

6.9 Phosgene Monitor/Analyzer Guideline

6.9.1 Purpose

The purpose of this section is to provide guidance towards the selection of phosgene monitor/analyzer equipment used to detect a loss of containment from phosgene processing systems.

6.9.2 Scope

The scope of this section includes site perimeter, secondary containment buildings, process and personnel devices that detect the presence of phosgene in areas defined as normally free of phosgene.

Monitoring equipment is placed in areas that are normally occupied by personnel who would be affected by a release of phosgene, as well as in remote areas to detect a loss of containment. These locations may include: secondary containment systems; perimeter locations around phosgene producing and handling facilities; and air intakes to heating, ventilating and air-conditioning (HVAC) systems for control rooms, etc.

A number of companies have found that linking fixed monitoring devices to a central alarm system offers a useful method of warning personnel about a loss of phosgene containment. Another option has been to integrate meteorological data and a grid of phosgene monitors (various technologies) with a PC-based modeling program. The network provides the capability of early leak detection and estimating downwind impact. Users may evaluate such approaches in development of monitoring systems that meet their individual situations.

For additional information on air monitoring, including the use of badges, refer to Section 4.2.3 of this Manual.

6.9.3 Definitions

Monitor – A piece of equipment used to detect the presence of phosgene outside process containment components. Examples of where monitors are sometimes used include: within enclosures, at a unit's perimeter, at a site's perimeter, in the vicinity of phosgene containing process equipment and as portable handheld devices.

Analyzer – A piece of equipment used to detect the presence of phosgene in process streams that are normally expected to be phosgene free but have the potential to contain phosgene if the process is operating improperly. Examples of where analyzers are sometimes used include:

scrubber outlets and the discharge location of certain vent systems such as the methylene chloride vent recovery systems.

6.9.4 Definitions of Service

Perimeter Monitors, Fixed and Portable - By definition, a perimeter monitor is located at the battery limits of a unit or plant that normally processes phosgene. Perimeter monitors are used to detect a loss of containment from the process. The monitors also identify external losses from phosgene secondary containment systems. There are two types of perimeter monitors. Fixed units are permanent installations that send information to the plant control systems. Portable units are used to verify a reading of a fixed unit and to detect the presence of phosgene outside secondary containment. Fixed systems are also installed to monitor areas in the immediate vicinity of phosgene containing equipment.

Mitigation System Process Analyzers – Mitigation system analyzers are used to detect a breakthrough of phosgene from a process such as through a process vent (that is, scrubber outlet or vent system discharge).

Secondary Containment Monitors - Secondary containment monitors are used to detect a loss of containment from process equipment housed within the phosgene enclosure systems, such as containment buildings, jacketed equipment and piping.

HVAC Monitors - HVAC monitors with alarms can be used to warn personnel of a loss of containment affecting their workspace (e.g., control rooms, laboratories, offices, etc.). The development of a response plan for personnel to follow should these devices activate helps reduce potential risks.

Personal Electronic Monitors – Personal Electronic Monitors can be used to help prevent personnel from entering phosgene-containing areas by identifying whether phosgene is present and/or the level of exposure. Audible alarms are available and can be set at an appropriate occupational exposure level.

Portable Monitors – Portable monitors can be used to locate phosgene leaks within and around phosgene-processing areas. Some of the more common locations at which portable monitors may be used include at flanges, at piping or equipment where failures can result in a gas release, and within secondary containment systems.

Badges – Colorimetric badges measure doses, and can be worn by workers or visitors in operating areas. Badges are sensitive to low doses

of phosgene and may be helpful in determining the extent of phosgene exposure.

Detector Tubes – Portable quantitative colorimetric devices are used for process measurements and emergency response situations.

6.9.5 Description of Monitor Types

The following monitor types are commonly used in monitoring programs.

Paper Tape Monitor – A paper tape monitor is a cabinet, stand-alone or portable instrument composed of a tape drive mechanism with paper tape, a vacuum pump with sample tubing, and a colorimetric analyzer. These instruments can monitor a single point or multiple sample points. Air samples are pumped to the unit and directed onto a chemically-impregnated paper tape that changes color in proportion to the amount of phosgene in the sample. Colorimetric changes are measured continuously and an output signal generated accordingly. Cassettes may require periodic replacement; for example, some cassettes are replaced on a monthly basis. Cassette measurement ranging from 0 to 1000 parts per billion is available; however, lower detection limit is often 7 parts per billion, but may change as technology improves. Some effects from other chemicals such as HCl are possible.

Chemical Cell Monitor – A chemical cell monitor is a stand-alone or portable instrument composed of an electrochemical cell open to the atmosphere or inserted into ductwork, coupled to a solid-state memory module and electronic transmitter. This type of monitor is a single-sample monitoring system. Phosgene gas enters the cell and reacts to change the electrochemical properties in the cell. The original chemical is eventually depleted and the cell must be replaced. Changes are measured continuously and an output signal generated accordingly. Chemical cell measurement ranging from 0 to 1000 parts per billion is available. The lower detection limit is often however 20 parts per billion. Again this is subject to change as technology improves. Chemical cell monitors are sensitive to interference gases.

Open-Path Monitors – Open-path monitors transmit an infrared or ultraviolet light beam along a path that may be hundreds of meters long, using the spectroscopic absorption properties of molecules to identify and quantify chemicals in the atmospheric path. Phosgene has a unique absorption signature that enables identification of phosgene among other gases that may be also present in the beam. One spectroscopic open-path monitor is also capable of detecting and simultaneously measuring most other gases that may be present along with the phosgene. The

sensitivity of Open-Path Fourier Transform Infrared Spectroscopy (FTIR) systems to phosgene has been tested to achieve detection limits as low as 0.5 parts per billion.

High-Range Phosgene Monitors – High-range phosgene monitors have the capability to monitor phosgene concentrations at levels of 1000 parts per million or higher, depending on the end user's requirements. Common technologies used for this type of application include: Fourier Transform Infrared and Magnetic Scanned Mass Spectrometers. Each of these devices is capable of monitoring a range of materials in addition to phosgene.

6.9.6 Monitor Selection Considerations

The general considerations discussed in this section may be helpful in selecting and developing phosgene monitoring programs. As with other sections of these Guidelines because the guidance is general by nature, it is not possible to identify all possible considerations that users may need to consider. Therefore, in selecting equipment, users must take into account their own specific needs and circumstances as different considerations may be relevant or required.

Chemical Interferences – Refers to the monitor's response to the presence of a chemical other than phosgene. Some persons believe chemical cell type monitors may be more susceptible to chemical interferences than paper tape monitors. The specific chemicals and concentrations that affect a monitor's response are manufacturer-specific. Common interference chemicals can include: H₂S, HCL, CL₂, SO₂, HCN, NO, NH₃ and H₂O. Proximity of other chemical facilities may introduce interference chemicals. Continued exposure to low levels of interference gasses may cumulatively deplete a chemical cell's ability to respond to phosgene, and warrant early cell replacement. Consult testing results on different monitors for further information on chemical interferences. Filters have been used for electrochemical cell technology to minimize the effect of interfering chemicals. Use of a filter may require recalibration of the detection cell and may impact response times. The manufacturer should be consulted on the application of any filter, technical details and applicability to its monitor.

Sensitivity – Refers to the lowest phosgene concentration the monitor can detect and respond to. Paper tape monitors are often able to detect lower phosgene concentrations than chemical cell type monitors, a capability which may be considered in relation to uses in and around phosgene-handling process areas where personnel are normally present.

A high sensitivity provides added protection of earlier warning of a phosgene leak.

Reliability – Refers to the ruggedness and ability of the monitor as a whole to continue to perform to specifications while subjected to normal or abnormal environmental stresses. Some monitor types include self-diagnostic features to alert the operator to internal malfunctions. Some monitor types require protective enclosures with controlled environment to function properly. Appropriate construction methods and high quality materials should be used in phosgene monitor installations.

Installation Issues – Refers to specific physical requirements or limitations of a monitoring system's components. Monitors that have an internal sampling pump often have sample line length limitations. It is important that the installation of paper tape monitor sample lines is done properly so that moisture does not collect in the system. Chemical cell monitors inserted in ductwork may have minimum flow requirements. Dust can also cause false readings in paper tape based systems. Filters should be considered for sample collection points.

Maintenance and Calibration Issues – Refers to procedures and methods for monitor upkeep to help assure continuous accuracy and reliability. Chemical cell monitors may have to be sent offsite for periodic replenishment of the cell and re-calibration with phosgene. Regularly scheduled "bump tests" with an interference gas can be used to help verify the chemical cell is still reactive. Paper tape monitors may require periodic sample line flow balancing and regular paper cassette tape replacement. Regular cleaning of sample collection systems has been shown to be beneficial in preventing false readings and other operations problems. Inlet and out sample tubing should also be considered in the maintenance of the sampling system as tubing leaks could affect the quality of the sample and the monitor's measurement results.

Cost Issues – Refers to initial installation, preventive maintenance, and upkeep/repair costs. Paper tape units may be the most expensive, and involve additional costs associated with running sample lines, purging, and conditioning the enclosure internal environment. Consumables include paper cassette tapes, sample line scrubbers, and particulate filters. Chemical cell monitors may be less costly to purchase and install, depending on physical location. Maintenance costs may include offsite services for calibration and chemical cell replacement.

6.9.6.1 Monitor Selection Considerations: Open-Path FTIR Monitors

One benefit provided by open-path monitors is that they can provide a continuous spatial coverage. Small plumes, which may

travel undetected between the positions of point monitors, may cross the light beam and can be detected by the open path systems. Thus a single open-path monitor may provide coverage not achievable by even a large number of point monitors.

Sensitivity – The open-path Fourier Transform Infrared systems may have the highest sensitivity with respect to large plumes. In the case of small plumes, the detection levels appear proportionately higher, but are generally in the range of the detection limits of paper tape and electrochemical monitors.

Reliability – Some recently developed open-path Fourier Transform Infrared instruments have shown a high degree of reliability. Older systems previously used for phosgene monitoring employed closed-cycle, cryogenic coolers that required frequent replacement that could result in low Mean-Time-Between-Failures (MTBF). The newer systems replaced closed-cycle coolers with automatic liquid nitrogen fill systems. These systems require replacement of the liquid nitrogen storage periodically (e.g., in some cases every 45 to 60 days). Some open-path Fourier Transform Infrared monitors that use these automatic fill systems have MTBF as high as 20,000 hours.

Chemical Interferences – The effect of chemical interferences on open-path Fourier Transform Infrared monitors is generally to raise detection limits and reduce the accuracy of the measurement. These monitors use a multi-component, least-squares algorithm (Classical Least Squares, “CLS”) to minimize the effects of interferences, and to enable (if desired) the individual quantitation of the interferences along with the main analyte, phosgene. Most chemicals absorb in the infrared region, but only a relatively small number happen to have absorption bands that occur in the narrow region of the phosgene band. Thus, these chemicals are potential interferences and the Classical Least Squares algorithm has been useful in minimizing the effect of these interferences on the quality of the phosgene detection and measurement.

Multi-Species Analysis – Most open-path Fourier Transform Infrared monitors can simultaneously monitor for any of the vast number of infrared absorbing chemicals in addition to phosgene. Some systems allow the simultaneous quantitation of up to 32 different chemicals.

Installation Issues – Action may be needed to protect installed open-path monitors and external optics from rain, wind and dust. Some systems require little additional protection, while others may

require environmental control within a narrow range of temperature and humidity. The monitor generally is located at the end of the planned monitored beam-path that has an unobstructed line-of-sight to the opposite end at which the retroreflector will be installed. Electric power must be provided at the monitor and conductive or optical fiber cables may be installed to bring the monitor output to a central control system.

Maintenance and Calibration Issues – Because the measurement technology behind open-path Fourier Transform Infrared monitors relies on a linear relationship in the absorption signal, calibration is inherent in the reference spectra for phosgene and other chemicals. In this respect, calibrations may be unnecessary. The calibration and response of the monitor can be checked by quality assurance procedures. Information on quality assurance procedures is outlined in the U.S. EPA Compendium Method for Open-Path Fourier Transform Infrared Monitors, TO-16.

Maintenance requirements depend on the environment of the installation. For example, while in many environments, cleaning the optics every six to twelve months is appropriate, other environments require alternative procedures. Aside from cleaning, some monitors only require the replacement of certain low-cost internal components on an annual basis; other monitors require replacement on a biannual basis.

Costs – The purchase cost of a single, open-path monitor may be higher than the cost of single-point monitors, but the information detected by the open-path monitor may be equivalent to, or better than, that received by a large number of point sensors. In addition, costs of ownership may be lower than ownership costs for point monitors. For some systems, maintenance requirements involve minimum on-site labor or off-site expense.

6.9.7 Sample Monitor Applications

The following examples are offered to help illustrate and apply information described earlier in the section.

Example 1 – Chemical Site A has eleven plants that produce or handle phosgene. The chemical plant bordering it on the south produces several chemicals that can interfere with chemical cell monitors given appropriate wind direction and concentrations. The chemical plant bordering it on the north also produces and uses phosgene. A high-traffic highway runs on the west. Unpopulated swampland borders its east side.

This site has paper tape monitor units installed in each of the eleven phosgene plants. Air sample points bracket the phosgene process area in each plant, and are tubed to a centrally located enclosure containing the monitors. This site also has six small secondary containment buildings with vessels containing liquid phosgene. These buildings are under slight vacuum pressure by means of a suction duct to the incinerator. A phosgene chemical cell monitor is inserted into the suction duct as it exits each building, to help detect any leak occurring inside. Similar duct-mounted chemical cell monitors are located in control room and lab heating, ventilating and air-conditioning systems throughout the plant. In addition, a network of multiple, stand-alone, chemical cell units monitor atmospheric air at regular intervals around the south, west and north site perimeter fence lines. These units serve to help verify containment of any leak within site borders. Wind speed and direction instruments are installed in several locations in the plant. All monitors are wired to a computer-based program where they are displayed, trended and alarmed. Interference chemicals from the neighboring plant to the south, coupled with specific wind directions, occasionally cause false phosgene alarms. Site-wide procedures are in place to help verify, evaluate and respond to any phosgene alarm.

Example 2 – Chemical Site B has one plant that produces phosgene. The site is remotely located in a generally rural setting. There are chemical plants nearby that produce chemicals that will interfere with electrochemical detectors. The area surrounding the chemical is mainly farmland. The closest major population is more than ten miles from the plant site.

Primary protection from phosgene exposure for the community and plant personnel is a secondary containment system that operates under a slight vacuum with continuous air flow from the secondary containment systems to a caustic scrubber designed to handle a “worst case” scenario release from the phosgene processing equipment that is installed inside.

Each secondary containment system is equipped with a paper tape phosgene monitoring system that continuously monitors the system for low-level phosgene concentrations. Each secondary containment system is monitored. A secondary monitoring system consisting of electrochemical cell detectors is installed as backup to the primary paper tape systems. Additional electrochemical cell monitors are located in the ductwork between the secondary containment system and the scrubber system. The outlet of the scrubber is equipped with redundant paper tape monitors to help detect any breakthrough in the event of a “worst case” release within the secondary containment system. A high range monitoring system is installed that systematically samples each secondary containment system. It can only sample one secondary containment

system at a time, but can be “locked-on” a single system if a leak is detected.

The last detection element is the perimeter monitoring system consisting of paper tape monitors located outside the secondary containment systems. The perimeter detection system is used to identify whether the secondary containment has been breached. The use of paper tape monitors is selected to help ensure the perimeter monitors are specific to only phosgene. The perimeter monitoring system consists of single-point and multi-point monitors. Placement of the monitors is based on meteorological data and proximity to the secondary containment systems.

The entire monitoring system consists of paper tape monitoring locations within the secondary containment system; electrochemical cell detectors within the secondary containment system; a single, multi-point high range monitoring system for the secondary containment system; paper tape monitors used for perimeter and HVAC inlet detection and paper tape systems on the outlet of the scrubber systems. The number and location of the monitors were selected after developing a monitoring strategy considered appropriate to the specific circumstances. All monitors transmit real-time information to the plant computer system where automated actions and administrative procedures are in place to respond to any type of phosgene leak detection. Portable (handheld) and mobile detection equipment is used if phosgene is detected outside the secondary containment system.

Example 3 - Chemical Site C has three plants that produce and handle phosgene. The three plants also provide a by-product for sales to other chemical plants surrounding its borders. The product is transported via pipeline directly and by tank truck.

The site has an Infrared Photometric monitor (analyzer) installed in each plant’s feed to the product delivery system. These Infrared Photometric monitors pull samples from the product feed lines at strategic points to provide quick reaction to prevent phosgene carryover into the product supply. Each plant has designed safety interlock systems, which are activated by the detection of phosgene concentration, to prevent the continuation of the product process. Additionally, the three plants have paper tape monitors, very similar to the ones in Example 1, that are used to monitor the Infrared Photometric monitor’s housing to help protect personnel from possible leaks within the analyzer housing. This approach has a dual effect because the product’s interference is also picked up on the tape, and therefore a leak in the housing is identifiable. The paper tape monitor also acts as a detection device of leaks on the span gas set-up used for calibration of the Infrared Photometric monitor.

Example 4 - Chemical Site D has three plants that produce and handle phosgene. Within each of these three plants are control rooms and administrative buildings that use air intake stacks for their heating, ventilating, and air conditioning systems.

Each intake stack has a pair of paper tape monitors installed in them for detection of phosgene gas. In addition, the control room is equipped with additional paper tape monitors for further detection of phosgene contamination. The stack detection monitors are used as a mechanism to shutdown the buildings' heating, ventilating, and air conditioning systems. The control rooms, because they are NOT evacuated buildings, are supplied with fresh air service for essential personnel. Site procedures are in place to help verify, evaluate and react to different levels of phosgene detection around and within these occupied buildings.