

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

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#### Amendments to 130/11

Note: The technical changes from the previous edition are underlined

#### 1 Introduction

The safe handling of toxic gases has always been a concern for EIGA members. The first edition of this document was published as an EIGA Technical Note in 1990. Over the years the content of the document has been extended to cover new aspects of the safe handling of toxic gases such as "security" and "user responsibility". Also the references to EIGA publications have been extended to include new publications relevant to the "principles" outlined in the document.

All the quoted EIGA publications are downloadable at https://www.eiga.eu

#### 2 Scope and purpose

#### 2.1 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 receptacles.

#### 2.2 Scope

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.

#### 3 Definitions

#### 3.1 Publications 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 Highly toxic gases

For this document, highly toxic gases are gases classified as Acute Toxic Category 1 according to EC Regulation 1272/2008 on Classification, labelling and packaging (CLP). See Appendix A.

#### 3.2.2 Toxic gases

For this document, toxic gases are gases classified as Acute Toxic Category 2 and Category 3 according to EC Regulation 1272/2008 on Classification, labelling and packaging (CLP). See Appendix A.

#### 4 Principles

#### 4.1 Principle 1 - Training

All personnel handling highly toxic gases shall be trained and competent. 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

- shall 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.

The gas supplier should support the customer and on request train customer staff in the safe handling and use of highly toxic and/or toxic gases. The training should include:

- Procedures for the safe use of toxic gases such as container connection and disconnection.
- Procedures for the recovery or disposal of highly toxic and/or toxic gases in the event of an emergency and liaison with the relevant emergency services.
- Driver training referencing the European Agreement concerning the International Carriage of Dangerous Goods by Road (ADR) and appropriate national regulations.

For more information, see the following EIGA documents:

Doc. N°	Title of Document				
23	Safety training of employees				
30	Disposal of gases				
39	The Safe preparation of gas mixtures				
78	Leak detection fluids - gas cylinder packages				
80	Handling gas container emergencies				
81	Road vehicle emergency and recovery				
129	Pressure receptacles with blocked or inoperable valves				
136	Selection of personal protective equipment				
161	Gas compatibility with Aluminium alloy cylinders				
188	Safe transfer of toxic liquefied gases				
199	Safe handling of electronic specialty gases				
913 *	Transport Security Guidance for EIGA Members				

<sup>\*:</sup> For EIGA members only

#### 4.2 Principle 2 – Supplier responsibilities

Suppliers shall take reasonable steps, typically as part of their social responsibility programme, to ensure that highly toxic gases are only supplied to competent users. Users shall 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. Whenever possible gas suppliers should support users in the development of their procedures.

For more information, see the following EIGA documents:

Doc. N°	Title of Document
920 *	Guidance for Qualifying Customers Purchasing Compressed Gases
919 *	Guidelines for the Preparation of Safety Data Sheets

<sup>\*:</sup> For EIGA members only

#### 4.3 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 (SDS) 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 Documents:

Doc. N°	Title of Document				
140	Code of Practice - Compressed fluorine and mixtures with inert gases				
162	Code of Practice - Phosphine				
163	Code of Practice - Arsine				
204	Code of Practice – Hydrogen Selenide				

#### 4.4 Principle 4 – Storage and use considerations

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

- An absence of excessive wear, rust or damage
- Valve protection and safety caps are intact and in place
- Cylinder labels are legible and list the contents, potential hazards, and precautions
- The cylinder is within test, i.e. the test date has not expired prior to filling

And

Should be tested for the absence of a gas leak, by the user, 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 receptacles, 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 receptacles in the open air or where this is not possible, with forced ventilation refer to Doc 189 for additional guidance.
- 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. refer to Doc 189 for additional guidance.
- The other hazards of the toxic gases shall also be considered when determining the separation distances in the storage areas. See dedicated COPs for silane, arsine, phosphine, etc. (see list under principle 3) for more guidance.

The specification and design of ventilation systems <u>shall</u> 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. <u>Operators handling highly toxic gases should wear portable gas detectors when no fixed gas detector is installed.</u> 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.

For more information, see the following EIGA document:

Doc. N°	Title of Document
189	The calculation of harm and no-harm distances for the storage and use of toxic gases in
	transportable containers.

#### 4.5 Principle 5 – Valve protection

Highly toxic gas receptacles 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 receptacle valve outlet significantly reduces the risk of leakage. According to Packing Instruction P200 of ADR, such a device shall be fitted at all times unless the gas receptacle is in use. Any gasket materials used shall be compatible with the gas and suitable for the service pressure.

It is a recognized industry practice 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. shall 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 receptacle valve with a chain. This ensures that the device is not lost whilst the receptacle is in use and is immediately available for refitting when the receptacle is disconnected from the equipment after use.

Highly toxic gas receptacle valves should be protected against mechanical damage at all times. When gas receptacles 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 receptacle shall be provided).

Note: The fitment of a flow limiting device in the valve outlet may be considered as a means of providing additional safety and may by imposed by national regulations in some countries, however such devices are unsuitable for certain applications e.g. liquefied corrosive gases and/or requiring high flow.

#### 4.6 Principle 6 – Security 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 documents:

Doc. N°	Title of Document
922 *	Site Security

<sup>\*:</sup> For EIGA members only

#### 4.7 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 receptacles. Such receptacles 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 shall be used, the load space shall be provided with adequate ventilation and there shall 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 shall <u>never</u> be transported in closed vans, private cars, etc. where the vehicle load space communicates with the driver's compartment. The security of the receptacles shall be considered and maintained during transport.

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

Doc. N°	Title of Document
913 *	Transport Security Guidance for EIGA Members

<sup>\*:</sup> For EIGA members only

#### 4.8 Principle 8 – Inventory requirements

An inventory of all highly toxic gases shall be kept in order to satisfy the requirements of the national legislation implementing the Directive Seveso III. 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.

For more information, see the following EIGA document:

Doc. N°	Title of Document
60	Seveso Documents – Guidance on Applicability, Assessment and Legal Documents for Demonstrating Compliance of Industrial Gases Facilities with Seveso Directive (s)

#### 4.9 Principle 9 - Safety management (Audit, inspection, risk assessment)

Periodic audits shall be performed 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.

For more information, see the following EIGA document:

Doc.N°	Title of Document	Title of Document		
102	Safety audit guidelines			

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

### (Informative)

Ula la Taria Ocean					
Highly 10	xic Gases	Toxic gases			
Acute Tox	icity Cat.1	Acute Toxicity Cat.2		Acute Toxicity Cat.3	
(LC50 rat.1h < 200 ppm)		(LC50 rat.1h < 1000 ppm)		(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	1 300
Hydrogen selenide	2	Chlorine trifluoride	299	Methyl mercaptan	1 350
Phosgene	5	Dichlorosilane	314	Carbonyl sulphide	1 700
Arsenic pentafluoride	20	Phosphorus trifluoride	320	Chlorotrifluoroethylene (R1113)	2 000
Arsine	20	Cyanogen	350	Sulphur dioxide	2 520
Phosphine	20	Carbonyl fluoride	360	Boron trichloride	2 541
Stibine	20	Boron trifluoride	387	Hexafluoroisobutene	2 650
Nitrosyl chloride	35	Silicon tetrafluoride	450	Hydrogen chloride	2 810
Sulphur tetrafluoride	40	Hexafluoroacetone	470	Hydrogen bromide	2 860
Selenium hexafluoride	50	Germane	620	Hydrogen iodide	2 860
Cyanogen chloride	80	Hydrogen sulphide	712	Ethylene oxide	2 900
Diborane	80	Bromomethane	850	Sulphuryl difluoride	3 020
Nitric oxide	115	Hydrogen fluoride	966	Carbon monoxide	3 760
Nitrogen dioxide	115			Ammonia	4 000
Chlorine pentafluoride	122				
Tungsten hexafluoride	160				
Fluorine	185				
Phosphorus pentafluoride	190				