6.9 Phosgene Monitor/Analyzer

Introduction

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

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

Phosgene monitoring equipment is routinely placed by companies 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.

For example, 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 4.0 *Health Factors, Industrial Hygiene, Medical Preparedness, First Aid and Protective Equipment* 4.2.3 *Air Monitoring* of the Guidelines.

NFPA 55, Standard for the Storage, Use, and Handling of Compressed Gases and Cryogenic Fluids in Portable and Stationary Containers, Cylinders and Tanks provides guidance on toxic gas requirements for monitoring and alarm/interlocks on detectors.

The information provided in this section should not be considered as a directive or as an industry standard that readers must adopt or follow. Instead, the information is intended to provide helpful ideas and guidance that users may wish to consider in a general sense (See Section 1.1 *Preface and Legal Notice*). Also included is a reference list of useful resources.

Contents

6.9.1 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 process solvent vent recovery systems.

6.9.2 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 process piping and equipment, and 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 the presence of phosgene 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.

Paper Tape – Colorimetric paper which is sensitive to low concentrations of phosgene may be helpful in determining phosgene emission points.

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.

6.9.3 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 phosgene sensitive 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 5 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 that may be designed to pump a sample of ambient air or allow ambient air to passively pass into the monitor. If phosgene gas enters the cell, it 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 on the order of 50 parts per billion, but varies by manufacturer. Again this is subject to change as technology improves. Chemical cell monitors are often 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.

6.9.4 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. In general, 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: H_2S, HCL, CL_2, SO_2, HCN, NO, NH_3 and H_2O. Proximity of other chemical facilities may introduce interference chemicals. Continued exposure to low levels of interference gases 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 the 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 outlet 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.

References

NFPA 55, Standard for the Storage, Use, and Handling of Compressed Gases and Cryogenic Fluids in Portable and Stationary Containers, Cylinders and Tanks