

Occupational Health Guideline for Phosphine

INTRODUCTION

This guideline is intended as a source of information for employees, employers, physicians, industrial hygienists, and other occupational health professionals who may have a need for such information. It does not attempt to present all data; rather, it presents pertinent information and data in summary form.

SUBSTANCE IDENTIFICATION

- Formula: PH_3
- Synonyms: Hydrogen phosphide; phosphorus hydride; phosphorated hydrogen
- Appearance and odor: Colorless gas with a characteristic fishy odor.

PERMISSIBLE EXPOSURE LIMIT (PEL)

The current OSHA standard for phosphine is 0.3 part of phosphine per million parts of air (ppm) averaged over an eight-hour work shift. This may also be expressed as 0.4 milligram of phosphine per cubic meter of air (mg/m^3).

HEALTH HAZARD INFORMATION

- **Routes of exposure**
Phosphine can affect the body if it is inhaled.
- **Effects of overexposure**
 1. **Short-term Exposure:** Inhalation of phosphine may cause coughing, shortness of breath, and severe breathing difficulty. This breathing difficulty may not appear until several hours after exposure has ceased. It may also cause thirst, nausea, vomiting, stomach pain, diarrhea, back pain, a feeling of coldness, fainting, and death.
 2. **Long-term Exposure:** Not known.
 3. **Reporting Signs and Symptoms:** A physician should be contacted if anyone develops any signs or symptoms and suspects that they are caused by exposure to phosphine.

- **Recommended medical surveillance**

The following medical procedures should be made available to each employee who is exposed to phosphine at potentially hazardous levels:

1. **Initial Medical Screening:** Employees should be screened for history of certain medical conditions (listed below) which might place the employee at increased risk from phosphine exposure.

—Chronic respiratory disease: In persons with impaired pulmonary function, especially those with obstructive airway diseases, the breathing of phosphine might cause exacerbation of symptoms due to its irritant properties.

2. **Periodic Medical Examination:** Any employee developing the above-listed conditions should be referred for further medical examination.

- **Summary of toxicology**

Phosphine gas is a severe pulmonary irritant and an acute systemic poison; it has caused both sudden death and delayed death due to pulmonary edema. Workers exposed intermittently to concentrations up to 35 ppm, but averaging below 10 ppm, complained of nausea, vomiting, diarrhea, chest tightness and cough, headache, and dizziness; no evidence of cumulative effects was noted. Single severe exposures cause similar signs and symptoms, as well as excessive thirst, muscle pain, chills, sensation of pressure in the chest, dyspnea, syncope, and stupor.

CHEMICAL AND PHYSICAL PROPERTIES

- **Physical data**
 1. Molecular weight: 34.04
 2. Boiling point (760 mm Hg): $-87.8\text{ C } (-126\text{ F})$
 3. Specific gravity (water = 1): Liquid = 0.75 at boiling point
 4. Vapor density (air = 1 at boiling point of phosphine): 1.17
 5. Melting point: $-134\text{ C } (-209\text{ F})$
 6. Vapor pressure at 20 C (68 F): Greater than 1 atmosphere

These recommendations reflect good industrial hygiene and medical surveillance practices and their implementation will assist in achieving an effective occupational health program. However, they may not be sufficient to achieve compliance with all requirements of OSHA regulations.

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Public Health Service Centers for Disease Control
National Institute for Occupational Safety and Health

U.S. DEPARTMENT OF LABOR
Occupational Safety and Health Administration

7. Solubility in water, g/100 g water at 20 C (68 F): 0.04

8. Evaporation rate (butyl acetate = 1): Not applicable

• **Reactivity**

1. Conditions contributing to instability: Overheated cylinders may explode.

2. Incompatibilities: Contact with air or any other oxidizer such as chlorine, etc., will cause ignition of phosphine. Phosphine reacts with acids, halogenated hydrocarbons, and moisture.

3. Hazardous decomposition products: Toxic gases and vapors (such as oxides of phosphorus, phosphoric acid mist, and hydrogen) may be released in a fire involving phosphine.

4. Special precautions: Phosphine is an unusually reactive and poisonous substance, and is usually handled in small quantities only.

• **Flammability**

1. Flash point: Not applicable

2. Autoignition temperature: Spontaneously flammable at room temperature

3. Flammable limits in air, % by volume: Data not available

4. Extinguishant: Shut off flow of gas. Carbon dioxide may extinguish the fire, but it will re-ignite spontaneously. If the fire is in a safe location, let the fire burn.

• **Warning properties**

1. Odor Threshold: May reports an odor threshold for phosphine of 0.02 ppm. Although Patty states that the limit of perceptibility is 1.5 to 3.0 ppm, the experience of industrial users confirms the odor threshold given by May.

2. Eye Irritation Level: Grant states that "although numerous instances of poisoning of human beings and experimental animals (from phosphine) have been reported, no characteristic ocular or visual effects are known."

3. Evaluation of Warning Properties: Since the odor of phosphine can be detected at a concentration well below the permissible exposure limit, it is treated as a material with good warning properties.

MONITORING AND MEASUREMENT PROCEDURES

• **General**

Measurements to determine employee exposure are best taken so that the average eight-hour exposure is based on a single eight-hour sample or on two four-hour samples. Several short-time interval samples (up to 30 minutes) may also be used to determine the average exposure level. Air samples should be taken in the employee's breathing zone (air that would most nearly represent that inhaled by the employee).

• **Method**

An analytical method for phosphine is in the *NIOSH Manual of Analytical Methods*, 2nd Ed., Vol. 5, 1979, available from the Government Printing Office, Washington, D.C. 20402 (GPO No. 017-033-00349-1).

RESPIRATORS

• Good industrial hygiene practices recommend that engineering controls be used to reduce environmental concentrations to the permissible exposure level. However, there are some exceptions where respirators may be used to control exposure. Respirators may be used when engineering and work practice controls are not technically feasible, when such controls are in the process of being installed, or when they fail and need to be supplemented. Respirators may also be used for operations which require entry into tanks or closed vessels, and in emergency situations. If the use of respirators is necessary, the only respirators permitted are those that have been approved by the Mine Safety and Health Administration (formerly Mining Enforcement and Safety Administration) or by the National Institute for Occupational Safety and Health.

• In addition to respirator selection, a complete respiratory protection program should be instituted which includes regular training, maintenance, inspection, cleaning, and evaluation.

COMMON OPERATIONS AND CONTROLS

The following list includes some common operations in which exposure to phosphine may occur and control methods which may be effective in each case:

Operation	Controls
Use as a doping agent in manufacture of solid-state components for electronic circuits and in manufacture of lasers	Local exhaust ventilation; personal protective equipment
Use in preparation of alkyl and aryl phosphonium halides in textile treatment; use in organic intermediates; use as curing catalysts for epoxy resins, polymerization initiators, and condensation catalysts	Process enclosure; local exhaust ventilation; personal protective equipment
Use as a fumigant for stored grain	Local exhaust ventilation; personal protective equipment

Liberation during drilling, machining, and grinding of ductile iron; during quenching of alloys or sludges; during cleaning of rusty metal in phosphoric acid; and during welding of steel coated with phosphate rust-proofing agents

Local exhaust ventilation; personal protective equipment

Liberation during manufacture and use of acetylene; during extraction of phosphorus, and use of inorganic phosphorus compounds use of phosphorus sesquisulfide in manufacture of safety matches and calcium phosphide in pyrotechnics

Local exhaust ventilation; personal protective equipment

EMERGENCY FIRST AID PROCEDURES

In the event of an emergency, institute first aid procedures and send for first aid or medical assistance.

• Breathing

If a person breathes in large amounts of phosphine, move the exposed person to fresh air at once. If breathing has stopped, perform artificial respiration. Keep the affected person warm and at rest. Get medical attention as soon as possible.

• Rescue

Move the affected person from the hazardous exposure. If the exposed person has been overcome, notify someone else and put into effect the established emergency rescue procedures. Do not become a casualty. Understand the facility's emergency rescue procedures and know the locations of rescue equipment before the need arises.

LEAK AND DISPOSAL PROCEDURES

• Persons not wearing protective equipment and clothing should be restricted from areas of leaks until cleanup has been completed.

• If phosphine is leaked, the following steps should be taken:

1. Ventilate area of leak to disperse gas.
2. Stop flow of gas. If source of leak is a cylinder and the leak cannot be stopped in place, remove the leaking cylinder to a safe place in the open air, and repair the leak or allow the cylinder to empty.

• Waste disposal method:

Phosphine may be disposed of by burning in a suitable combustion chamber equipped with an appropriate effluent gas cleaning device.

REFERENCES

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RESPIRATORY PROTECTION FOR PHOSPHINE

Condition	Minimum Respiratory Protection* Required Above 0.3 ppm
Gas Concentration	
3 ppm or less	Any chemical cartridge respirator with a cartridge(s) providing protection against phosphine. Any supplied-air respirator. Any self-contained breathing apparatus.
15 ppm or less	A chemical cartridge respirator with a full facepiece and a cartridge(s) providing protection against phosphine. A gas mask with a chin-style or a front- or back-mounted canister providing protection against phosphine. Any supplied-air respirator with a full facepiece, helmet, or hood. Any self-contained breathing apparatus with a full facepiece.
200 ppm or less	A Type C supplied-air respirator operated in pressure-demand or other positive pressure or continuous-flow mode.
Greater than 200 ppm or entry and escape from unknown concentrations	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode. A combination respirator which includes a Type C supplied-air respirator with a full facepiece operated in pressure-demand or other positive pressure or continuous-flow mode and an auxiliary self-contained breathing apparatus operated in pressure-demand or other positive pressure mode.
Fire Fighting	Self-contained breathing apparatus with a full facepiece operated in pressure-demand or other positive pressure mode.
Escape	Any gas mask providing protection against phosphine. Any escape self-contained breathing apparatus.

*Only NIOSH-approved or MSHA-approved equipment should be used.