Phosgene Safety Practices
for design, production and processing

Part 3
Related information and special safety practices

Section 2: Phosgene in the laboratory

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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.

1 Scope, diphosgene and triphosgene, authorisation of laboratories

This text deals with the handling of phosgene in the laboratory, such as in the analysis of samples and the use of phosgene in synthesis. Included in the text is a section specific to the use of diphosgene or triphosgene. Diphosgene and triphosgene are, in effect, derivatives of phosgene and are potential sources of phosgene: phosgene may be released from them in transport or storage under unfavourable conditions, e.g. at higher temperatures or when containing impurities. Triphosgene has a specific toxicity of its own; see also part 3 sections 3.1.3 and 3.5.

Authorisation of a laboratory using phosgene, diphosgene or triphosgene use may be required by a regulator or other body. To comply, in either case, it may be necessary to conduct a safety analysis before the laboratory is authorised for such use. Factors to be considered in the safety analysis include energy failures and off-gas handling as well as an emergency action plan.

Reviewing the safety analysis on a routine basis is advisable.

2 Phosgene actions: procedures and documentation

A phosgene action is any test, transfer or experiment with phosgene at occupational exposure levels. For TLV levels see part 3 section 4.2 “Working place limits”.

It is important that laboratories handling phosgene have written operating procedures which may be either general operating instructions or procedures for specific phosgene actions. Considerations to be included in the safety procedures may be sections regarding accident prevention as well as provisions of when to abort the phosgene action and a corresponding plan for emergency shutdowns.

It is suggested that operating instruction or procedures for specific phosgene actions include a safety checklist which is signed off by the person carrying out the test or experiment and by the supervisor. This may not be necessary for small experiments or for analytical measurements.

The collection and handling of phosgene-containing samples in production units are described in Part 2 - section 3.3. It is important that procedures include directions on transporting phosgene-containing samples to the laboratory, for disposal of residual phosgene-containing materials and for decontaminating the sample containers used.

It is important that the facility supervision ensure that all current regulations and agreed safety procedures are in place before work with phosgene commences.

3 Qualifying to work in a phosgene laboratory

It is advisable that before using phosgene in a laboratory, personnel are trained, demonstrated competence and that this is documented. Checking for competence at appropriate intervals thereafter is important.

Training/qualifying could typically include:

- Understanding the hazards associated with phosgene and what to do practically in an emergency.
- Participate in an emergency exercise to test response to alarms.
- On the job training under supervision of experienced personnel.
- Discussion of procedures and instructions before the work starts.
- Observation of the phosgene action.
- Assist during an experiment.
- During one or more experiments, carry out the experiment with supervision of experienced personnel.

Personnel working adjacent to a phosgene laboratory

It is advisable that personnel working in laboratory or office areas adjacent to the area where phosgene is present be trained on how to respond to a phosgene emergency. That emergency plans be a written document and reviewed with personnel at appropriate intervals, is important.

4 Phosgene area: design, equipment, procedures

4.1 Design

It is important that the scale of phosgene actions be minimised in order to limit potential phosgene exposure. This includes the size of equipment and of the quantities of material.

It is recommended that when handling **larger quantities** of liquid phosgene (pure or in solution) or phosgene as gas, the process is carried out in a dedicated area. Preferably this is an enclosed area which is specially designed for handling phosgene, having a slight under-pressure and equipped with:

- Purpose-designed fume hoods with sash windows
- Flow meters, each with an alarm function to monitor the hood performance
- A ventilated area or cabinet for storage of phosgene cylinders
- A caustic soda scrubbing system, or other phosgene decomposition system, capable of destroying any phosgene present in the exhaust of each fume hood. This system should be active when work with phosgene is being carried out and equipped with the necessary controls and alarms to guarantee performance.
- A phosgene feed system in the hood to connect cylinders has been pressure tested before use. It is typically equipped with a flow controller, automatic shut-off valve and a connection, to allow nitrogen purging of the system before the cylinder is disconnected. The automatic shut-off valve will be activated if there is a malfunction of a) the ventilation system or b) the decomposition system or c) there is a power failure. The automatic shut-off valve cannot be opened as long as malfunction exists.
- A phosgene detection system which monitors:
  – the air in the area
  – the phosgene storage area or cabinet, to detect any leakage from the cylinders
  – the exhaust from the hoods

  If values above the TLV are measured (although detection limit is much lower) it activates:
  – a phosgene alarm system (both acoustic and flashing lights)
  – the decomposition system (if not active already)
  – the phosgene supply shut-off valve
  – an alarm to a room where 24 hours monitoring/emergency response is available
- A button near the exits of the area which can be used to switch off all the electrical equipment present in the hood in case of an emergency. This also means that experimental setups should be designed in such a way that in case of an emergency the experiment can be aborted immediately.
- An electrical power back-up for the ventilation, phosgene decomposition including an alarm system, in case of power failure.

Written procedures to ensure safe operation in this area could include the following rules:

- When handling phosgene carried out in the hood: all samples containing phosgene to be kept within the hood.
- In case of a phosgene alarm, evacuate the area immediately. Consider switching off the equipment with the emergency button. Any release of phosgene can then be extracted and destroyed in the phosgene decomposition system.
- Entrance to the area during a phosgene alarm is allowed only with the use of air breathing equipment.

If all of the above requirements be met, the precautions mentioned the other part of section 4 should be reviewed.

When handling **smaller quantities** of liquid phosgene (pure or in solution) or phosgene as gas, the above preferred design and procedures basically apply. In this situation one could consider not automating the shut-off valve or consider making other alarm and back-up arrangements, depending on the actual situation.

4.2 Hoods

Besides meeting local regulations, it is important that hoods are designed as per the above recommendation. The flow velocity in an opening where one sash window is open is best between 0.25 and 0.4 m/sec, minimising the backflow of vapour from the hood. It advisable to check national regulations for required air flow rates.

A device such as a flow meter with flow direction indication that monitors the hood performance should be used. It is recommended that the front window of a hood be capable of opening horizontally to minimize the open space during the phosgene action. And that the hood sash is closed to the degree that the experiment allows to minimize the risk of phosgene exposure.

4.3 Pressurised phosgene cylinders

Pressurised phosgene cylinders for laboratory use are if possible best stored outside the laboratory and protected from overheating (< 50 °C). If this is not possible, it is important that the cylinders be stored in hoods or in continuously ventilated fume cabinets equipped with phosgene monitoring devices and protected from temperatures exceeding 50 °C.

Pressurised gas cylinders can be safely moved only when the cylinder valve is closed, and the valve cap (with gasket) and the cylinder cap in place.

It is important that pressurised phosgene cylinders are connected and operated only in hoods or suction-vented cabinets. Consider the need for breathing air when disconnecting or connecting a cylinder.

It is advisable that the cylinder valve (hand valve) is opened only after a second block valve has been attached. For better control of the flow and pressure, appropriate needle valves or a pressure regulator compatible with phosgene can be used (do not use brass). It is important that the needle valve stem is secured to prevent it becoming unscrewed. Use a properly sized wrench to attach or remove the valve and thread protector and use a new gasket suitable for use with phosgene each time a valve is connected. Lead gaskets are not recommended because they can be pressed into the valve opening.

It is important that the cylinder valve (hand wheel) only be opened and closed by hand and that cylinders that cannot be opened without the use of force (tools or levers) are returned to the supplier with appropriate documentation.

It is advisable to fully open the main valve on a gas cylinder only after a leak test has been performed with the needle valve closed and the main valve slightly open. The leak test can be conducted using:

- a gas testing tube such as a Draeger tube
- phosgene indication paper
- an electronic phosgene indication instrument

Brass valves may not be suitable for phosgene service. After phosgene gas has been taken from cylinder, incursion of foreign substances into the valve or into the cylinder is to be avoided.

After a gas cylinder has been disconnected a leak test is advisable before returning to the supplier.

It is advisable to keep the pressure regulator valves in the fume hood for decontamination.

Notify the supplier immediately if it is no longer possible to close a cylinder tightly and await instructions from the supplier.

4.4 Phosgene detection and measurement in the laboratory

It is important that personnel working or visiting laboratories where phosgene is in use wear a phosgene detection badge located close to the breathing zone and that laboratories where phosgene actions are carried out are equipped with air monitoring systems, preferably with alarms. Examples of systems are listed below:

- A stationary phosgene detector (e.g. paper tape, electrochemical) that can measure phosgene concentrations at or below the TLV .
- A personal warning device, for example a Monitox instrument (Compur 4100) can be used for concentrations near to the TLV
- Phosgene indicator badge paper may be placed at strategic points around the apparatus and inside the hood to indicate phosgene leaks. The colour can give a semi-quantitative indication of the leak using a colour comparator.
- Draeger tubes which can detect phosgene in the sub-ppm range

4.5 Destruction of phosgene

It is advisable that personnel involved with decomposition of phosgene wear proper protective equipment including supplied breathing air.

4.5.1 Decomposition of phosgene gas

Decomposition of gaseous phosgene in the off-gas from laboratory phosgenation can be accomplished by hydrolysis of phosgene on activated carbon. With this method, any amount of phosgene that could be harmful to the environment is eliminated.

Alternatively, a caustic soda scrubbing system can be used for this purpose.

4.5.2 Composition of phosgene solutions with solids (adsorption)

Spilled phosgene solution can be decomposed by adsorbing the spilled material on non-flammable mineral adsorbents (e.g. Oil-Dri or Vermiculite) and covering it with calcium hydroxide. It is important that the liquid is adsorbed with minimum twice the amount of adsorbent to the spilled phosgene solution. The adsorbent can then be covered with at least six-fold excess of calcium hydroxide (based on the amount of phosgene or phosgene solution). It is **important** to maintain this sequence: first the adsorbent, then the calcium hydroxide. Complete decomposition of the phosgene necessary before the decomposition medium can be properly disposed off.

An alternative to mineral adsorbent/calcium hydroxide is to use crystalline urea.

4.5.3 Decomposition of phosgene solutions with solutions

An aqueous ammonia solution is suitable for decomposition of phosgene in solutions if the phosgene solution is miscible with water. Phosgene solutions that are not miscible with water can be decomposed with minimum three-fold excess of a mixture containing:

- 1 part aqueous, concentrated (25%) ammonia solution,
- 1 part water
- 1 part iso-propanol (low flash point of the decomposition solution)

These decomposition solutions should always be used in excess amounts.

To decompose large amount of a phosgene-containing solution, it may be necessary to cool the phosgene solution and add it to a cooled decomposition solution.

Small quantities of phosgene, samples for example, can be directly neutralized with an appropriate neutralizing agent ($NaOH$ or NH_4OH)

4.6 Control of phosgene releases

When a phosgene release is evident in any apparatus in a hood it is advisable that the following actions are taken:

- use the proper PPE, which could include supplied breathing air
- close the hood to the extent possible
- warn others
- evaluate the situation and take the appropriate action:

- In case of **minor problems**, such as a loose stopper, ground joint, or stirrer guide, with release of gaseous phosgene, a person should be able to reach inside the hood to fix the problem. Consider the need for wearing breathing air. The horizontal pane of the hood should be opened as little as possible to avoid/minimize any phosgene release.
- If the experiment takes place in a **walk-in hood**, evacuating the hood is advisable. Then a minimum of two people using supplied breathing air and other PPE can attempt to fix the problem. If the leak cannot be fixed it is advisable to abort the reaction and to take appropriate measures to decompose the remaining phosgene.
- In case of damaged equipment or emission of larger amounts of phosgene solution, it is important to activate the laboratory alarm and evacuate the laboratory while implementing the prescribed emergency action appropriate for the situation.
- If the phosgene emission is **not restricted to the laboratory** area (when off-gas from the hood or the laboratory is blown to the atmosphere, for example), an alarm could be activated while implementing the prescribed emergency action appropriate for the situation.

It is best not to discharge hood effluent containing phosgene to the atmosphere untreated. A phosgene destruction method can be used to prevent phosgene release from laboratory hoods.

4.7 Personal Protective Equipment

It is important to consider the need for supplied breathing air when:

- connecting or disconnecting phosgene gas cylinders
- handling an emergency, including emergency shutdown
- when making repairs or fixing leaks

Personnel standing outside the hood to observe/monitor the reaction should not need to use supplied breathing air: however, it would be advisable for it to be within easy reach and a second qualified person to have supplied air equipment available in case of an emergency. Personnel working outside a hood not completely closed are advised to wear a full face breathing air mask, or at least a filter mask fitted with an acid vapour canister. See Part 2, section 3.1 on personal protection.

It is advisable that persons within an area (section, room, etc.) where phosgene work is performed wear phosgene indicator badges and keep escape packs or full-face masks with them.

5 Examples of phosgene actions

5.1 Phosgenation using phosgene from gas cylinder

5.1.1 Overview

It is recommended that a phosgene experiment is monitored by a person during the entire experiment process and that it not be left unattended. It is advisable that an additional qualified employee with proper personal protective equipment is also available in case of an emergency. During the entire experiment period (from connecting the phosgene gas cylinder until any excess phosgene at the end of the experiment has been destroyed) the work and the area will be monitored for phosgene.

It is advisable that each phosgenation apparatus be monitored by at least one employee, possibly with the exception of screening experiments in research and development laboratories when very small quantities are used. If two phosgenations are to be performed simultaneously, it is recommended that they be monitored by two employees.

Flushing of apparatus after phosgenation with nitrogen may be carried out in the same hood as a phosgenation experiment.

It is recommended that only phosgene reactions be performed in the phosgenation hood and that other experimentation not be performed in these hoods at the same time and that the reaction off-gas from the test equipment (from phosgenation or other degassing equipment, for example) is sent to an off-gas system with phosgene destruction, before it is released to the atmosphere.

5.1.2 Sample size and equipment

It is good practice to minimize the size of samples containing phosgene. When analysing for components other than phosgene, it is best to remove the phosgene prior to analysis by purging with nitrogen. Decomposition of the phosgene in the nitrogen purge is recommended prior to release to the hood exhaust.

In some cases it may be necessary to analyze prior to decomposition of the phosgene in order to get an accurate analysis.

Handling phosgene in glass equipment may be used in the laboratory only when the following conditions are met:

- The amount of phosgene may not exceed the capacity of the decomposition system in case of a sudden release.
- Remove only the amount of phosgene actually needed for the experiment from a pressurised cylinder in gaseous form which might be either condensed or dissolved in solvent.
- It is not recommended to take liquid phosgene directly from a pressurised cylinder since solid particles such as rust may get into the valve preventing it from closing tightly.
- It is advisable that the flask/vessel containing condensed phosgene remain connected to the apparatus until the condensed phosgene has been consumed. It is not recommended to manually manipulate the apparatus, such as disconnecting the lines and apparatus, weighing the flask and the liquid phosgene, before all condensed phosgene is consumed.

- It is important to take precautions to prevent backflow of the reaction mixture into the liquid phosgene and to mitigate spills in the event the glass breaks.

5.1.3 Phosgene equipment

It is important that the equipment selected for use with phosgene reactions is inspected for suitability (wall thickness, cracks, materials of construction etc.). It is recommended that joints be clamped. To prevent undesirable overpressure, it is advisable that a liquid seal loop, vented to a phosgene decomposition system, be installed between the phosgene cylinder and the reaction equipment. With the safety seal loop in place, test may be performed under slight positive pressure (0.1 bar overpressure maximum).

Experiments at higher pressure may require special purpose-designed equipment.

Sulphuric acid or white mineral oil may be used as seal liquids (proper disposal should be assured; phosgene is easily dissolved in both). Water or mercury is not recommended as seal liquids.

It is recommended that adequately sized containers with inorganic absorption agents be placed underneath the reaction vessel to contain the vessel contents in case the vessel breaks.

5.1.4 Phosgene solution storage

Occasionally, a master batch of phosgene solution needs to be prepared to be used in several separate experiments. This is usually in research and development laboratories having experience in handling phosgene.

The phosgene solution is usually prepared by dissolving phosgene in a solvent (such as monochlorobenzene or toluene). Important considerations for storing phosgene solutions could include:

- Written safety instructions specifying the phosgene monitoring plan and instruction on dealing with an emergency situation.
- Storing the solution in a hood equipped with a phosgene detector that continuously monitors the space and is capable of measuring concentrations to 0.1 ppm (volume) and will activate an alarm possibly to a (control) room where 24/7 coverage is available.
- It is advisable to store the solution in a sealed container that is placed in a container large enough to contain the entire contents of the storage container plus enough solid absorbent or liquid decontamination solution to absorb or neutralize all of the phosgene. Direct contact between the sealed solution container and the absorbent/decontamination solution is best to be avoided.

5.2 Diphosgene or triphosgene

5.2.1 Overview

Diphosgene and triphosgene are hazardous chemicals which in effect are condensed forms of phosgene, capable of releasing high concentrations of phosgene in unfavourable conditions, which can potentially occur also during transportation and storage. It is important to understand the hazardous nature of these chemicals and be prepared in the event of an emergency.

Diphosgene and triphosgene are sometimes used in laboratories as phosgene-generating reagents. Diphosgene and triphosgene are usually stable at room temperature, but will decompose to generate phosgene if heated to certain temperature (if a catalyst is present, the decomposition temperature is much lower). An advantage of using these chemicals is that the phosgene generated this way is usually directly dissolved in a solvent or consumed instantly in the reaction vessel, so there is no gaseous phosgene transfer involved in between flask/lines. For the principal physicochemical differences between phosgene and the phosgene congeners, see also Table 1 in part 3 section 3.1.3.

5.2.2 Storage and Handling

It is important to store di- and tri-phosgene in a cool area with good ventilation, i.e. in a hood or ventilated cabinet with the container closed and sealed. Storage in a freezer or fridge is not necessary and better avoided. A check for phosgene can be done prior to opening the container using phosgene indicator paper or Draeger tube. It is advisable to open the container carefully and in a hood since when diphosgene or triphosgene is stored it is possible that phosgene may be released with an increase in pressure inside the container. It is advisable to monitor the containers on a regular basis. It should be noted here that phosgene detectors may be suitable to show the presence/absence of congeners of phosgene, but only in a dichotomous, non-quantitative manner. See Part 3 section 3.5

5.2.3 Additional Safety Considerations

Important safety considerations are:

- Written safety instruction which specifies steps to take in case of phosgene release, including emergency actions, and the decomposition of off-gas
- Experimentation is carried out in a hood.
- Those monitoring the experiment wear a phosgene badge and have escape mask within reach.
- Continuously monitor the hood for phosgene.
- Provisions for off-gas handling and phosgene decomposition.

6 Use of phosgene including di- and tri-phosgene

6.1 Foreword

Phosgene is a useful but potentially hazardous and toxic material that could lead to fatal consequences if not stored and used properly. While di- and tri-phosgene are stable under normal conditions there is a potential for them to decompose releasing phosgene and therefore are not considered to be "safe" phosgene equivalents. The toxic effect might be delayed compared with phosgene, see also Part 3 section 3.5.

It is advisable that any incident/accident be considered as a phosgene exposure with appropriate measures taken. Important considerations for handling phosgene and/or di- and tri-phosgene can be summarised as follows:

- A written Standard Operating Procedure (SOP) for the use and storage be available with emergency measures specified
- It is advisable that a safety representative is responsible for the development and implementation of a site-specific safety procedure.
- Only experienced persons with adequate training will handle phosgene or di- and tri-phosgene.
- It is strongly advised to do the handling, including weighing, etc, in a fume hood.
- It is advisable that phosgene indicator badges be worn by all personnel with potential exposure to phosgene vapours
- The use of an electronic phosgene detector next to the experiment is recommended.
- The use of a safety tray/receiver large enough to contain the entire contents of the reaction equipment is recommended (loaded with urea and vermiculite or any other suitable adsorption material).
- It is important that no phosgene, di- or tri-phosgene be emitted in the off-gas (off-gas treatment via a decomposition tower recommended).
- It is important that respiratory protection be readily available.
- It is important that phosgene decomposition solution be readily available.
- It is recommended that central storage of the compounds and the safety equipment on the site be established (tracking of the material is recommended) with the amounts stored minimized. It is important that only authorized individuals have access to the storage facility.
- In incidents where personnel are exposed to phosgene vapours, e.g. badge discoloration, it is important that the employee be seen by a medical provider (physician or nurse) who after assessing exposure history and badge discoloration will decide upon disposition of the patient. See also Part 3 section 1: “First aid, medical intervention and emergency response” (under preparation).

6.2 Standard Operating Procedure (SOP) for phosgene/ diphosgene / triphosgene

It is recommended that a written standard operating procedure (SOP) be developed and implemented for each individual use of phosgene, di- or tri-phosgene including some or all of the following considerations:

- **Responsibilities**
  Delineate the responsibilities of those personnel who either directly or indirectly will be involved with the phosgene action.
- **Safety Precautions**
  Delineate steps to be taken by the various personnel in the event of an incident.
- **Personal Protective Equipment**
  Describe in detail the PPE that will be required by those personnel who are either directly or indirectly involved with the phosgene action.
- **Organisation**
  Describe the labelling in the work area, the training and qualification of technicians and the number and responsibilities of technicians
- **Storage and Transport**
  Describe safe storage regulations (site and governmental) and restrictions and procedures to be followed when transporting these compounds
- **Experimental Set up**
  Describe in detail the set up of the experimental equipment including ancillary equipment used in the event of a phosgene excursion and to prevent phosgene vapours from escaping to the atmosphere
- **Preparation and Performance of the Experiment**
  Describe in detail the procedure to be followed in the experiment including sampling techniques
- **Analysis**
  Describe in detail the procedures to be used to analyse the various samples including in-process samples.
- **Disruption of the Operation**
  Describe in detail the actions to be taken by various personnel in the event of a disruption of the operation due to equipment failure power failure or any other cause.
- **Emergency Action Plan**
  Describe in detail what actions will be taken and by whom in the event of an emergency; including alarms, notifications evacuation plans and routes, etc.

7 Abbreviations and Acronyms

BAR	A unit of pressure which is about the same as atmospheric pressure (1 bar = 14.054 psi)
°C	Degree Celsius
NaOH	Sodium hydroxide
NH4OH	Ammonium hydroxide
PPE	Personal Protective Equipment
PPM	Parts per Million
PPM-MIN	PPM times Minutes
PSI	Pounds per Square Inch
SOP	Standard Operating Procedure
TLV	Threshold Limit Value