EIGA

CODE OF PRACTICE ARSINE

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EUROPEAN INDUSTRIAL GASES ASSOCIATION AISBL

AVENUE DE L'ASTRONOMIE 30 • B – 1210 BRUSSELS
Tel: +32 2 217 70 98
E-mail: info@eiga.eu • Internet: www.eiga.eu

CODE OF PRACTICE ARSINE

As part of a programme of harmonisation of industry standards, the European Industrial Gases Association (EIGA) has issued *Code of Practice Arsine*, jointly produced by members of the International Harmonisation Council and originally published by the Asia Industrial Gases Association, (AIGA) as AIGA 050, *Code of Practice Arsine* and the Japanese Industrial and Medical Gases Association (JIMGA) as JIMGA-T-S/37, *Arsine*.

This publication is intended as an international harmonised publication for the worldwide use and application by all members of the Asia Industrial Gases Association (AIGA), Compressed Gas Association (CGA), EIGA, and Japan Industrial and Medical Gases Association (JIMGA). Regional editions have the same technical content, however, there are editorial changes primarily in formatting, units used and spelling. Regional regulatory requirements are those that apply to Europe.

EUROPEAN INDUSTRIAL GASES ASSOCIATION AISBL
Avenue de l'Astronomie 30 B 1210 Brussels Tel +32 2 217 70 98
E-mail: info@eiga.eu Internet: www.eiga.eu

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Note: Technical changes from the previous edition are underlined

1 Introduction

Arsine is a toxic, colourless gas with a garlic-like odour. It is shipped as a liquefied compressed gas under its own vapour pressure of 1.515 MPa, abs (219.7 psia). It is also supplied in a gaseous state, diluted with other gases under pressure. It is flammable and highly toxic. The issue of the safe handling of arsine is a very important and relevant topic to the compressed gas industry as well as the user community of this specialty gas.

Arsine 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 arsenide layer. Arsine can be inadvertently generated in mining and manufacturing processes involving arsenic compounds and paints and herbicides containing arsenic compounds.

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

NOTE In this publication, arsine 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 arsine and its handling equipment. The publication includes guidance for design of equipment, selection of cylinders and valves, and handling controls and safety practices. Guidelines on the operational steps associated with the use of arsine and arsine mixtures as well as fire protection, gas detection, ventilation, and related safeguards are also included. The manufacture, purification, and analysis of arsine is 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 arsine where the consequences of improperly handling arsine could cause injury, death, and/or facility damage. This publication provides an understanding of the potential hazards involved in handling arsine and the guidelines to take 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, and non-return valves (check valves) used with compressed gas.

3.2.3 Containers

Vessels of various shapes, sizes, and materials of construction such as cylinders, portable tanks, or stationary tanks, and of designs meeting the specifications of 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.

3.2.4 Critical temperature

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

3.2.5 Cylinder

Transportable pressure receptacle having a water capacity that does not exceed 150 L (5.3 ft^3) that can be filled with a gas under pressure.

3.2.6 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.

3.2.7 Flammable gas

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).

3.2.8 Gas

Gas or gas under pressure as defined in the 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 vapour pressure greater than 300 kPa; or (b) Is completely gaseous at 20 °C at a standard pressure of 101.3 kPa.

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 parts per million (ppm) for a 1 hr exposure, which includes gases classified as Acute Toxicity Category 1 according to UN GHS [2]. Refer to LC_{50} definition.

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 may be in serious danger from physical hazards such as fire, explosion, or chemical exposure.

NOTE Generally, only firefighters and emergency response team who are members of a specialized hazmat team will enter the hot zone.

3.2.14 Inert gas

Gas that is not toxic, does not 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 animal population.

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

3.2.16 Lower flammable limit or lower flammability limit (LFL)

Lower limit of flammability (point at which a flame just starts to propagate) of a gas or vapour at ordinary ambient temperatures and pressures expressed in percent of the gas or vapour 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 their 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 (PRD)

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 over pressurization.

3.2.21 Safety data sheet (SDS)

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

3.2.22 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).

3.2.23 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 [3].

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 hr exposure, which includes gases classified as Acute Toxic Category 2 and 3 according to UN GHS [2].

3.2.25 Upper flammable limit or upper flammability limit (UFL)

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

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

3.2.26 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.

3.2.27 Valve protection cap

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

4 Gas properties

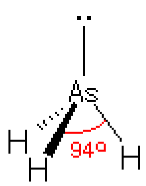
4.1 General

Arsine is a metal hydride gas with the chemical formula AsH_3. It is highly toxic with an LC50 1 hour of 178 ppm and LC_{50} 4 hour of 89 ppm. In addition to its toxicity, it is also flammable and is capable of forming flammable mixtures when mixed with air. It is not considered to be corrosive. It possesses a garlic-like odour [4, 5, 6].

Arsine is routinely shipped in seamless steel or aluminium alloy cylinders. For reasons of safety, cylinders used for arsine will have a test pressure of 4.2 MPa (609 psi). Some national bodies mandate higher test pressures. The vapour pressure of arsine is approximately 1.515 MPa, abs at 21.1 °C (219.7 psia at 70 °F) [4].

Table 1 shows properties of arsine.

Table 1 Properties of arsine

Property	SI Units	U.S. Units	Reference
Synonyms	arsenic trihydride, hydrogen arsenide, arsenic hydride, arsenous hydride		
Chemical formula	AsH_3		
CAS number	7784-42-1		
UN number	UN 2188		
Physical state	Gas		
Colour	Colourless		[4, 5, 6]
Odour	Garlic-like odour		[4, 5, 6]
Molecular weight	77.945		
Boiling point at 1 atm	–62.5 °C	–80.5 °F	[4]
Freezing point at 1 atm	–116.9 °C	–178.4 °F	[4]
Decomposition temperature range	230 °C to 300 °C	446 °F to 572 °F	[4, 6, 10, 11]
Critical temperature	99.9 °C	211.8 °F	[4]
Critical pressure	6599 kPa, abs	957 psia	[4]
Critical volume	132.5 cm^3/mol	8.086 in^3/mol	[4]
Critical density	588.3 kg/m^3	36.73 lb/ft^3	[4]
Critical compressibility factor	0.274		[10]
Density of liquid at 21.1 °C (70 °F)	1.335 kg/m^3	83.55 lb/ft^3	[4]
Density of gas at 20 °C (68 °F) and 1 atm	3.24 kg/m^3	0.2025 lb/ft^3	[4]
Specific density of the gas at 21.1 °C (70 °F) and 1 atm (air=1)	2.69		[4]
Specific volume of the gas at 21.1 °C (70 °F) and 1 atm	5.0 ft^3/lb		
Vapour pressure at 21.1 °C (70 °F)	1.515 Mpa, abs	219.7 psia	[4]
Solubility in water (vol gas/vol water)	0.23 in^3/in^3		[4]
pH	Not applicable		
Volatility	Not applicable		
Odour threshold (varies with impurities)	0.5 ppm		[11, 13]
Evaporation rate	Not applicable		
Flash point	Not applicable		
Flammable limits in air (% by volume)	3.9% to 78%		[4, 16]
Latent heat of vaporization at –62.48 °C (–80.46 °F)	214 kJ/kg	92 Btu/lb	
Autoignition temperature	285 °C	545 °F	[8, 9]
Molecular shape	trigonal pyramidal		
Dipole moment	0.20 D		[3]
Standard enthalpy of formation at 25 °C, $\Delta_f H^0_{gas}$	+66.44 kJ/mol		[3]
Structure			

4.2 Physical properties

Decomposition of arsine is possible in the presence of light.

Arsine is decomposed by the effect of ultraviolet rays and it decomposes more rapidly as the ultraviolet ray intensity increases [7].

Although arsine has positive heat of formation (+66.44 kJ/mol), stability tests showed that even with input of 100 J decomposition did not take place in the cylinder.

Avoid sources of ignition, sparks, and flames due to the flammable properties of arsine. Arsine poses a severe fire hazard and a moderate explosion risk. Refer to Table 1.

A flammable mixture of arsine in air requires an ignition source to ignite because it is not pyrophoric. The autoignition temperature of arsine is 285 °C (545 °F) [8, 9].

Arsine is stable at room temperature and begins to decompose at approximately 230 °C (446 °F) with complete decomposition at approximately 300 °C (572 °F) [5, 10, 11, 12, 13].

4.3 Chemical properties

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

Arsine is not known to polymerize.

4.4 Flammability properties

Refer to 5.1.

4.5 Health properties

Refer to 5.2.

4.6 Environmental properties

With controls, releases of arsine can be minimized. If arsine enters the environment through an accidental release, it can contaminate land, water, and air. Many countries have strict regulations and measures to be taken if a release occurs. The users of arsine shall review applicable regulations.

- Arsenic compounds including arsine are considered hazardous air pollutants (HAPs). These pollutants are known or suspected to cause cancer or other serious health effects such as reproductive effects and birth defects or adverse environmental effects [14];

- Arsine 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 fulfil this mission, local governments may require that the person or organization responsible for arsine use notify the government when the amount on-site reaches a predetermined limit; Arsine is listed in Seveso III, Annex I, part 2, named substances.

- If a release or spill of arsine occurs, the government can require additional notifications be made. These requirements vary by governments;

- 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 can vary considerably depending upon the type and extent of exposure. Arsine 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 risk. 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.

Table 2 shows the published data for arsenic.

Figure 1 and Figure 2 show the arsine vapour pressure versus temperature using SI Units and U.S. customary units.

Table 2 Published data for arsenic

Arsenic CAS number: 7784-42-1			
Risk assessment values or standards	**Value**	**Units**	**Reference**
Inhalation cancer risk value (potency)	0.0043	ug/m^3	[16]
Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) reporting limit	45 100	kg lb	[17]
Ingestion cancer risk value (potency)	1.5	mg/kg/day	[16]
Ingestion noncancer risk value (reference dose)	0.0003	mg/kg/day	[16]
National water quality standard	0.01	mg/L	[18]

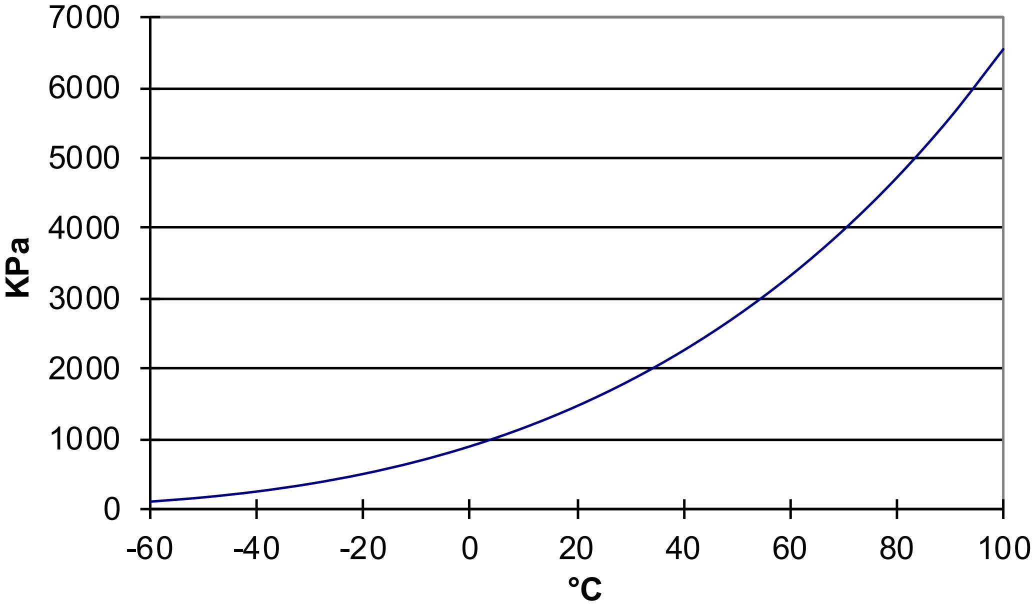


Figure 1 Arsine pressure versus temperature (SI units)

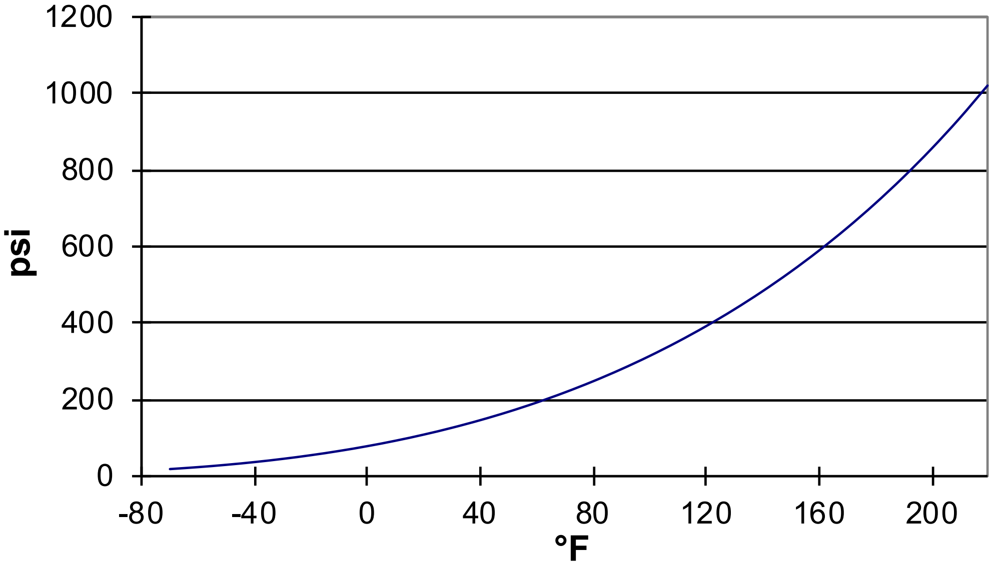


Figure 2 Arsine pressure versus temperature (U.S. Units)

5 Gas major hazards

5.1 Fire and explosion hazards [19, 20, 21, 22]

Arsine is flammable. By-products of arsine combustion are toxic arsenic oxides (solids). These arsenic oxides can be absorbed by the skin. Therefore, personnel shall wear protective clothing and self-contained breathing apparatus (SCBA) when fighting arsine fires. Only trained personnel should respond to arsine 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.

In order for an arsine ignition to occur, three conditions need to occur simultaneously:

- concentration of arsine is within its flammable limits;
- presence of sufficient air or an alternate oxidizing source; and
- existence of an ignition source.

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

Arsine has a flammable range nearly equivalent to that of hydrogen.

Arsine can begin to slowly decompose into its elements of arsenic and hydrogen at temperatures of 230 °C to 240 °C (446 °F to 464 °F) [4, 6, 10, 11]. A temperature of 300 °C (572 °F) is recognized as the temperature where decomposition is fully accelerated [5, 10, 11, 12, 13].

If the flow of arsine cannot be stopped, let it burn until the fire stops naturally, keeping adjacent cylinders and equipment cool. If an arsine fire is extinguished and the flow of arsine is not stopped, a hazardous combustible mixture can continue to form. It is possible that the mixture can be ignited, 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 an arsine fire shall not be extinguished until the flow of arsine is stopped, water sprays should be used to extinguish any secondary fire and to prevent the spread of fires. The arsine containing equipment can be kept cool by water sprays to decrease the rate of arsine release or to prevent further damage. This is best done at a distance. Water used in firefighting could become contaminated 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 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 toxic properties of arsine. They also should communicate and cooperate with personnel who are familiar with materials in the area of the emergency. Unexpected conditions can require special actions.

If a cylinder of arsine or supply piping system is ruptured so that quantities of arsine 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—As a result of a fire, oxides of arsenic (for example, arsenic trioxide and arsenic pentoxide) can form, can deposit as a dust over the affected facility, and can be carried downwind of the fire. Such oxidized arsenic is toxic by inhalation, ingestion, and absorption.

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

5.2 Toxicology

5.2.1 Arsine exposure

Arsine has a garlic-like odour with an odour threshold of about 0.5 ppm [6, 23]. Cases of arsine intoxication have been recorded without the subject being aware of exposure.

The primary route of entry is inhalation. Arsine is a highly toxic systemic poison. The primary effect is massive destruction of red blood cells resulting in acute kidney failure. The odour of arsine is not always detected during serious exposures as symptoms can be delayed. All exposure victims should be evaluated at a medical facility. Symptoms of acute exposure can be delayed from 2 hours up to 48 hours depending on exposure intensity.

The literature in the following sections has been reporting the symptoms of arsine poisoning by exposure for a long time, but its acute toxicities to humans are not known well. In this publication, some reports are shown for the reference as follows.

Wald and Becker reported that exposures to 250 ppm of arsine are instantly lethal, exposure to 25 ppm to 50 ppm is lethal after 30 minutes, and 10 ppm is lethal after longer exposures [12].

Henderson and Haggard reported that 250 ppm concentrations of arsine could be fatal after exposure for 30 min; 16 ppm to 60 ppm concentrations could be dangerous after exposure for 30 min to 1 hr; 3 ppm to 10 ppm can cause slight symptoms after exposure for several hours [24].

NOTE Arsine exposure is primarily inhalation and is not absorbed by the skin. Arsenic oxide after burning or oxidizing arsine can be absorbed by the skin.

For more information, see the gas supplier's safety data sheet (SDS) [3].

The major hazards associated with exposure to arsine are massive hemolysis and associated acute renal failure. Symptoms can be delayed up to two days and can include:

- headache;
- dizziness;
- shortness of breath on exertion;
- garlic-like odour of breath;
- numbness, coldness, tingling of hands and feet;
- nausea;
- vomiting,
- abdominal cramping;
- abdominal tenderness and rigidity;
- bronzing of the skin;

- puffiness of the jaws and eyelids;
- pulmonary oedema;
- jaundice and hepatomegaly;
- anaemia and leukocytosis;
- shock; and
- delirium and coma [5, 25, 26].

Table 3 shows regulatory exposure information for arsine.

NOTE Combustion products resulting from the exposure of arsine to a flame are toxic.

Within the body, arsine is oxidized to other arsenic species. Arsenic and arsenic compounds are recognized by many countries as carcinogenic to humans and induce genotoxic effects in experimental systems and in humans.

Measurement of arsenic levels in the urine (greater than 0.2 mg/L) is a diagnostic test for exposure.

Table 3 Regulatory exposure information for arsine

Arsine CAS number: 7784-42-1			
	Value	**Units**	**Reference**
LC_{50} rat 1 hour	178	ppm	[27]
Time-Weighted Average-Permissible Exposure Limit (TWA-PEL)	0.050 0.2	ppm mg/m^3	[11] [25]
Recommended Exposure Limit Ceiling 15 minutes	0.002	mg/m^3	[11, 24]
NIOSH Immediate Danger to Life and Health (IDLH) Concentration	3	ppm	[11, 24]
Acute Exposure Guideline Levels (AEGLs) AEGL-1 (30 min) AEGL-2 (30 min) AEGL-3 (30 min)	 NR 0.21 0.63	 ppm ppm ppm	[28]
NOTES 1 OSHA limits are the legal exposure limits allowed by U.S. law and are enforceable. 2 NR: Not recommended 3 For occupational exposure limits (OELs) for European countries, refer to EIGA's SDS 005 for arsine at www.eiga.eu			

5.2.2 Medical treatment for arsine exposure

There is no antidote for arsine poisoning. Treatment is symptomatic and consists of measures to support respiratory, vascular, and renal function. If haemolysis develops, urinary alkalinisation is initiated.

Detailed prehospital and hospital management practices for treatment of arsine exposures can be found in *Medical Management Guidelines for Arsine* [6].

Victims exposed only to arsine gas do not need decontamination before medical treatment as they pose no serious risks of secondary contamination to personnel outside the hot zone. Although small amounts of arsine can be trapped in the victim's clothing or hair after an overwhelming exposure, these quantities are not likely to create a hazard for response personnel outside the hot zone.

6 Gas handling equipment – General considerations

The equipment used to handle arsine 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 arsine (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 arsine systems. As arsine is a highly toxic and flammable gas, consideration should be given to the following issues when designing systems to handle arsine:

- 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 vents; and
- regulators.

6.1 Materials of construction

Selection of metals and non-metals shall be made taking into account the compatibility guide in Table 4. It is extremely important that all gas control equipment is 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 arsine service and is thought to be compatible, it should be tested first to confirm suitability prior to use under defined temperature, pressure, and flow conditions.

Table 4 provides a material compatibility guide that is prepared for use with dry arsine at normal operating temperature of 21.1 °C (70 °F). This information may vary if different operating conditions exist.

Table 4 Material compatibility guide [29]

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

2 If used, some plastics and elastomers absorb arsine.

3 ISO 11114-1, *Gas cylinders—Compatibility of cylinder and valve materials with gas contents—Part 1: Metallic materials* addresses concerns for hydrogen embrittlement and it is also acknowledged that UN Model Regulations P-200 requires an "H" stamp for steel cylinders charged with arsine; however, there is no conclusive proof that arsine is an embrittling gas [30, 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 arsine under normal or upset conditions. Refer to vendor supplied data.

6.3 System pressures and overpressure protection

System pressures are low due to the low vapour pressure of arsine, which is 1.515 MPa at 21.1 °C (219.7 psia at 70 °F). Design should address conditions where system pressure can be subjected to sub atmospheric conditions and draw in air or other gas stream contamination that is used in the system. Due to the hazardous nature of arsine, a conservative engineering and design approach shall be applied to the system design as applicable whether for pure arsine or arsine mixtures.

Gaseous mixtures of arsine are routinely packaged at pressures at or below the rated cylinder working pressure. Gas panels typically use a gas regulator to reduce the cylinder pressure to the operating condition.

Care is needed to 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 safety relief devices 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) (see Section 11).

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

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

6.4 Valve types and filter types

Metal diaphragm valves and bellows valves provide better leak-tightness as compared to packed valves. The use of non-metal material for diaphragms or bellows is not recommended due to the permeation potential of arsine thru the non-metal. Ball valves, butterfly valves, gate valves, needle valves, or packed valves are not recommended for use in arsine 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.

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, these filters are 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 would 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 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 wherever possible.

6.6 Purification materials

Arsine 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.

System purge shall be done prior to the use or removal of the purifier.

6.7 System leak tests and purge

After installation or maintenance, systems and components shall be leak checked and purged prior to commissioning.

Connections that are routinely remade in the process (for example, cylinder pigtail or other connections) shall be leak checked at a pressure higher than maximum usage pressure prior to system purging.

The best purge systems are those that are automated. The number of purge cycles is a function of the inert purge gas 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 arsine. 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 arsine can operate at varying temperatures depending on the application. Some systems can require an external heat source for the cylinder and process lines in order 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 vapour pressure versus temperature relationship as 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 arsine is flammable, 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, vapours, or gases will normally be 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 vapours of flammable gas, flammable liquid-produced vapour, or combustible liquid-produced vapour mixed with air are normally prevented by having forced mechanical ventilation, which is under negative pressure. This could become hazardous through the failure or abnormal operation of the ventilating equipment.

6.10 Monitoring systems

6.10.1 Gas monitoring

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

Arsine is a colourless, flammable, and highly toxic gas. It has a garlic-like odour that can be detected at concentrations greater than or equal to 0.5 ppm [6, 12]. This level of detection does not provide warning of hazardous levels. Because arsine is non-irritating and produces no immediate symptoms, persons exposed to hazardous levels can be unaware of its presence. A gas monitoring system continuously monitors primary locations for arsine including but not limited to the following areas:

- storage;
- operator areas;
- gas cabinets;
- 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 arsine. 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 arsine include:

- photo-absorption;
- photo-ionization;
- electrochemical;
- colorimetric tape;

- thermal conductivity; and
- catalytic bead.

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

6.10.2 Flame and smoke monitoring

Under normal circumstances, most flammable gases should be monitored for concentrations within the flammable range or for detection of flame or smoke. However, the greater hazard with arsine is its high toxicity. The toxic concentrations of arsine are well below the flammable range and therefore it is recommended to monitor for sub-ppm levels.

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.

6.13 Regulators

Refer to 10.2.

7 Process and operation

7.1 Life safety control (gas detection and alarm systems)

Procedures shall be in place to control worker exposure to arsine and its by-products. Compliance with these procedures will 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 a 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 should be installed to trigger emergency response actions in compliance with national regulations.

7.1.2 Life safety system

- Periodic review of heating, ventilation, and air conditioning (HVAC) air balance through building, fume hoods, gas cabinets, and abatement systems—With time, air flows/exhausts can change and required capture velocities can 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 arsine is a flammable gas, firefighting systems shall be considered and follow national regulations;

- 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 areas should be designed with more than one exit.

7.1.3 Management

- Work clothing management—Daily change outs, a place for contaminated clothing, separate locker room from manufacturing environment;

- Training and recertification in use of personal protective equipment (PPE)—Workers required to wear respiratory protection shall be medically evaluated and fit tested to confirm worker ability and clearance for use;

- Training and emergency response—Training should be conducted on the emergency response to situations that involve the possible release or exposure to arsine and its by-products;

- General awareness training—Personnel involved in the manufacturing, processing, maintenance, handling, storage, and/or transportation of arsine and its by-products shall be trained on the exposure effects (signs, symptoms, medical treatment) using the SDS and other safety information related to the environment and to personnel. Additional training can be required by local jurisdictions, which could include personnel safety, preventive maintenance (PM), 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;

- For all workers, inclusion in a periodic medical surveillance program is recommended and may be required by specific regulations. Documented work history as well as medical history should be captured. Medical surveillance can also consist of an annual chest X-ray, examination of skin for the presence of chronic skin lesions, fingernail and hair clipping, and blood work review;

- Labelling 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 arsine. These work instructions should describe in sufficient detail the information needed to perform a specific task. These work instructions shall be written in 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 consulted and trained when procedures are changed. A risk assessment should be carried out on all operations involving arsine. Any changes to these procedures shall be reviewed under management of change (MOC) practices.

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

- contamination of the gasket by the natural oils found on the skin; and
- contamination of the operator from residual arsine by-products found on the used gasket.

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

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

7.3 Ventilation

Ventilation is required for storage areas, gas cabinets, fume hoods, and areas where arsine is processed, stored, or handled. Regulations may vary by country but common guidelines are as follows.:

7.3.1 Necessity of ventilation for arsine

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

7.3.2 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 national 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 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 across the face of the small valve manipulation opening is recommended for normal operating conditions. In the United States, the average ventilation velocity at the face access port or opening shall not be less than 1.02 m/s (200 ft/min) with a minimum of 0.76 m/s (150 ft/min) at any point of the access port or opening;
- The number of air exchanges per hour (inside the gas cabinet or exhausted enclosure) may be regulated by local authorities;
- 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 such as arsine, exhaust should be taken near the floor;
- For some arsine mixtures (helium, hydrogen) that are lighter than air, exhaust should be taken near the ceiling;
- 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 vapours;
- Exhaust ventilation should not be recirculated within the room or building if the cylinders, containers, or tanks stored are capable of releasing hazardous gases such as arsine;
- 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 labelled as follows: 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 will activate in the event of the loss of ventilation.

7.4 On-going maintenance and preventive maintenance (PM) programmes

It is essential that arsine handling equipment is maintained.

Attention should be provided to any replacement parts for compatibility with arsine and other system products.

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

8 Gas cylinder filling and 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

Arsine is routinely packaged in seamless steel cylinders or aluminium alloy cylinders with a minimum test pressure set by a regulatory body. Low pressure welded cylinders may be accepted for this service, with a special approval that has been granted by the regulatory body. Conversion of arsine cylinders to other gas services is strongly discouraged. Refer to ISO 11621, *Gas cylinders—Procedures for change of gas service* or CGA C-10, *Guidelines to Prepare Cylinders and Tubes for Gas Service and Changes in Gas Service* for further information [31, 32].

The cylinder size for arsine and its mixtures are limited by local government regulations. In Japan, maximum cylinder size is 49 L and in the United States, maximum cylinder size is 57 L except for mixtures less than 10 vol%. Company policy may further limit the fill quantity for arsine based on a risk assessment.

Generally, cylinders that are used in high purity electronic arsine service have special internal pre-treatment to maintain gas purity. This treatment is provided by the gas supplier.

Containers shall be certified and tested regularly in compliance with national standards. Container retest shall follow national 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 they can be repaired to meet the standards, they may be put back to use; otherwise they shall be scrapped. In some countries, arsine cylinders cannot be used in other services.

Prior to fill, ensure that a container has not been damaged. Prefill inspection of containers and correct verification of their pressure rating prior to filling is very important.

8.2.2 Valves and pressure relief devices

It is recommended that diaphragm seal valves be used for arsine as it provides 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.

There are different types of valve outlets that are used for arsine 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 ensure a leak-tight connection. In accordance with DOT and UN, transport regulations (*European Agreement concerning the International Carriage of Dangerous Goods by Road/Rail* (ADR/RID), *International Maritime Dangerous Goods* (IMDG) *Code*, etc.) require that valve outlets of gas cylinders containing pyrophoric and/or highly toxic gases or gas mixtures are fitted with a gas-tight plug or cap [33, 1, 34]. The use of adapters to connect cylinder valves to the cylinder outlet is not recommended.

There are a variety of different cylinder valve inlets that are in use today for arsine. 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, because of the toxicity of arsine, PRDs are prohibited. The use of PRDs for cylinder valves with arsine is required in some countries. In other countries, PRDs are optional but it is recommended to avoid using PRDs.

8.2.3 Filling ratio

Containers shall be filled with arsine and mixtures in accordance with the requirements of authorities having jurisdiction.

- The United Nations P200 Packaging Instruction currently permits a maximum fill ratio of 1.1 kg/L for arsine packaged in cylinders with a test pressure of 300 bar (30 MPa) [1];
- The maximum fill ratio for arsine in Japan is 0.416 kg/L;
- In the United States, the maximum fill ratio based on liquid full cylinder at 54.4 °C (130 °F) is 1.26 kg/L; however, most customers have it filled in the range of 0.50 kg/L to 0.60 kg/L due to local regulations or insurance requirements; and

The maximum filling ratio for Europe is 1.1 kg/l.

8.3 Filling equipment

Many countries regulate the disposal of arsenic contaminated wastes. Any equipment or materials in contact with arsine 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.

8.3.1 Manifolds

Manifold components in contact with arsine filling shall be designed with compatible materials listed in this publication. When not under arsine pressure, manifolds should be backfilled with an inert gas such as helium, nitrogen, argon and plugged to ensure that any contaminants are excluded from the manifold system. Filling manifolds should be located in well-ventilated areas. To reduce the potential quantity of gas released in an incident and to reduce waste, small diameter tubing and lengths are preferred. The filling manifold should be made using welded fitting and metal face seal fitting. <u>The use of threaded fitting should be avoided. The use of mechanical fittings should be minimized</u>.

Refer to 6.7 for system leak tests and purge practices.

8.3.2 Compressors

Since arsine is a liquefied gas, compressors are not normally used for pure gas.

8.3.3 Vacuum pumps

Vacuum pumps in contact with arsine are typically either dry pumps or those using an oil sealed pump. However, oil sealed pumps risk oil contamination by arsine and waste management and PPE are required.

Dry pumps are recommended due to no potential oil contamination. Oil sealed (wet) pumps have the potential for oil back streaming if back streaming barriers are not maintained. If back streaming occurs, arsine (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 arsine.

8.3.4 Pressure gauges

Pressure gauges are used to monitor the pressure within the arsine system. Analogue 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 arsine is flammable, the use of digital pressure gauges (operated by electricity) should be at low voltage intrinsically safe (via low voltage or electrical barriers) to avoid ignition source potential.

9 Storage and handling

The following are good practices for storage and use of arsine.

9.1 General guidelines

- All facilities shall have an emergency response plan, which should include the plan for gas releases and emergency evacuation (more information is available in EIGA Doc 80, *Handling gas container emergencies* and EIGA Doc 30, *Disposal of gases*) [35, 36];

- 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;
- Arsine 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 vapours (for example, bleach or seawater); and
- Container valves shall be securely closed, outlet seals tightly installed, and valve protection caps in-place during all storage and handling operation.

9.2 Storage

9.2.1 Segregation

- Full and used 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; and
- Arsine shall be stored in well-ventilated areas, away from incompatible gases, oxidizers, pyrophoric gases, flammable gases, open flames, sparks, and sources of heat. Incompatible groups shall be separated by required distance or by fire partition. If the local jurisdiction does not specify the distance, separation of at least 6 m is recommended. Refer to EIGA Doc 189, *The Calculation of Harm and No-Harm Distances for the Storage and Use of Toxic Gases* and NFPA 55, *Compressed Gases and Cryogenic Fluids Code*, Chapter 7 for more information [37, 22].

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 51.7 °C (125 °F);
- The quantity of arsine stored shall not exceed the design of the facility and shall comply with national 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; and
- 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.

9.3 Handling

9.3.1 Essentials

- Personnel handling arsine cylinders should receive training;
- Use materials of construction compatible for handling arsine. 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 (capped) 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 a gas filter or SCBA) shall be considered and determined after a risk assessment; and
- All piping, cabinets, and equipment used to handle arsine shall be electrically earthed/grounded.

9.3.2 Precautions

- The filling and use of arsine shall be done in exhausted enclosures or rooms with the discharge treated to below acceptable levels before emission into the atmosphere. To determine safety distances, refer to EIGA Doc 189 [37];
- Remove valve outlet cap or connections 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;
- Always open valves slowly and carefully; and
- Containers with residual gas should be treated as if they were full.

9.3.3 Checking

9.3.3.1 Container

- Check cleanliness of the valve outlet and pigtails;
- Leak check containers and connection before use; and
- Prior to 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.

9.3.3.2 Piping

Always purge piping systems with inert gas:

- before the introduction of arsine; and
- before the disconnection of arsine cylinders.

9.3.4 Prohibition and restriction

- Do not use adaptors to connect containers;
- Do not overtighten valves. 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;
- The 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 in the vicinity of arsine or arsine mixtures is of the appropriate electrical classification. Consult International Electrotechnical Commission (IEC) or NFPA 70, *National Electrical Code*® (NEC) [38, 21]; and
- Non-sparking tools are recommended to be used when working around arsine and are required by some jurisdictions.

9.4 Security

Since the consequences of exposure to arsine are severe and can be widespread, security measures should be implemented to prevent access to arsine cylinders by unauthorized personnel. For more details, refer to AIGA 003 *Security Guidelines,* EIGA Doc 907 *Security Guidelines*, CGA P-50, *Site Security Standard*, or CGA P-51, *Transportation Security Standard for the Compressed Gas Industry* [39, 40, 41, 42].

A sale policy for arsine shall be in place. It shall be ensured by a thorough review prior to the purchase being approved and the delivery being made that the customer has a valid reason to purchase arsine and that the tracking records during shipment of arsine 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 arsine 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 arsine 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 arsine, 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 will avoid the risk of backfeeding via the purge gas system into another incompatible process gas supply system.

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

10.2 Regulators

Regulators are used in arsine 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 arsine 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 arsine in semiconductor processes are typically constructed of 316 or 316L stainless steel (SS) and at times are electropolished. Regulators with stainless steel diaphragms should be used to avoid the potential of arsine diffusion through porous elastomer diaphragms and the potential diffusion of contaminants that are adsorbed on elastomeric diaphragms. Once a regulator has been used in arsine service, it should not be used for other gas service. A regular bonnet vent shall be piped to a safe disposal abatement system.

11 Gas abatement systems

Since arsine is a highly toxic 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 arsine 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 utilizing chemical abatement may offer better solutions. Such an abatement system could be capable of dealing with other contaminates in the system. Disposal of arsine 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 EIGA Doc 30 [36].

A competent person knowledgeable in the handling and processing arsine 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
  $2\,AsH_3 + 3\,O_2 \rightarrow As_2O_3 + 3\,H_2O$ and/or
  $2\,AsH_3 + 4\,O_2 \rightarrow As_2O_5 + 3\,H_2O$

- Oxidation via wet scrubber
  $AsH_3 + Oxidant + 4\,H_2O \rightarrow AsO_4^{-3} + 11H^+ + 8\,e^-$

- Absorption/adsorption and reaction on a treated solid (with metallic oxides)
  $3\,CuSO_4 + 2\,AsH_3 \rightarrow Cu_3As_2 + 3\,H_2SO_4$ or
  $6\,FeCl_3 + AsH_3 + 3\,H_2O \rightarrow 6\,FeCl_2 + H_3AsO_3 + 6\,HCl$

  - Physical adsorption on solid media
    $AsH_3 + C \rightarrow C\left[AsH_3\right](C : \text{Activated Carbon})$

11.1.1 Reclamation or recovery

Reclamation of arsine is not a disposal method, as usually understood. This technique is for reclaiming residual gas and returning the arsine safely to suitable containers. Once reclaimed, arsine has to be re-processed, purified and analysed before being reused.

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 arsine. Arsine should not be reclaimed to a container and returned without the written authority of the owner of the container.

Some users collect arsine into cylinders for treatment off-site.

11.1.2 Oxidation via incineration

While burning the arsine molecule can be done satisfactorily, capturing the toxic solid by-product requires extensive equipment. Clean-up procedures and employee protection from the arsenic oxide dust is critical.

For complete reaction, arsine shall be introduced directly into the burning flame.

11.1.3 Oxidation via wet scrubber

The typical wet scrubber used for arsine 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. Factors to be taken into account when utilizing a wet scrubber include:

- Arsine input flow rate;
- pH control of the absorbent liquor;
- Temperature of the absorbent liquor;
- Provisions should be made to monitor both the inlet and outlet stream for arsine concentration;
- Flow control should be installed in the waste arsine stream to enable the gas flow to be matched to the capacity of the scrubber;
- Pressure control should be installed in the waste arsine 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 arsine 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 and work well for low concentrations of arsine.

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

Arsine is fed directly into a vessel containing a bed of solid adsorbent. There are many solid absorbents available which strongly and readily adsorb/absorb and react with arsine. Simplicity and portability of a small solid-state absorber may favour the choice of this method under certain emergency conditions.

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 arsine disposal rate;
- Quantity of arsine to be disposed;
- Acceptable frequency of changing the absorbent bed or system;

- Concentration of the arsine stream delivered into the absorber bed;
- Temperature rise effects from reaction between the arsine and the absorbent;
- Distribution system within the absorber bed to prevent channelling and premature breakthrough of unreacted arsine;
- Absorbent particle size—Generally small particles give a high contact area, which corresponds to greater efficiency. However, small particle sizes can lead to plugging or high pressure drops and a tendency of channelling and premature breakthrough of unreacted arsine;
- Provisions should be made to monitor both the inlet and outlet stream for arsine concentration;
- Flow control should be installed in the waste arsine stream to enable the gas flow to be matched to the capacity of the absorber bed;
- Pressure control should be installed in the waste arsine 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

Arsine is fed directly into a vessel containing a bed of solid media. There are many types of solid media available that adsorb arsine. Adsorption capacity varies with solid type, for example, using granular activated carbon, arsine capacities approach to 18% (by weight) of the total carbon weight.

Off-gassing of arsine from solid media can occur so it is important to have controls and arsine monitoring in place. Heat is generated during arsine adsorption as a function of adsorption rate and arsine 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 favour 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 arsine 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 arsine;
- physical properties of abatement material;
- toxicological properties of arsine;
- characteristics of arsine; and
- operating documents.

11.3 Waste stream disposal

Dispose of in accordance with all applicable regulations. Waste streams can contain arsenic and be considered a toxic, hazardous waste. Management and control of waste is required. Refer to local and government regulations as they apply to waste management.

11.4 Waste management

Nearly every operational process leaves behind some residual waste. Pressure to conserve 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 can 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 has spilled, leaked, or been improperly disposed.

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

- Source reduction or waste prevention—Any practice that reduces the amount or toxicity of waste generated;
- Recycling—Conserve disposal capacity and preserve 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—Reduces 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 arsine 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 could 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.

Arsine 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 can 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 arsine is usually one of the first steps in responding to an incident.

12.1.2 Evaluation

The responder will predict the behaviour and anticipated problems associated with the material. Anticipated problems that could extend beyond the company property will 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 neighbourhood. 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 PPE is worn. 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 [35, 36, 37].

Off-site 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 EIGA Doc 80, *Handling Gas Container Emergencies,* and the *Emergency Response Guidebook* (ERG) [35, 19]. Also refer to EIGA Doc 30 [36].

13 References

Unless otherwise specified the latest edition shall apply.

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NOTE—This publication is part of an international harmonization program for industry standards. The technical content of each regional document is identical, except for regional regulatory requirements. See the referenced document preface for a list of harmonized regional references.

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