PRINCIPLES FOR THE SAFE HANDLING AND DISTRIBUTION OF HIGHLY TOXIC GASES AND MIXTURES

AIGA 026/13

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1 Introduction

1.1 Scope and purpose

The purpose of this document is to set out basic principles for the safe handling and distribution of highly toxic gases and mixtures. These principles are in addition to those, which are normally applied to the handling of gases and containers.

It is recommended that these principles should apply to all highly toxic gases. Appendix A gives examples of such gases.

In addition, it is recommended, as far as it is reasonably practicable, to extend the application of the principles set out in this document to all toxic gases.

Whilst this document is primarily aimed at gas suppliers and distributors, it is recommended that gas users also observe the principles.

1.2 Definitions

Highly toxic gases: For this document, highly toxic gases are gases classified as Acute Toxic Cat.1 according to EC Regulation 1272/2009 on Classification, labelling and packaging (CLP). See Appendix A.
Toxic gases: For this document, toxic gases are gases classified as Acute Toxic Cat.2 and Cat.3 according to EC Regulation 1272/2009 on Classification, labelling and packaging (CLP). See Appendix A.

2 Principles

2.1 Principle 1 – Training

All personnel handling highly toxic gases shall be trained. It is important to ensure that all personnel are trained to a level which is commensurate with their involvement with highly toxic gases. The minimum requirements is that all personnel (including vehicle drivers) handling highly toxic gases must be able to recognise the gases they are handling, be aware of the appropriate properties and hazards and the action to take in the event of an emergency. Such personnel should be provided with appropriate safety equipment and training in its use.
Those manufacturing, distributing and using toxic gases should be trained in the safe handling and use of the toxic gas. The training should include:

- Procedures for the recovery or disposal of toxic gases in the event of an emergency and liaison with the relevant emergency services.
- Driver Training will meet the International Carriage of Dangerous Goods by Road and appropriate local or national requirements.

For more information, see the following EIGA *(AIGA)* documents:

Doc.N°	Title of Document
23	Safety training of employees - *(AIGA 009)*
30	Disposal of gases - *(AIGA 083)*
39	The Safe preparation of gas mixtures - *(AIGA 047)*
69	Transport emergency instructions
78	Leak detection fluids - gas cylinder packages - *(AIGA 070)*
80	Handling gas container emergencies - *(AIGA 004)*
81	Road vehicle emergency and recovery
103	Transporting gas cylinders or cryogenic receptacles in "enclosed vehicles"
129	Pressure receptacles with blocked or inoperable valves - *(AIGA 025)*
161	Gas compatibility with Aluminium alloy cylinders
913	Transport security guidelines - *(AIGA 043)*

2.2 Principle 2 – Supplier responsibilities

Suppliers shall take reasonable steps, typically as part of a responsible care programme, to ensure that highly toxic gases are only supplied to competent users. Users must be aware of the hazardous properties of the gases they are handling and should have trained personnel and adequate facilities and procedures for safe handling and dealing with emergency situations. Users should be provided with appropriate gas data and safety information and it is recommended that they are asked to confirm that they have the necessary facilities and procedures in place before they are supplied with highly toxic gases.

2.3 Principle 3 – User responsibilities

The users of toxic gases shall do a risk assessment of the conditions under which these gases are used in the actual working environment. They shall take into account the information contained in the safety data sheets received from their suppliers. In particular, they shall verify that their conditions of use are covered by the conditions of use described in the SDS and in the attached exposure scenarios if any.

The user shall have an emergency plan in place and consider the maximum quantity of highly toxic gas stored and used on-site. Users should return unused toxic gases to the supplier or dispose of the toxic gases as hazardous waste when the toxic gases are no longer required.

For more information on the handling of specific toxic gases, see the following EIGA *(AIGA)* Documents:

EIGA Doc.	AIGA Doc.	Title of Document
140	053	Code of Practice - Compressed fluorine and mixtures with inert gases
162	051	Code of Practice – Phosphine
163	050	Code of Practice – Arsine

2.4 Principle 4 – Storage and use considerations

All toxic gas containers/cylinders should be visually inspected to ensure:

- An absence of excessive wear, rust or damage
- Valve protection and dust caps are intact and in place
- Cylinder labels are legible and list the contents, potential hazards, and precautions

And

- Should be tested for the absence of a gas leak, by the customer, immediately following delivery.

Cylinders that do not meet incoming inspection requirements should be quarantined for return to the supplier and emergency plans activated if there is a possibility of danger.

All areas where highly toxic gases are filled into containers, used or stored shall be well ventilated. It is important to ensure that the ventilation is adequate. Ventilation requirements will be determined by the operation, for example:

- Storage of highly toxic gas containers in the open air or where this is not possible, with forced ventilation of at least 10 air changes per hour.

- Filling and use of highly toxic gas receptacles normally requires additional localised extraction, such as that provided by a fume cubicle, gas cabinet or ventilation hood.

The specification and design of ventilation systems should be undertaken by competent personnel who take into account the toxicity and physical / chemical properties of the gas and the potential risks and possible magnitude of any gas leakage. In enclosed storage areas there should be gas detectors

with automatic alarm systems to detect any leaks. When completing maintenance work in the storage areas a permit to work system shall be used.

2.5 Principle 5 – Valve protection

Highly toxic gas containers shall be checked to ensure that they are free of leaks, shall have their valve outlets fitted with a gas tight cap nut or plug and shall have their valves protected against mechanical damage. The fitment of a gas tight cap nut or plug to the gas container valve outlet significantly reduces the risk of leakage. Such a device should be fitted at all times unless the gas container is in use. Any gasket materials used must be compatible with the gas and suitable for the service pressure.

It is recommended that for additional safety, the nut or plug should be provided with a bleed hole (or other suitable arrangement) that allows gas discharge (of gas accumulated in the valve outlet) before complete removal of the cap nut or plug. The provision of bleed holes etc. must not affect the ability of the cap nut or plug to provide a leak-free seal on the valve outlet when correctly fitted and tightened.

It is also recommended that such devices are made “captive” by securing to the container valve with a chain. This ensures that the device is not lost whilst the container is in use and is immediately available for refitting when the container is disconnected from the equipment after use.

Highly toxic gas container valves should be protected against mechanical damage at all times. When gas containers are in use, they should be properly secured to prevent them falling. A valve protection device such as a valve cover or guard should be fitted at all other times. (Note: where this is not practicable, e.g. for lecture bottles, an adequate ventilated packaging for the gas container must be provided).

Note: The installation of a flow limiting device in the valve outlet may be considered as a means of providing additional safety, however such devices are unsuitable for certain types of gases and applications e.g. corrosive gases, during the filling of the container.

2.6 Principle 6 – Security of highly toxic gases

Highly toxic gases shall be stored securely in locked cages, compounds or stores. In addition to ensuring ventilation requirements are adequate for the storage of highly toxic gases, it is important that access to the store is restricted to authorised and competent personnel only. This will necessitate the provision of lockable storage areas to minimise the risk of unauthorised persons gaining access.

For more information, see the following EIGA /AIGA documents:

EIGA Doc.	AIGA Doc	Title of Document
907 (Note 1)	003 (Note 1)	Security Guidelines

Note 1: for EIGA and AIGA members only

2.7 Principle 7 – Transportation

Toxic gases shall only be transported on well ventilated vehicles. Good ventilation at all times is of paramount importance when handling toxic gas containers. Such containers shall only be transported on suitable vehicles where the load space is well ventilated and separated from the driver’s compartment by a gas tight bulkhead. Open vehicles are recommended, however, where closed vehicles must be used, the load space must be provided with adequate ventilation and there must be a procedure for entering the load space (e.g. the use of additional ventilation before the load space is entered).
It is recommended that the following notice is displayed on the doors into the load space "WARNING NO VENTILATION OPEN WITH CAUTION"
Toxic gases must never be transported in closed vans, private cars, etc. where the vehicle load space communicates with the driver’s compartment. The security of the containers must be considered and maintained during transport.

For more information, see the ADR and the following EIGA /AIGA documents:

EIGA Doc.	AIGA Doc.	Title of Document
913 (Note 1)	043 (Note 1)	Transport Security Guidelines

Note 1: for EIGA and AIGA members only

2.8 Principle 8 – Inventory requirements

An inventory of all highly toxic gases shall be kept. Any losses in storage or transport shall be immediately identified and investigated. It is important to closely monitor the storage and movement of highly toxic gases to ensure that they do not get into the wrong hands (e.g. through theft, mistaken delivery, falling off a vehicle in transit, etc.)

The system for controlling the storage and movement of highly toxic gases shall be audited periodically to ensure its correct operation.

2.9 Principle 9 – Safety management (Audit, inspection, risk assessment)

Perform periodic audits to determine compliance with applicable regulations, codes of practice and work instructions.

Such audits shall include:

- Ventilation testing - to ensure that gas cabinets, fume extraction cabinets and storage areas meet the minimum requirements for safe operation.
- Gas detector testing – to ensure detectors and alarms work in line with vendors specifications.
- The inspection of security systems, such as access control, locked storage areas, lighting and other related requirements, to ensure that the area is protected from unauthorized entry.
- Records of the inspections.

Appendix A - List of toxic gases according to their CLP Classification for acute toxicity

Acute Toxicity Cat.1 (LC50 $_{rat.1h}$ < 200 ppm)		Acute Toxicity Cat.2 (LC50 $_{rat.1h}$ < 1000 ppm)		Acute Toxicity Cat.3 (LC50 $_{rat.1h}$ < 5000 ppm)	
Name	**LC50/rat.1h**	**Name**	**LC50/rat.1h**	**Name**	**LC50/rat.1h**
Hydrogen telluride	2	**Chlorine**	293	**Hexafluoro-1,3-Butadiene**	1300
Hydrogen selenide	2	**Chlorine trifluoride**	299	**Methyl mercaptan**	1350
Phosgene	5	**Dichlorosilane**	314	**Carbonyl sulphide**	1700
Arsenic pentafluoride	20	**Phosphorus trifluoride**	320	**Chlorotrifluoroethylene (R1113)**	2000
Arsine	20	**Cyanogen**	350	**Sulphur dioxide**	2520
Phosphine	20	**Carbonyl fluoride**	360	**Boron trichloride**	2541
Stibine	20	**Boron trifluoride**	387	**Hexafluoroisobutene**	2650
Nitrosyl chloride	35	**Silicon tetrafluoride**	450	**Hydrogen chloride**	2810
Sulphur tetrafluoride	40	**Hexafluoroacetone**	470	**Hydrogen bromide**	2860
Selenium hexafluoride	50	**Germane**	620	**Hydrogen iodide**	2860
Cyanogen chloride	80	**Hydrogen sulphide**	712	**Ethylene oxide**	2900
Diborane	80	**Bromomethane**	850	**Sulphuryl difluoride**	3020
Nitric oxide	115	**Hydrogen fluoride**	966	**Carbon monoxide**	3760
Nitrogen dioxide	115			**Ammonia**	4000
Chlorine pentafluoride	122				
Tungsten hexafluoride	160				
Fluorine	185				
Phosphorus pentafluoride	190				