

Phosgene Safety Practices

for design, production and processing

Part 2

Key elements of safety practices - long version

Section 3: Operational requirements

Table of contents

- 3. [Operational requirements](#)
 - 3.1 [Personal protection, first aid and medical intervention](#)
 - 3.1.1 [Operating staff \(unit personnel\)](#)
 - 3.1.2 [Service and contractor personnel with reasonable routine](#)
 - 3.1.3 [Service and contractor personnel without reasonable routine](#)
 - 3.1.4 [Visitors in a unit](#)
 - 3.1.5 [Phosgene indicator badges](#)
 - 3.1.6 [Medical intervention](#)
 - 3.2 [Safety Procedures](#)
 - 3.2.1 [Phosgene work procedures](#)
 - 3.2.2 [Work permit](#)
 - 3.2.3 [Standard procedures for de-phosgenation, clearing and cleaning of phosgene containing equipment](#)
 - 3.3 [Sampling](#)
 - 3.3.1 [General requirements for taking samples](#)
 - 3.3.2 [Routine samples](#)
 - 3.3.3 [Non-routine samples](#)
 - 3.3.4 [Gas sampling](#)
 - 3.3.5 [Phosgene solutions](#)
 - 3.4 [Training](#)
 - 3.4.1 [Visitor instruction](#)
 - 3.4.2 [Basic training for new employees](#)
 - 3.4.3 [Ongoing training for employees who operate phosgene-containing equipment](#)
 - 3.4.4 [Training for employees \(company or long-term contractors\) who maintain phosgene-containing equipment](#)
 - 3.4.5 [Laboratory technicians](#)
 - 3.4.6 [Documentation](#)
 - 3.4.7 [Miscellaneous](#)

[\(Abbreviations and acronyms\)](#)

III caveat

The information herein is presented in good faith, is believed to be accurate and reliable, but may well be incomplete and /or not applicable to all conditions or situations that may be encountered.

No representation, guarantee or warranty is made as to the accuracy, reliability or completeness of this report, or that the application or use of any of the information, analysis, methods and recommendations herein will avoid, reduce or ameliorate hazard, accidents, losses, damages or injury of any kind to persons or property. Readers are therefore cautioned to satisfy themselves as to the applicability and suitability of said information, for the purposes intended, prior to use.

3 Operational requirements

3.1 Personal protection, first aid and medical intervention

It is good safety practice to admit personnel into phosgene producing or using plants only after receiving safety instructions and then only with the prescribed Personal Protective Equipment (PPE). It is advisable that personnel using breathing air get a medical check-up and a physician's approval prior to working and those check-ups are repeated at regular intervals. Local regulation may also apply to work done while using breathing air.

People, who are entering the units, can be divided into four groups:

- Operating Staff (including unit management)
- Company service and contractor personnel regularly working in phosgene areas
- Company service and contractor personnel infrequently working in phosgene areas
- Visitors

For basic first aid for first-aiders, paramedic, physician and patient see Part 3 - section 1 "First aid, medical intervention and emergency response" (in preparation).

3.1.1 Operating staff (unit personnel)

It is advisable that employees use the company specified protective clothing and equipment before entering the unit, including a phosgene indicator badge (with the employee's name and date) affixed near the breathing zone. It is also good practice that each employee carries an escape device at all times.

Escape devices are meant to be only used in an emergency case when it is necessary to evacuate the unit. These devices are not a substitute for breathing air systems which are used when performing work in the units.

It can be dangerous to perform any operation on phosgene-containing equipment, where there is a possibility of phosgene being released, unless an independent breathing air supply is used and additional safety measures, as described in detail in standard operation procedures and work permits, are adhered to.

Training for unit personnel on the use of the personal protective equipment, which is refreshed on a regular basis and considers local regulations and restrictions is important.

It is good practice for employees to check that their escape device is in good condition (e.g. the expiration dates of the filter cartridges) before entering the unit.

Conducting regular drills involving plant personnel, the fire brigade, medical responders and personnel in neighbouring plants is a good safety practice. (See also Part 2 - section 3.4 "Training")

3.1.2 Service and contractor personnel regularly working in phosgene areas

It is important that service and contractor personnel regularly working in phosgene service areas are provided with the same training as Operating Staff and that it be documented and refreshed. The work permit will specify whether a contractor can work alone. (See also Part 2 - section 3.4 "Training")

3.1.3 Service and contractor personnel infrequently working in phosgene areas

It is important that personnel from the service departments and contractor companies working for the first time or only occasionally in phosgene service areas, receive extensive safety training concerning the hazards of the unit and the proper PPE required before starting any work. The work permit will specify whether a contractor can work without supervision.

3.1.4 Visitors in a unit

Visitors are persons entering phosgene service areas who are not directly involved in working activities.

It is good safety practice to provide visitors entering phosgene-containing units with basic information and training about what to do in an emergency and be equipped with the appropriate personal protective equipment. Training in the practical use of the escape device is especially important.

It is important that visitors be accompanied by a unit staff member at all times who will be responsible for the visitor in case of an emergency. (See also Part 2 - section 3.4.1 "Visitor instruction")

3.1.5 Phosgene indicator badges

In the unlikely event of uncontained phosgene releases inside or outside the facility it is necessary to assess personal exposure to phosgene in order to take appropriate and effective medical action for immediate emergency treatment.

A good way to assess personal exposure is from personal phosgene indicator badges showing a dose of exposure usually calibrated ppm*min worn by personnel in areas where phosgene exposure is possible.

The reading displayed on the badge follows an organic chemical reaction between reactants and phosgene forming colours in different shades of red so that medical staff, with the help of a comparator, will be able to make a precise assessment of the dose inhaled. This assessment may generate further medical actions and activities.

In order to make this assessment reliable it is important to adhere to the following:

- Badges are part of PPE and should be made readily available. Correct storage and usage is important.
- Badges worn close to the nose and the mouth provide the best indication of the exposure.
- It is good practice that the badge has the person's name and date on which it was worn and be replaced as per the badge manufacturer's instructions.
- It is prudent to check cross-sensitivities against any other chemicals, like chlorine, HCl, NOx, etc., as well as moisture and UV light depending on manufacturer of badge and site conditions.
- Badges may also be worn inside masks and goggles as a check of tight fit.
- It is important that any discoloration of the badge be reported to the responsible person in charge and to the medical staff with subsequent action taken according to internal procedures.

Quite frequently, indicator badges are used for leak detection or monitoring for traces of phosgene inside and outside the plant. This is generally permissible if not explicitly excluded by internal procedures, but limitations according to sensitivity, accuracy etc are a consideration. Phosgene indicator paper could also be considered.

However indicator badges are not a suitable substitute for monitoring devices installed inside the unit or at plant or fence line boundaries.

It should be noted here that phosgene detectors may be suitable to show the presence/absence of congeners of phosgene, like triphosgene, but only in a dichotomous, non-quantitative manner. See Part 3 section 3.5

3.1.6 Medical intervention

See also Part 3 - section 1 "First aid, medical intervention and emergency response" (in preparation).

3.2 Safety procedures

Because of the extremely hazardous nature of phosgene it is suggested that the area within a plant where phosgene is used be clearly defined, that strict operating discipline be enforced and that written procedures be audited and updated routinely.

3.2.1 Phosgene work procedures

Phosgene work area definition

Phosgene areas are typically those sections of a unit containing phosgene and mixtures containing it in liquid or gaseous form, i.e. those areas of the unit located inside the secondary containment boundary. Other toxic gases such as carbon monoxide and chlorine could also be used in the phosgene work area.

Phosgene work procedures

It is important that procedures for work (especially non-routine work) in phosgene service / phosgene work areas consider the following main elements:

- Appropriate Personnel Protection Equipment needed with respect to the hazard of the work
- Adequate instructions about the work to be performed, including risk evaluation
- Attendance of a safety guard during line breaking work
- Warning announcements for the hazardous area before, during and after the work.

3.2.2 Work permit

It is important that a work permit be issued for all work where a primary barrier of the phosgene units is opened. A work permit will normally contain detailed instructions for the preparation and performance of the work to be done, as well as the technical and organisational precautionary measures for the work area and its surroundings.

That only authorised personnel issue work permits is important. To follow the 4-eyes-principle, it is recommended that work permits not be completed and signed by the same person.

Avoid deviations from the work sequence as they can be dangerous. If the permitted work cannot be completed as planned, it is important to stop the work and secure the area until a new plan can be approved with a new work permit issued per the new plan.

In the event of a phosgene emission to the atmosphere, unit personnel are expected to respond according to emergency response procedures.

3.2.3 Standard procedures for de-phosgenation, clearing and cleaning of phosgene-containing equipment

If equipment that has contained phosgene needs to be opened for maintenance, cleaning or inspection proper preparation and decontamination is important to avoid phosgene emissions and unacceptable risk for the working personnel.

Standard detailed procedures for shutdown, de-phosgenation and cleaning equipment in phosgene service are recommended and could include the following for each type of equipment:

- Segregate the equipment from the rest of the process
- Flush equipment with an appropriate solvent
- Purge equipment with nitrogen
- Pull vacuum on the equipment to evaporate liquid residues
- Purge with steam
- Purge with ammonia or caustic soda
- Flood equipment with water, caustic soda or ammonia water
- Empty and purge with nitrogen or another inert gas
- Connect equipment to a decomposition system during de-phosgenation and / or opening
- Careful decontaminate catalyst used for generating phosgene prior to disposal
- Gaskets or solid residues may contain trapped phosgene
- Enter equipment after clearing, i.e. for removing tower internals, only with proper PPE including breathing air

3.3 Sampling

3.3.1 General requirements for taking samples

Reduced sampling will minimize the potential of releasing phosgene to the environment. It is important that when phosgene-containing samples are taken, appropriate safety systems are in operation and that written procedures are available and followed.

Proper PPE including supplied air is advisable for personnel taking any phosgene-containing sample not only in production units but also in laboratories and pilot plants. Safety is increased when sample points are easily accessible, ergonomically sound and when spot ventilation is used to remove any escaping vapours.

3.3.2 Routine samples

Samples from the production units that are included in a sample plan are considered “routine”, even though the frequency of sampling may be monthly, quarterly, etc.

For routine liquid samples, such as phosgene solutions, the best option for a sampling station is an enclosure (box) that is equipped with a venting system and a means to ensure that the venting system is working prior to taking any samples.

It is important that enclosures be of an approved design that permits their use in explosive atmospheres, that the valves inside the enclosure are operable from the outside and that the dead volume inside the sampler is minimised. To avoid purging before taking a sample valves with a “zero” clearance space can be used. It is recommended that samplers with a defined sample volume be used to prevent uncontrolled amounts of the product from entering the collection vessel.

It can be dangerous if samples are taken using open sample containers outside of the enclosure (i.e., open to the atmosphere). However, the use of threaded jars in an approved sampling station is permissible even though the cap is applied after the sample has been taken. The cap is to be tightened prior to transport. A basket is normally used for carrying.

Self-contained sample stations with fixed volume samplers, such as those provided by Dopak or Texas Sampler, have been used successfully over the years and are considered excellent examples of a contained sampling station. If other supplied stations are to be used, specifications equal to/or exceeding those of the two sampling stations mentioned above are recommended.

It is important that the sampling process adhere to a written procedure that has been reviewed and approved for safety

3.3.3 Non-routine samples

Any sample that is not in the production unit's sample plan is considered “non-routine”.

If liquid samples are obtained from phosgene-containing streams on a non-routine basis, it is important that appropriate sampling stations be designed and utilised. Stainless steel sample cylinders (bombs) or other contained method can be used when taking non-routine samples, but open sample containers are not recommended.

It is important that the sampling process adhere to a written procedure that has been reviewed and approved for safety

3.3.4 Gas sampling

Sampling of gas streams is performed but is uncommon. When sampling gas streams, stainless steel cylinders are the usual vessel of choice and the sampling method is designed to prevent a phosgene release.

Sampling designs can make use of process bypasses and maintenance decomposition/spot vent systems for the clearing of lines before detaching the sample cylinder.

It is important that the sampling process adhere to a written procedure that has been reviewed and approved for safety.

3.3.5 Phosgene solutions

Minimize sampling of pure phosgene solutions (i.e. phosgene and solvent only) by using on-line analysis. If a phosgene solution must be analysed, the best way to obtain the sample is with a sampler that neutralizes the phosgene at the source. This may be accomplished by using a fixed-volume sampler containing a pre-weighed amount of sodium hydroxide that will react with the phosgene. The phosgene concentration is then calculated after back titration with HCl. This neutralisation method alleviates the need for secondary containment of the sample while in transport because the sample no longer contains phosgene.

An alternative to neutralisation is to dilute the phosgene solution using pre-weighed solvent in the container with the fixed-volume sampler. However, this sample still contains phosgene, which requires a secondary containment during transportation.

3.4 Training

3.4.1 Visitor instruction

Important considerations for visitors to phosgene operating areas prior to entering the area:

- Inform visitors of the basic characteristics of phosgene (smell, gas density, etc.).
- Issue phosgene indicator badges to visitors and inform them about the proper use and care of them.
- Instruct visitors about the general alarm plan for the area they are visiting as well as exit/evacuation procedures. This can be accomplished by means of a safety video if available.
- Instruct visitors on the use of the escape device used by the area being visited.
- Accompany visitors with unit personnel, who are responsible for their safety.

3.4.2 Basic training for new employees

It is important that the operation and maintenance of phosgene generating and processing units be assigned to well trained and experienced operations and maintenance personnel.

Once a new employee has finished any general technician training, unit specific training may be required, which could involve details of the various physical, chemical and hazardous characteristics of phosgene as well as standard operating procedures of the phosgene equipment and processes. This training could include the following:

- Start-up procedures
- Shutdown procedures
- Normal operating parameters and procedures
- Consequences of operating outside of normal operating parameters
- Emergency procedures / actions

It is important that the training plan include on-the-job training, consisting of specific unit operations for which competency can be demonstrated by the trainee.

Since units may operate for long periods between major shutdowns, it may be possible that employees who have passed the initial training period may still not have firsthand experience with some basic unit operations (e.g., start-up, shutdown, upset conditions, etc.). To provide this experience special training in the form of tabletop drills, discussions with experienced operators, emergency drills or other means may be required.

When a scheduled shutdown is planned, consideration should be given to ensure that employees that may not have experienced certain operations are available to obtain this experience.

Note: The use of training simulators and programs could provide valuable training for these unit operations.

3.4.3 Ongoing training for employees who operate phosgene-containing equipment

- Once an employee has been certified to operate phosgene-containing equipment, tabletop drills that pertain to unit operations and upset conditions for phosgene-containing portions of the unit can be performed to enhance operating skills.
- Regular evacuation drills with attention given to ensure all shifts participate in these drills are advisable.

3.4.4 Training for employees (company or long-term contractors) who maintain phosgene- containing equipment

It is important that the maintenance of phosgene generating and processing units be assigned to well trained and experienced maintenance personnel.

Prior to beginning work in the phosgene unit it is important that all personnel have been instructed about:

- the potential hazards of working in a phosgene area,
- aspects of the work planned,
- the planned response in the event of a release or other emergency

And that they are issued the proper PPE and ensure that their escape device is in proper working condition.

3.4.5 Laboratory technicians

Training of laboratory technicians is covered in Part 3 - section 2 'Phosgene in the Laboratory'.

3.4.6 Documentation

It is important that participation at instructions, training courses and other qualifications activities be controlled and documented. It is advisable that if training occurs for an entire operating shift, all personnel who participated in the training be documented and that a shift member who is unavailable to participate, should be required to make up the missed training and be documented.

3.4.7 Miscellaneous

It is advisable, that contract employees, who are used in the same role as company technicians, should obtain the same training as company employees.

(Abbreviations and acronyms)

HCl	Hydrogen chloride
NO _x	Nitrogen oxides
PPE	Personal Protective Equipment
PPM	Concentration in Parts per Million
PPM-MIN	Dose in PPM times Minutes
UV	Ultraviolet