictions, where forced ventilation is provided, a manual shutoff switch should be provided outside of the room in a position adjacent to the principal access door to the room or in an approved location. The switch shall be the break-glass or equivalent type and shall be labeled VENTILATION SYSTEM EMERGENCY SHUTOFF;
- Where mechanical ventilation is provided, the system shall be operational, at a minimum, during the time the building or space is occupied; and
- There shall be an alarm system that activates if there is loss of ventilation.

7.4 On-going maintenance and preventive maintenance programs

It is essential that equipment in which phosphine is handled is held to a high standard and maintained in a routine, controlled, and safe manner. Particular attention should be provided to any replacement parts for compatibility with phosphine and other system products.

Preventive action is directed at eliminating potential causes of equipment failure before they occur. The manufacturer's equipment manual provides guidelines for preventive maintenance (PM) management of their equipment. It is the responsibility of each user to ensure control exists. Users of phosphine should have a PM program installed and implemented at all sites that process or handle phosphine.

8 Gas cylinder filling/packaging

8.1 Filling facility consideration

Refer to Section 9 for information on good practices for filling facilities.

8.2 Containers

8.2.1 Cylinders

Phosphine is routinely packaged in seamless steel cylinders or aluminum alloy cylinders with a minimum test pressure set by the regulatory body. Low pressure welded cylinders may be accepted for this service, with special approval that has been granted by the regulatory body. Conversion of phosphine cylinders to other gas services is not recommended unless following an approved procedure. Refer to ISO 11621:1997, *Gas cylinders—Procedures for change of gas service* and CGA C-10, *Guidelines to Prepare Cylinders and Tubes for Gas Service and Changes in Gas Service* for further information [35, 36].

The cylinder size of phosphine and its mixtures are limited by local government regulations. In Japan, maximum cylinder size is 49 L and in the United States is 57 L except for mixtures less than 10 vol%.

Cylinders that are used in high-purity electronic phosphine service, generally have a special internal pretreatment to maintain gas purity. This pretreatment is provided by the gas supplier.

Containers shall be certified and tested regularly in compliance with applicable standards. Container retest shall follow applicable standards or the container manufacturer's country laws and regulations, whichever is more stringent. Containers failing to meet these standards shall be removed from service. If the container can be repaired to meet the standards, it can be put back to use; otherwise it shall be scrapped.

Before fill, care shall be exercised to ensure that a container has not been damaged. Prefill inspection of containers and correct verification of their pressure rating before filling are very important.

8.2.2 Valves and pressure relief devices

It is recommended that diaphragm seal valves be used for phosphine because they provide a level of leak tightness that is not normally achievable with a packed valve. The diaphragm valve can be either a diaphragm packless or a tied diaphragm valve. Some jurisdictions such as the United States and Europe, mandate the use of the diaphragm valve such as the United States and Europe.

There are different types of valve outlets that are used for phosphine in Asia, North America, and Europe. It is important that the ancillary equipment used to connect to the cylinder valve be of the same thread configuration as the cylinder valve outlet to insure a leak-tight connection. The use of adapters to connect to the cylinder valve outlet is not recommended. Transportation of dangerous goods regulations such as those for DOT, ADR/RID, *International Maritime Dangerous Goods* (IMDG) *Code,* and UN TDG Model Regulations, require that the valve outlets of gas cylinders containing pyrophoric and/or highly toxic gases or gas mixtures are fitted with a gas-tight plug or cap [3, 37, 1].

There are a variety of different cylinder valve inlets that are in use today for phosphine as well as all gases. There are also a variety of cylinder neck threads that are used worldwide. The threads on the valve inlet shall match the threads on the container neck. It is very dangerous to match cylinders and valves that have been manufactured to different national inlet thread standards since the possibility exists that the valve, under pressure, could be ejected from the cylinder. This practice shall be forbidden.

In most countries, PRDs are prohibited because of the toxicity of phosphine. The use of PRDs for cylinder valves with phosphine is required in some countries. In other countries, PRDs are optional but it is recommended to avoid using PRDs.

8.2.3 Fill density

Containers shall be filled with phosphine and mixtures in accordance with the requirements of the AHJ:

- The UN P200 packaging note currently permits a maximum fill density of 0.45 kg/L for phosphine packaged in cylinders with a test pressure of 30 MPa (300 bar) and 0.30 kg/L for a cylinder with a test pressure of 20 MPa (200 bar) [2];
- The maximum fill density for phosphine in Japan is 0.207 kg/L;
- In the United States, the maximum fill density based on liquid full cylinder at 54.4 °C (130 °F) is 0.30 kg/L; However, under a special permit, 0.45 kg/L of fill density with the test pressure of the cylinder over 15.1 MPa (2188 psi) is allowed by DOT; and
- The maximum filling ratio for Europe is 0.3 for 225 bar of the gauge test pressure and 0.45 for 250 bar of the gauge test pressure.

8.3 Filling equipment

Many countries regulate the disposal of phosphine contaminated wastes. Any equipment or materials in contact with phosphine should be treated as a hazardous waste when the time comes for disposal unless proven otherwise. Clean-up procedures and employee protection guidelines should be documented and understood.

The by-products of phosphine oxidization typically are phosphorus oxides or oxyacids. Peroxide washing is a suitable cleaning method of contaminated equipment.

8.3.1 Manifolds

Manifold components in contact with phosphine filling shall be designed with compatible materials listed in this publication. When not under phosphine pressure, manifolds should be backfilled with an inert gas (for example, helium, nitrogen, argon) and plugged to ensure that any contaminates are excluded from the manifold system.

Filling manifolds should be located in well-ventilated areas. To reduce potential quantity of gas released in an incident and reduce waste, small diameter tubing and lengths are preferred. The filling manifold should be made utilizing welded fitting and metal face seal fitting. The use of threaded fitting should be avoided. The use of mechanical fittings should be minimized.

For system leak tests and purge practices, refer to 6.7.

8.3.2 Compressors

Since phosphine is a pyrophoric and liquefied gas, compressors are not normally used for pure gas.

8.3.3 Vacuum pumps

Vacuum pumps in contact with phosphine are typically dry pumps although oil sealed pumps may be used. Dry pumps are recommended to eliminate oil contamination concerns. The use of a hydrocarbon oil pump does not present a hazard and can be used. However, wet pumps risk oil contamination by phosphine and waste management and PPE are required. Any possible air reaction can quickly foul the vacuum pump and could cause a serious incident under higher phosphine concentrations.

Oil sealed (wet) pumps have the potential for oil backstreaming if backstreaming barriers are not maintained. If backstreaming occurs, phosphine (and system manifold) contamination can occur and downtime/clean up can be lengthy. Personnel shall exercise care when performing vacuum pump maintenance, especially for oil sealed (wet) pumps where the oil has absorbed phosphine.

8.3.4 Pressure gauges

Pressure gauges are used to monitor the pressure within the phosphine system. Analog and digital pressure gauges may be used as necessary. However, the pressure gauge dead volume should be considered along with ease of inert gas purge. Gauges shall be placed so they are easily monitored by the operator. Since phosphine is flammable, the use of digital pressure gauges (operated by electricity) should be intrinsically safe (via low voltage or electrical barriers) at low voltage to avoid ignition source potential.

9 Storage and Handling

Good practices for storage and use of phosphine are listed in the following sections.

9.1 General guidelines

- All facilities shall have an emergency response plan that includes the plan for gas releases and emergency evacuation (more information is available in AIGA 004, *Handling gas container emergencies* and CGA P-63, *Disposal of Gases*) [38, 11];
- SDS shall be available for reference;
- Good housekeeping is essential, for example, keeping combustible material away from container storage or use areas;
- Check for insects or foreign material before removing the valve protection cap;
- Phosphine cylinder valve outlet caps shall be installed except when being filled or in use;
- Always secure (nested, palletized, or chained) the containers whether during transportation, storage, or use;
- Never strike an arc (with welding electrode) on the container;
- Never allow containers to contact electrical circuits;
- Never expose containers to corrosive chemicals or vapors, for example, bleach or seawater; and

- Container valves shall be securely closed and valve protection caps in-place during all storage and handling operations.

9.2 Storage

9.2.1 Segregation

- Full and empty containers should be segregated. Containers with residual gas should be treated as if they were full;
- Group containers according to the gas hazard they pose;
- Phosphine shall be stored in well-ventilated areas, away from incompatible gases (oxidizers, pyrophoric gases, etc.), flammable gases, flammable liquids, open flames, sparks, and sources of heat. Incompatible groups shall be separated by required distances or by fire partition. If the local jurisdiction does not specify the distance, at least 6 m (20 ft) separation is recommended. Refer to EIGA Doc 189, *The Calculation of Harm and No-Harm Distances for the Storage and Use of Toxic Gases,* CGA P-1, *Standard for Safe Handling of Compressed Gases in Containers*, and NFPA 55, *Compressed Gases and Cryogenic Fluids Code*, Chapter 7 [39, 40, 24]; and
- A 5 m (16.4 ft) separation of phosphine from electrical devices that are not electrically classified explosion-proof is recommended in the absence of any regulatory direction.

9.2.2 Storage condition

- Practice first in, first out (FIFO) cylinder management;
- Containers should be stored under dry conditions;
- Containers should be stored on level ground to minimize toppling;
- Store containers to prevent the temperature of the containers from exceeding the national guideline;
- The quantity of phosphine stored shall not exceed the design of the facility and shall comply with applicable regulations;
- Cylinders when stored vertically shall be secured (nested, palletized, or chained) to prevent accidental tip over. Standard compressed gas cylinders are designed to be stored vertically. In these cases, precaution shall be taken to ensure that they are secured from falling;
- Other small cylinders such as lecture bottles are more conveniently stored horizontally. However, some local regulations may require vertical storage for toxic liquefied gases, especially when equipped with PRDs;
- Damage limiting construction such as an energy relief wall or blast roof should be incorporated into the room design if flammable gases are stored in large quantities indoors. This wall or roof is designed to allow dissipation of pressure arising from an explosion; and
- There are countries that do not permit outdoor storage of phosphine. In the United States, outdoor storage is allowed under specific circumstances.

9.3 Handling

9.3.1 Essentials

- Personnel handling phosphine cylinders shall be trained;
- Use materials of construction compatible for handling phosphine. This information can be obtained from the SDS and 6.1 and 6.2. of this publication;

- Always wear PPE when handling gas containers. Steel-toed safety shoes, safety glasses with side shields, and leather gloves shall be worn. Additional PPE (for example, flame-resistant/antistatic clothing, respiratory protection such as gas filter or SCBA) shall be considered and determined after a risk assessment; and
- All piping, cabinets, and equipment used to handle phosphine shall be electrically earthed/grounded.

9.3.2 Precautions

- Filling and use of phosphine shall be done in exhausted enclosures or rooms with the discharge treated to less than acceptable levels before emission into the atmosphere. To determine safety distances, refer to EIGA Doc 189 [39];
- Remove valve outlet cap or connection(s) slowly only in exhausted enclosures or using respiratory protection and look for signs of leakage before removing completely;
- Always stand at the side of the valve outlet cap or connection when removing the cap or breaking a connection; and
- Always open valves slowly and carefully.

9.3.3 Checking

9.3.3.1 Container

- Inspect for cleanliness of the valve outlet and pigtails;
- Leak check containers and connection before use;
- Before entry, enclosed spaces containing highly toxic gas, including shipping containers, should be checked for leaks of the toxic gas in the absence of a maintained stationary detection system; and
- If any problems are found, replace and secure the outlet cap and contact your supervisor or the cylinder supplier.

9.3.3.2 Piping

- Always purge piping systems with inert gas:
  - Before introduction of phosphine
  - Before disconnection of phosphine cylinders; and
  - Application of a vacuum is also recommended to aid in the purging system.

9.3.4 Prohibition and restrictions

- Users shall not use adaptors to connect containers;
- Do not overtighten valves, handwheels, connections, or outlet caps. Follow manufacturer’s recommendations;
- Never drag or slide the containers;
- Never lift the container by the valve protection cap;
- Use cylinder trolleys or moving devices to minimize rolling of cylinders;
- Never use cylinders as a roller to move equipment;
- Use of portable electronic devices (for example, cellular phones and walkie-talkies) may be prohibited depending on the electrical classification of the area;

- Prohibit sources of ignition (for example, cigarette smoking);
- Ensure that electrical equipment near phosphine or phosphine mixtures is of the appropriate electrical classification. Consult International Electrotechnical Commission (IEC) or NFPA 70, *National Electrical Code®* (NEC) [41, 25]; and
- Non-sparking tools are recommended to be used when working around phosphine and are required by some jurisdictions.

9.4 Security

Since the consequences of exposure to phosphine are severe and can be widespread, security measures should be implemented to prevent access to phosphine cylinders by unauthorized personnel. For more details, refer to AIGA 003, *Security guidelines,* EIGA Doc 907 *Security guidelines,* or CGA P-50*, Site Security Standard* [42, 43, 44].

A sale policy for phosphine shall be in place. It shall be verified by a thorough review before the purchase being approved and the delivery being made that the customer has a valid reason to purchase phosphine and that the tracking records during shipment of phosphine shall be issued and kept.

10 Gas supply to point-of-use

Gas supply systems shall be located in a well-ventilated area. Gas cabinets or ventilated enclosure shall be used for phosphine supply systems. Provision shall be made to deal with emergencies such as leaks in the supply system.

10.1 Process line control

A dedicated inert purge gas shall be used to purge the phosphine system during commissioning of the system, before and after maintenance, and before and after cylinder change. To ensure that the purge gas supply does not become contaminated with phosphine, a backflow prevention device shall be provided in the purge system. A dedicated purge system may consist of a cylinder, a bundle, or a separate high pressure supply line that may be a part of a larger system. This can avoid the risk of backfeeding via the purge gas system into another incompatible process gas supply system.

Precautions should be taken to ensure that phosphine does not inadvertently come into contact with any oxidizer or a source of ignition.

10.2 Regulators

Regulators are used in phosphine delivery systems to reduce and control the pressure from a high pressure source to a safe working pressure for use. All internal regulator parts should be compatible with phosphine under normal operating conditions.

A regulator for semiconductor applications is functionally the same, but has different features than those of a regulator designed for general duty use. Regulators designed for controlling phosphine in semiconductor processes are typically constructed of 316L stainless steel (SS) or other compatible alloys and may be, at times, electropolished. Phosphine being a pyrophoric gas requires additional safeguards in material construction. Elastomer diaphragms shall not be used to avoid the potential of phosphine diffusion and the potential diffusion of contaminants that are adsorbed on elastomeric diaphragms. Once a regulator has been used in phosphine service, it should not be used for other gas service. The regulator bonnet vent shall be piped to a safe disposal abatement system or safe location. See 6.3.

11 Gas abatement systems

Since phosphine is a highly toxic and pyrophoric material, a gas abatement system shall be used to control any emission whether anticipated or not.

The best method of abatement depends on whether the phosphine is being handled as a pure product, diluted in a mixture, or mixed with other by-products. Full product recovery tends to be practiced at manufacturing facilities. After use in a process, contamination and other issues using chemical abatement may offer better solutions. Such an abatement system could be capable of dealing with other contaminates in the system. Disposal of phosphine by any means shall be done in an environmentally acceptable manner in compliance with all applicable regulations. For more information on disposal of gases, refer to CGA P-63 [11].

A competent person knowledgeable in the handling and processing phosphine should design the equipment.

11.1 Basic principles of abatement

The following are the typical chemical reactions and physical adsorptions:

- Reclamation or recovery via cryogenic recovery
- Oxidation via incineration

  $2\,PH_3 + 4\,O_2 \rightarrow P_2O_5 + 3\,H_2O$

- Oxidation via wet scrubber

  $P_2O_5 + 3\,H_2O \rightarrow 2\,H_3PO_4$ or

  $PH_3 + 4\,OCl^- \rightarrow H_3PO_4 + 4\,Cl^-$

- Absorption/adsorption and reaction on a treated solid (with metallic oxides)

  $3\,CuSO_4 + 2\,PH_3 \rightarrow Cu_3P_2 + 3\,H_2SO_4$ or

  $6\,FeCl_3 + PH_3 + 3\,H_2O \rightarrow 6\,FeCl_2 + H_3PO_3 + 6\,HCl$

- Physical adsorption on solid media

  $PH_3 + C \rightarrow C[PH_3]\,(C: \text{Activated Carbon})$

11.1.1 Reclamation or recovery

Reclamation of phosphine is not a disposal method, as usually understood. This technique is for reclaiming residual gas and returning the phosphine safely to suitable containers. Once reclaimed, phosphine has to be reprocessed, purified, and analyzed before being reused. However, due to the pyrophoric characteristic of phosphine, the typical phosphine user should not perform reclamation of phosphine.

All types of reclamation are strongly recommended both in the interests of the environment and the conservation of materials and energy.

The supplier of the material who has the necessary product handling and container filling expertise is best suited for reclamation of gaseous phosphine. Phosphine should not be reclaimed to a container and returned without the written authority of the owner of the container.

Some users collect the phosphine into cylinders for treatment offsite.

11.1.2 Oxidation via incineration

While burning the phosphine molecule can be done satisfactorily, capturing the oxidized by-product requires additional equipment. When phosphine burns, it produces a dense white cloud of phosphorus pentoxide (P_2O_5) fumes. Secondary neutralization and cleanup of the phosphorus oxides or oxyacids is critical to employee protection.

For follow up abatement actions for the oxidized phosphine by-product generated, refer to 11.1.3.

11.1.3 Oxidation via wet scrubber

The typical wet scrubber used for phosphine is a counter current packed tower.

Suitable arrangements should be made to ensure the system is monitored and shut down in the event of waste gas breakthrough or uncontrolled flammable concerns. Because the phosphine can autoignite on contact with air, even with low ppm phosphine concentrations (much less than 1% concentration to avoid the autoignition point). Factors to be taken into account when utilizing a wet scrubber include:

- Phosphine input flow rate;
- pH control of the absorbent liquor;
- Phosphine concentrations in ppm and much less than 1%;
- Temperature of the absorbent liquor;
- Provisions should be made to monitor both the inlet and outlet stream for phosphine concentration;
- Flow control should be installed in the waste phosphine stream to enable the gas flow to be matched to the capacity of the scrubber;
- Pressure control should be installed in the waste phosphine stream to enable the gas flow to be matched to the operating capacity of the scrubber;
- Use of inert purge as necessary to facilitate process line clean up; and
- Consideration of discharge point from the scrubber exhaust, well away from air intake systems, downdrafts, and personnel areas.

To prevent the risk of absorbent liquor sucking back into the system, controls should be in place. Consideration should be given to the use of non-sparking equipment as phosphine is flammable. To ensure safe and efficient performance, monitoring of process conditions as well as the scrubber gas discharge effectiveness should be carefully considered.

Oxidizing solutions may consist of liquid solutions of potassium permanganate or sodium hypochlorite or caustic solutions and work well for low concentrations of phosphine.

Use of a wet scrubber with higher concentrations of phosphine (greater than 1%) should be carefully engineered to address the pyrophoric characteristic of phosphine.

11.1.4 Absorption/adsorption and reaction on a treated solid (with metallic oxides)

Phosphine is fed directly into a vessel containing a bed of solid adsorbent. It is critical to keep the gas stream under an inert environment to prevent autoignition of the pyrophoric phosphine. There are many solid absorbents available that strongly and readily absorb/adsorb and react with phosphine. Simplicity and portability of a small solid-state absorber may favor the choice of this method under certain emergency conditions. However, capacity is very limited to the amount of phosphine that can be absorbed/adsorbed on the media.

In this publication, the terms absorption and adsorption are used interchangeably.

Factors to be taken into account when utilizing the solid-state absorber include:

- Required phosphine disposal rate;
- Quantity of phosphine to be disposed;
- Acceptable frequency of changing the absorbent bed or system;
- Concentration of the phosphine stream delivered into the absorber bed;

- Temperature rise effects from reaction between the phosphine and the absorbent;
- Distribution system within the absorber bed to prevent channeling and premature breakthrough of unreacted phosphine;
- Absorbent particle size: Generally small particles give a high contact area, which corresponds to greater efficiency. However, small particle sizes can lead to pluggage or high pressure drops and a tendency of channeling and premature breakthrough of unreacted phosphine;
- Provisions should be made to monitor both the inlet and outlet stream for phosphine concentration;
- Flow control should be installed in the waste phosphine stream to enable the gas flow to be matched to the capacity of the absorber bed;
- Pressure control should be installed in the waste phosphine stream to enable the gas flow to be matched to the operating capacity of the absorber bed;
- Use of inert purge as necessary to facilitate process line clean up; and
- Consideration of discharge point from the absorber bed exhaust, well away from air intake systems and personnel areas.

11.1.5 Physical adsorption on solid media

Phosphine is fed directly into a vessel containing a bed of solid media. It is critical to keep the gas stream under an inert environment to prevent autoignition of the pyrophoric phosphine gas. There are many types of solid media available that adsorb phosphine. Adsorption capacity varies with solid type, for example, using granular activated carbon, phosphine capacities approach to 1% to 3% (by weight) of the total carbon weight.

Off-gassing of phosphine from solid media can occur so it is important to have controls and phosphine monitoring in place. Heat is generated during phosphine adsorption as a function of adsorption rate and phosphine concentration. Temperature profiles through the bed containing solid media that are flammable shall be monitored to prevent the solid media from igniting.

Simplicity and portability of a small solid-state absorber may favor the choice of this method under certain emergency conditions. Factors to be taken into account when adsorption on carbon are similar as those identified in 11.1.4.

11.2 User requirements

All personnel involved with the handling of phosphine shall be trained in the procedures for abatement control used at the site. A thorough knowledge of the product and its associated hazards is required. This would include, but is not limited to:

- physical characteristics and toxicological properties of phosphine;
- physical properties of abatement material; and
- operating documents.

11.3 Waste stream disposal

Dispose in accordance with all applicable regulations. Disposal of pure phosphine is considered a toxic hazardous waste. Waste streams can contain phosphorous oxides or other metallic oxides and be considered a toxic, hazardous waste. Management and control of waste is required. Refer to local and national regulations as they apply to waste management.

11.4 Waste management

Nearly every operational process leaves behind some residual waste. Accelerating pressure on conserving natural resources, the impact of new technologies on resource use, increasing waste generation, and the need for more sustainable approaches to using natural resources represent new challenges to our society.

Local and government authorities may regulate all this waste under various programs. Only those companies licensed by the government are allowed to process these wastes. Evaluating, selection, and monitoring of the waste disposal company is a very important program with which the hazardous waste generator shall comply . Full documentation of hazardous waste generation, shipments, and final processing is critical to ensure compliance and control.

The goals of waste management are to:

- protect society from the hazards of waste disposal;
- conserve energy and natural resources by recycling and recovery;
- reduce or eliminate waste; and
- clean up waste that could have spilled, leaked, or been improperly disposed.

Users shall promote and encourage the use of combined methods to manage solid waste.

These methods are:

- Source reduction or waste prevention—any practice that reduces the amount or toxicity of waste generated;
- Recycling that conserves disposal capacity and preserves natural resources by preventing potentially useful materials from being thrown away;
- Landfilling—landfills are well-engineered facilities that are located, designed, operated, and monitored to ensure compliance with regulations. Solid waste landfills shall be designed to protect the environment from contaminants that can be present in the solid waste stream; and
- Waste combustion—waste combustion can reduce the quantity of waste considerably. However, concerns of what types/quantities of toxics exit the scrubbers can become a local debate.

12 Emergency response

12.1 Preparation

The purpose of preparation is to establish a system and assign responsibility in the event of an incident or other emergency situation.

The phosphine user shall have procedures in place to address emergency situations that affect public health and environmental concerns in the event of an incident. The emergency plan identifies potential emergencies that are reasonably foreseeable, and specifies actions to prevent, prepare for, respond to, and recover from these emergencies. The emergency plan includes methods used to prevent and mitigate environmental impacts, which could be associated with emergency situations.

The emergency plan shall be reviewed and updated periodically as applicable. Updated copies are provided to the local emergency planning committees and government officials as applicable. Training is provided for all personnel who may be involved with emergency response.

The emergency plan is tested periodically to ensure its effectiveness, including tests of related leak detection equipment, PPE, protective systems, and emergency communications. The emergency contact list is reviewed and updated with each change as applicable. Latest versions shall be maintained.

Phosphine incidents vary considerably and the emergency plan shall consider the chemicals and quantities involved, types of hazard, response efforts required, number of responders needed, and effects produced. Incidents may require immediate control measures (emergency) or long term activities (remedial action) to restore acceptable conditions. The plan activities are divided into interacting elements:

- recognition;
- evaluation;
- control;
- information; and
- safety.

12.1.1 Recognition

Recognizing the type and degree of the hazard presented by phosphine is usually one of the first steps in responding to an incident.

12.1.2 Evaluation

The responder can predict the behavior and anticipated problems associated with the material. Anticipated problems that extend beyond the company property may require support/involvement from local officials. The SDS or other product information can be used to help evaluate the nature and affect to the environment and public health.

12.1.3 Control

Control refers to those methods that prevent or reduce the impact of an incident. Control is addressed by remedial action in the form of documented procedures (plans). It is the responsibility of each facility and its personnel to ensure procedures are in place and followed.

12.1.4 Information

An integral component of response is information. Notification of employees, local emergency response officials, corporate compliance, corporate safety, and government agencies is completed per established procedures. All incidents are documented and reviewed by the safety committee and/or emergency response team to determine the root cause, to implement the corrective actions of the incident, the effectiveness of the response, corrective action warranted, and notification to prevent repeat occurrence. Reference documents may include:

- SDS;
- Emergency plan;
- Standard operating procedures (SOPs);
- PHA reviews; and
- Technical gas data books.

12.1.5 Safety

All hazardous material responses pose varying dangers (health and safety) to responders, the environment, and the neighborhood. Safety considerations are an input to every activity that is undertaken and are an outcome of each response taken. It is the responsibility of all employees to work in a safe manner and follow established safety rules and regulations.

12.2 Response

Ensure that personnel responding to an emergency situation are trained and wearing required PPE before attempting any emergency response. Only those employees trained in responding to an incident shall do so and only to the level of their training. The company's emergency plan shall identify the procedures and policies that will be followed in an emergency response [33, 34, 38].

Offsite response requires interaction with other company's emergency plan. It could occur during transportation or at the customer site. Whether on-site or offsite, detailed information on how to handle such issues can be found in AIGA Doc 004 and the *Emergency Response Guidebook* (ERG) [38, 45, 21]. Also refer to CGA P-63 [11].

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