



SAFE TRANSFER OF TOXIC LIQUEFIED GASES

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Prepared by WG-4 Special Gases

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Amendments to 188/14

Section	Change
	Document is updated to the new template
3	Definitions are updated to the new template and some technical definitions have been updated
	The old paragraph 4 and related old section 13.2 – examples of toxic gas releases related to liquified gases – have been taken out. The information was outdated.
5.8	The chapter about fire fighting has been rewritten

NOTE Technical changes are shown underlined

Additional change: change of reference: EIGA doc. 97 to ISO/TR 11364

1 Introduction

EIGA members are filling toxic liquefied gases in different types of transportable gas containers (cylinders, cylinder bundles, pressure drums, ISO-containers, etc...). The liquefied gases are usually transferred via the liquid phase in order to reduce the duration of the operation. EIGA members supply toxic liquefied gases under pressure to customers who withdraw these products from the liquid phase or the vapour phase. Accidental releases of the liquid phase of these products present greater risks than vapour phase release since the flow rates can be significantly higher.

The toxic liquefied gases that are usually handled in large quantities by EIGA members include ammonia, chlorine, hydrogen chloride and sulphur dioxide. Their use has recently increased for new applications in the semiconductor and photovoltaic industries.

2 Purpose and Scope

2.1 Purpose

The objective of this document is to describe the best practices for the safe transfer and use of toxic liquefied gases in transportable gas containers; in particular the filling of small containers (e.g. cylinders) with toxic liquefied gases from large containers (e.g. ISO-containers and pressure drums).

2.2 Scope

This code of practice describes guidelines for the filling and use of toxic liquefied gases in transportable receptacles:

- design safety features for a safe operation of the installation,
- safety measures to operate such installations,
- operator knowledge requirements.

The recommendations in this document should also be considered for the transfilling of toxic gases in the liquid phase for the preparation of gas mixtures.

The use includes the placement of the container into service by connecting it to the piping or the pressure control systems. It excludes the use of the product in process operations but includes safety measures to avoid cross-contamination from the user's installation.

Toxic liquefied gases are defined in section 3. The filling of bulk static storage and large transportable equipment (e.g. Multiple-Element Gas Containers (MEGCs), ISO containers) with toxic liquefied gases is outside the scope of the document.

The filling of toxic gases in cylinders with an adsorbed material is also outside the scope of this document.

3 Definitions

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

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 and Need not

Indicate 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 Toxic liquefied gases

For the purpose of this document, toxic gases are gases and gas mixtures that are classified according to Regulation (EC) No 1272/2008 (*Classification, labelling and packaging of substances and mixtures - CLP*) as Acute Toxic, category 1, 2, or 3. This corresponds to the gases having a $LC50_{rat1h} < 5000 \text{ vppm}$ or a $LC50_{rat4h} < 2500 \text{ vppm}$ and to the definition of "Toxic" according to the *European Agreement concerning the International Carriage of Dangerous Goods by Road* (ADR). [1,2]¹.

ADR defines a liquefied gas as a gas which when packaged under pressure for carriage is partially liquid at temperatures above -50 °C.

The main liquefied toxic gases handled by EIGA members are listed in Appendix A of this document. More data including the full CLP classification of the toxic gases handled by EIGA members is given in EIGA Doc 169, *Classification and Labelling Guide in accordance with EC Regulation 1272/2008 (CLP Regulation)* [3].

3.2.2 Gas containers

For the purpose of this document, gas containers include the gas receptacles and the MEGCs as defined in the ADR:

- Gas cartridges: any non-refillable receptacle containing, under pressure, a gas or a mixture of gases. It may be fitted with a valve. The capacity of receptacles made of metal shall not exceed 1 000 ml; that of receptacles made of synthetic material or of glass shall not exceed 500 ml.
- Cylinder: a transportable pressure receptacle of a water capacity not exceeding 150 litres.
- Bundle of cylinders: an assembly of cylinders that are fastened together and which are interconnected by a manifold and carried as a unit. The total water capacity shall not exceed 3 000 litres except that bundles intended for the carriage of toxic gases of Class 2 (groups starting with letter T according to 2.2.2.1.3) shall be limited to 1 000 litres water capacity.
- Pressure drum: a welded transportable pressure receptacle of a water capacity exceeding 150 litres and of not more than 1 000 litres, (e.g. cylindrical receptacles equipped with rolling hoops, spheres on skids).
- Tube: a seamless transportable pressure receptacle of a water capacity exceeding 150 litres and of not more than 3 000 litres; tubes are also called "ton containers" in the US.
- Multiple-element gas container (MEGC): a unit containing elements which are linked to each other by a manifold and mounted on a frame. The following elements are considered to be elements of a multiple-element gas container: cylinders, tubes, pressure drums and bundles

¹ References are shown by bracketed numbers and are listed in order of appearance in the reference section.

of cylinders as well as tanks for the carriage of gases of Class 2 having a capacity of more than 450 litres.

- Portable Tank/Tank container: a transport unit comprising a shell and items of equipment and when used for the carriage of gases having a capacity of more than 0.45 m³ (450 litres). Portable Tanks/Tank containers are also called "ISO Containers" or "ISO Modules" in the Industry jargon.

3.2.3 Filling ratio

Means the ratio of the mass of gas to the mass of water at 15 °C that would fill completely a pressure receptacle fitted ready for use. Filling ratios for the gases are defined in Section 4.1.4.1 P200 of ADR.

3.2.4 LC50

LC 50 (50% lethal concentration) means the concentration of a chemical in air or of a chemical in water which causes the death of 50% (one half) of a group of test animals.

4 Methods of transferring liquefied gases

This section describes the different methods of transfilling:

- Liquid phase transfer by pump
- Transfer of liquid using gas top pressure
- Transfer by warming up the supply receptacle
- Transfer by cooling down the receiving receptacle

There are several different methods that can be used for the transfer of toxic liquefied gases. It is important that a risk assessment is undertaken before any such transfer is carried out and the transfer is undertaken using equipment that has been specifically designed for this purpose. Where a system is to be used to transfer several different products, the risk assessment shall also examine compatibility of the products to be transferred with each other and with the components making up the transfer system. See section 6 "Operational Requirements".

Although there are variations in the designs of equipment used, they all share a common principle for filling liquefied gases, namely the use of a weigh scale to determine the amount of gas filled into the receiving pressure receptacle. The flow diagrams in the following paragraphs are schematics only that illustrate the general principles and main equipment needed in the 4 methods of transfilling. They do not replace detailed Piping and Instrumentation Diagrams (P&IDs) based on Hazard and Operability Study (HAZOP) and other risks analysis.

Before commencing the transfer of toxic liquefied gases, pre-fill inspection of both the filling equipment and the receiving pressure receptacle shall be undertaken. See section 6 "Operational Requirements".

Generic operational recommendations for all methods of transfer:

- The weigh scale to be used shall be of suitable dimensions, range and accuracy for the size of receiving receptacle to be filled and shall be calibrated.
- Prior to commencing the transfilling operation, the functionality of the weigh scale should be confirmed using a range of check weights.
- Before commencing the transfilling operation, leak testing of the filling system shall be undertaken, with special focus on cylinder connections. Leak testing can be undertaken using a number of different techniques for example, pressurisation with an inert gas and check for a pressure drop over a known period of time.
The method of leak testing to be used should be subjected to an operational risk assessment prior to implementation.
The system shall be designed so as to minimise the risk of liquid becoming trapped within sections of pipe work and components, leading to a possible failure of the system due to over pressurisation. Where relief devices are installed to offer protection, these devices shall relieve to a safe location such as an abatement system.
- The venting of toxic liquefied gases to atmosphere shall not be permitted. Therefore, an abatement system is an integral component within the transfilling system. The method of

abatement shall be compatible with the liquefied gas being transfilled. The abatement system should have sufficient capacity to accommodate both routine venting of substances and quantities of substances released during a non-routine event, for example a release due to leakage or failure of a component of the filling system.

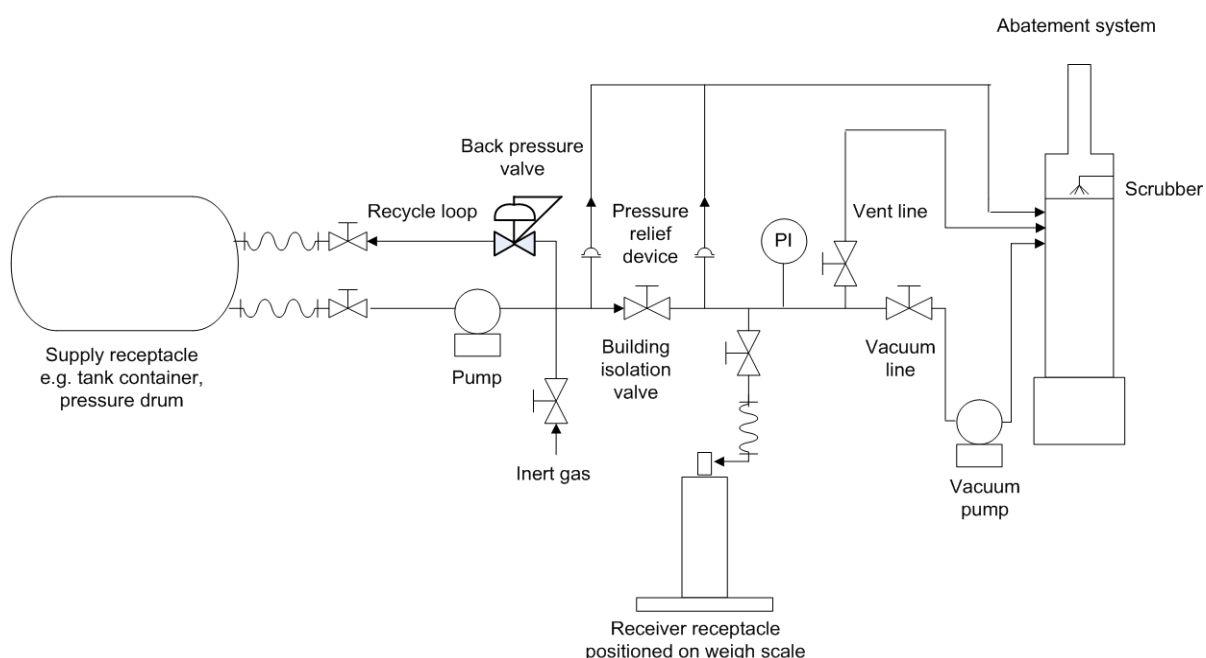
- The risk assessment shall determine additional measures for liquid containment in case of leak from pump and/or receptacle.

Upon completion of the transfer of toxic liquefied gases, irrespective of transfer method used, post fill inspection of the receiving receptacle shall take place. See section 6 “Operational Requirements”.

4.1 Liquid phase transfer by pump

Pumping the product is the most common method of transferring the liquefied gas into the receiving pressure receptacle. For chemically unstable substances (e.g. ethylene oxide) transfer by pressure is preferred.

4.1.1 Schematic arrangement



4.1.2 Description of the method

Liquefied product is transferred from the supply receptacle (e.g. tank container, pressure drum, cylinder etc) to the receiving pressure receptacle using a pump. The receiving receptacle is positioned on a calibrated weigh scale in order that the quantity of transferred product can be measured and safeguards be implemented to prevent over filling. Valves located along the system are used to control the flow of product.

A pressure recycle loop is installed downstream of the pump discharge and allows product to be recycled into the pump suction in the event that the pump is “dead ended” (for example upon completion of filling the receiving receptacle). This protects the pump.

Upon completion of product transfer to the receiving receptacle, the filling line (hose / pigtail) or connector shall be vented and evacuated/purged to allow safe disconnection. Given the toxic nature of the products being handled, such venting has to be done via a suitable scrubbing medium.

Toxic liquefied gases shall not be vented to atmosphere.

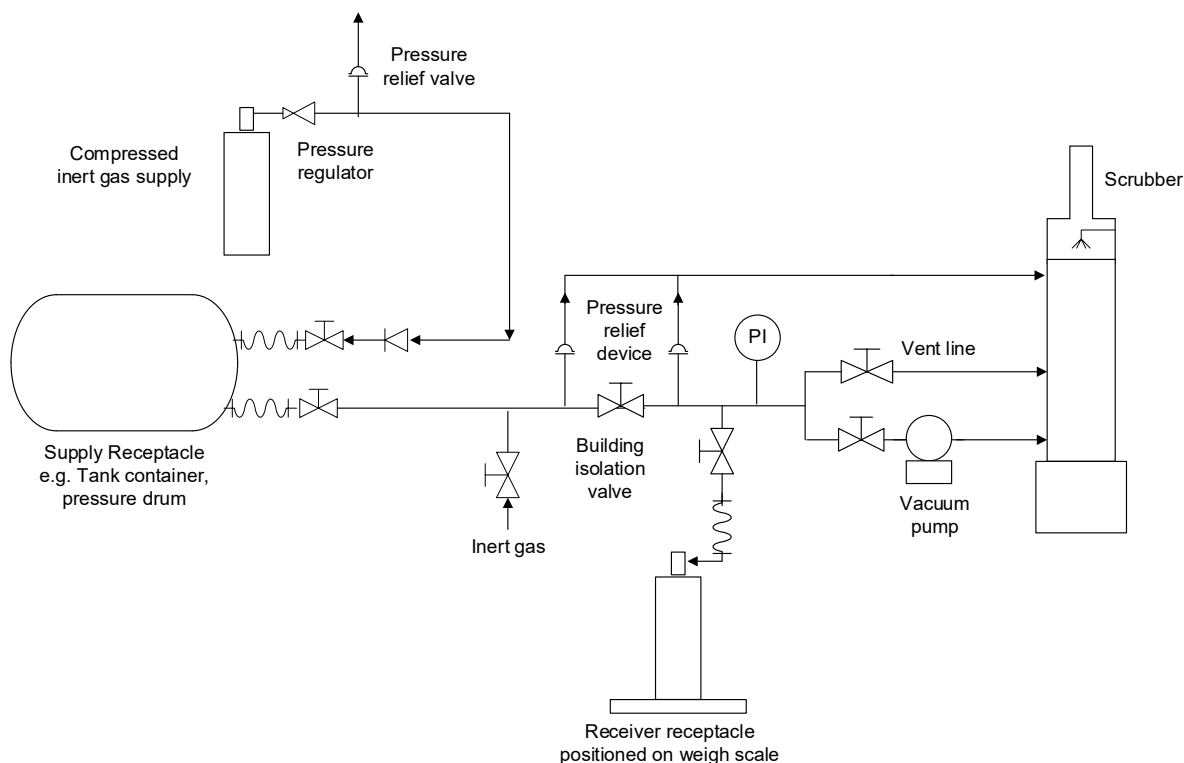
4.1.3 Design and operational precautions

When designing and operating a system that utilizes liquid phase transfer using a pump, a number of factors need to be considered:

- The pump to be used shall be compatible with both the chemical and physical properties of the liquefied gas to be transferred.
- The pump should be of suitable size and capacity for the system in order to minimise the risk of overfilling the receiving receptacle.
- The system should be designed to minimise the risk of the pump being run dry or “dead ended”. Both scenarios can result in damage which can compromise the integrity of the pump.
- The risk of the pump creating a vacuum condition and potential implosion of the supply receptacle should be addressed.

4.2 Transfer of liquid using inert gas top pressure

4.2.1 Schematic arrangement



4.2.2 Description of the method

Another method of transferring toxic liquefied gases is by pressure. In this method, the supply receptacle has a “top” pressure of a compressed inert gas such as nitrogen applied to it. The pressure of the supply receptacle is greater than the pressure of the receiving receptacle, this difference in pressure being the driving force which pushes the liquefied gas from the supply to the receiving receptacle.

When this type of operation is performed, it is important that the pressure limitations of the supply receptacle are not exceeded. The supply receptacle shall be protected by the installation of suitably rated pressure relief valves in order to prevent over pressurisation with the compressed inert gas being used.

The receiving receptacle is positioned on a calibrated weigh scale in order that the quantity of transferred product can be measured and safeguards be implemented to prevent over filling. Valves located along the system are used to control the flow of product.

Upon completion of product transfer to the receiving receptacle, the filling line (hose/pigtail) or connector has to be vented to allow safe disconnection. Given the toxic nature of the products being handled, such venting shall be done via a suitable scrubbing medium.

The quality of the inert gas used to establish the “top” pressure is of the utmost importance. Impurities present in the inert gas (water, oxygen, etc) do not only have an effect on the overall quality of the transferred liquefied gas, they can also create hazardous situations.

For example, if high concentrations of moisture are present in an inert gas used in the transfer of a corrosive liquefied gas, the rate at which damage due to corrosion takes place within the filling system increases significantly. This can result in failure of components in the filling system.

Therefore, before connection to the transfer system, the identity and the quality of the inert gas shall be verified with respect to safety and quality critical impurities.

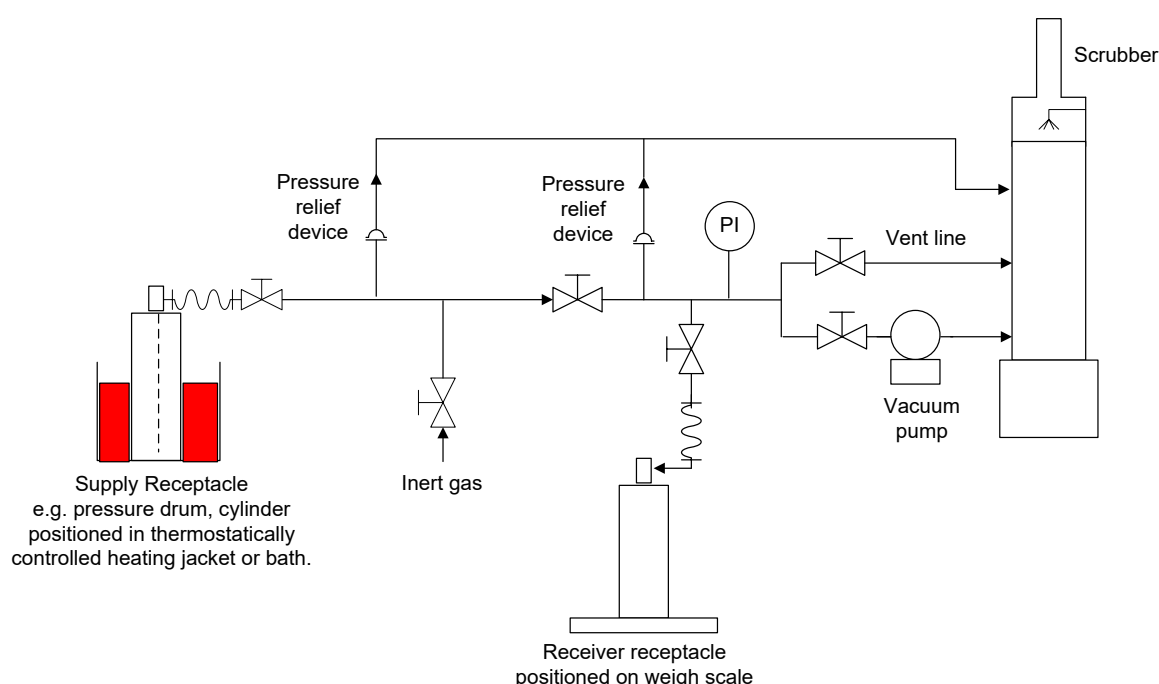
Non return devices should be fitted to the inert gas supply to minimise the risk of back flow of product. The supply of inert gas should where possible be dedicated to the system it is being used on so as to avoid cross contamination and the potential for the mixing of chemically incompatible substances resulting in the creation of potentially hazardous situations.

4.2.3 Design and operational precautions

- The inert gas supplied to the supply receptacle shall be at an equal or lower pressure than the working pressure of the transfilling system and the receptacle. Where the inert gas supply pressure is regulated, a pressure relief device shall be fitted downstream of the regulator, designed in order to protect the exceeding the working pressure of the receptacle and of the transfilling system in the event of failure of the regulator.
When transfilling corrosive liquefied gases utilising an inert gas top pressure, the moisture content of the inert gas is of great importance. The presence of moisture may result in corrosion damage to the transfilling system and formation of impurities. Prevention is critical in systems handling high purity products.
- The inert gas supply system shall be fitted with check valves or some other means of preventing possible back flow of liquefied gas from the supply receptacle to the inert gas source. Check valves or other devices designed to prevent back flow should be maintained in accordance with manufacturer's recommendations.
- Upon completion of product transfer the pressure in both the supply and receiving receptacles shall be checked and reduced if required. The reduction in pressure shall be achieved by venting gases to the abatement system.

4.3 Transfer by warming up the supply receptacle

4.3.1 Schematic arrangement



4.3.2 Description of the method

This method is most commonly used when transferring liquefied gases from a small supply receptacle such as a pressure drum or cylinder. It is also used to avoid the inert gas for pressurization being dissolved in the transferred product.

If transfer of liquid is to be undertaken, the supply receptacle shall be fitted with an internal dip tube. Vapour can be transferred from receptacles that do not have a dip tube fitted. For efficient transfer rates the receiving cylinder additionally is cooled to condense the vapour phase (refer to 4.4). It should be noted that some designs of receptacle have the ability to deliver both liquid and vapour. These receptacles are either fitted with more than one valve (one valve delivers liquid, one valve delivers vapour), or a single dual port (outlet) valve. The supply receptacle is heated, thereby generating an increase in vapour pressure within the receptacle. The receiving receptacle can be at either ambient temperature or cooled. It is the pressure differential created by the difference in temperature between the two receptacles that provides the driving force which pushes the liquefied gas from the supply to the receiving receptacle.

The supply receptacle is preferably heated using a heating jacket. Other means such as the use of a water bath can be used.

Whichever method of heating is used, there are a number of safety factors to consider:

- Any heating system should not allow the temperature of the supply receptacle to exceed 65°C (in accordance to ADR packing instruction P200). The system shall be thermostatically controlled and be designed to fail "cold".
- If used in the transfer of flammable liquefied gases, the heating system should be ATEX compliant and not provide a source of ignition to any possible product leakage.
- The use of heated water baths should be avoided when handling corrosive liquefied gases, as the humid conditions that can be produced by such systems can accelerate the rate at which corrosion damage occurs in the event of a leakage of product.

The receiving receptacle is positioned on a calibrated weigh scale in order that the quantity of transferred product can be measured and safeguards be implemented to prevent overfilling. Valves located along the system are used to control the flow of product.

Upon completion of product transfer to the receiving receptacle, the filling line (hose/pigtail) or connector shall be vented and evacuated/purged to allow safe disconnection. Given the toxic or flammable nature of the products being handled, such venting shall be done via a suitable disposal system.

4.3.3 Design and operational precautions

The selection of the heating media to be used should be the subject of a risk assessment during the design of the transfilling equipment.

The following safety factors shall be considered during the risk assessment:

- There are different types of heating media available including electrical heating jackets, hot water baths and steam boxes. Where flammable products are being transfilled and electrical heating systems are to be used, it is important to define hazardous area classification (zone NE, zone 2, zone 1 or zone 0) considering safety barriers according to ATEX Directive 1999/92/EC, minimum requirements for improving the safety and health protection of workers potentially at risk from explosive atmospheres and ensure that electrical components in these heating systems comply with the requirements of the ATEX Directive 2014/34/EU, *equipment and protective systems intended for use in potentially explosive atmospheres* implemented by each EU member state [4,5].
Where corrosive products are to be transfilled using hot water baths or steam boxes, it should be noted that in the event of product leakage, the rate of corrosion to both the supply receptacle and filling equipment will be accelerated.
- The method of heating the supply receptacle shall be thermostatically controlled. The temperature shall not be greater than the maximum operating temperature of any of the components constituting the supply receptacle (cylinder or drum tank, valves etc) as specified by the manufacturer (see also 4.3.2). This is so as to minimise the risk of heat damage to the supply receptacle.
- The risk of polymerization of the gas.
- The critical temperature.