THE CHLORINE INSTITUTE

Pamphlet 73

Atmospheric Monitoring Equipment for Chlorine

Edition 7

A LEGACY OF SAFETY STEWARDSHIP since 1924

June 2003

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1. INTRODUCTION

1.1 Purpose

Edition 7 of Atmospheric Monitoring Equipment for Chlorine reflects modest changes to this publication from Edition 6. This pamphlet provides information on the experiences of Chlorine Institute member companies in the design, installation, maintenance, and benefits of ambient chlorine monitoring equipment. This information is basically unchanged from Edition 6.

The primary changes are information about chlorine monitoring equipment. This information is presented in revised Appendices 10.1 and 10.2.

Personal monitors are beyond the scope of this pamphlet.

1.2 Responsible Care

The Institute is an American Chemistry Council (ACC) Responsible Care® Partnership Association. In this capacity, the Institute is committed to: Fostering the adoption by its members of the Codes of Management Practices; facilitating their implementation; and encouraging members to join the Responsible Care® initiative directly.

Chlorine Institute members who are not ACC members are encouraged to follow the elements of similar responsible care programs through other associations such as the National Association of Chemical Distributors' (NACD) Responsible Distribution Program or the Canadian Chemical Manufacturers Association's Responsible Care® Program.

1.3 Background

As of the publication date, there are no federal regulations within the United States which mandate the installation of ambient chlorine monitors. However, state and local rules may require the use of monitors for specific situations. Several non-domestic Chlorine Institute member indicated in the survey that they have been required to install monitoring systems. Within the United States, the choice to install monitoring systems is an individual company consideration.

The Environmental Protection Agency has recommended in its report to Congress "Review of Emergency Systems" (9.1), that industry be encouraged to conduct research to develop and refine cost effective, reliable, chemical detection monitoring systems that do not require frequent calibration. During the Special Emphasis Program of 1986, the Occupational Safety and Health Administration questioned chlorine manufactures concerning their anticipated use of chlorine monitors for occupational safety.

Additionally, facilities producing, using or otherwise handling chlorine may be affected by one or both OSHA's Process Safety Management Rule for Highly Hazardous Chemicals (PSM) (9.2) or EPA's Accidental Release Prevention Requirement; Risk Management Programs (RMP) (9.3).

Depending on site-specific factors, the use of ambient chlorine monitors may assist the facility in meeting the requirements of one or both of these regulations. The use of ambient chlorine monitors may also assist a facility in implementing security measures.

1.4 Worker/Community Alert

Chlorine monitors have proven to be effective leak detection devices. Many Chlorine Institute members have installed perimeter systems, source systems or a combination of the two to provide early warning of leaks for plant personnel and the surrounding community. Although perimeter and source monitors are not intended to take place of personal exposure monitoring, they can play a significant role in an overall plant safety program. Early warnings of leaks may allow plant personnel to take appropriate safety precautions and to mitigate the chemical release. Data from source chlorine monitors also may be used in industrial hygiene programs to identify plant areas where additional personnel exposure monitoring or engineering controls may be necessary.

Early detection of chemical releases is also an extremely important part of any Community Awareness and Emergency Response (CAER) Program. Early discovery of chemical releases allows for prompt community notification and timely discussion of the appropriate emergency response. Information exchange between industry and the community is a requirement of the Emergency Planning and Community Right-to-Know Act, Title III of the Superfund Amendments and Reauthorization Act (EPCRA). Perimeter and source chlorine monitors may play an important role in a plant's personnel and community safety programs.

1.5 Methodology

The Chlorine Monitoring Task Group, which developed Edition 5 of this pamphlet, surveyed member companies of The Chlorine Institute. The 1990 survey attempted to summarize experiences with specific perimeter and/or source monitoring systems. It was not intended to review or evaluate personnel monitors. The survey also asked for input which could improve existing monitoring systems.

In mid-2002, Institute staff surveyed members to determine what chlorine monitors had been installed since mid 1996. The results of this survey are shown in Appendix 10.1.

Between mid 2002 and early 2003, Institute staff surveyed known chlorine monitoring equipment manufacturers. The search for manufacturers was extensive, but not exhaustive. Each was asked to provide characteristic system data in a standardized format as was done in previous editions. However, some manufacturers declined to provide information stating that it was in danger of being outdated. Updated information could readily be provided by contacting the manufacturer at its website address. In addition, several vendors declined to respond to the request. Accordingly, Appendix 10.2 has been modified to include only vendor address information. Readers of this pamphlet are reminded that there are most likely other manufacturers of such monitoring equipment.

1.6 Disclaimer

The information in this pamphlet is drawn from sources believed to be reliable. The Institute and its members, jointly and severally, make no guarantee and assume no liability in connection with any of this information. Moreover, it should not be assumed that every acceptable procedure is included or that special circumstances may not warrant modified or additional procedure. The user should be aware that changing technology or regulations may require a change in the recommendations herein. Appropriate steps should be taken to insure that the information is current when used. These recommendations should not be confused with federal, state, provincial, municipal or insurance requirements, or with national safety codes.

1.7 Approval

The Institute's Plant Operations and Safety Committee approved this pamphlet on April 15, 2003.

1.8 Revisions

Suggestions for revisions should be directed to the Secretary of the Institute.

1.9 Reproduction

2. DEFINITIONS

The following are definitions of terms as used in this pamphlet.

Word	Definition
Accuracy	Absolute correctness of the response of the analyzer.
Alarm Only Monitor	Detects the presence of chlorine and activates an alarm if the concentration exceeds a preset limit.
Ambient Air	Atmospheric gas which chlorine analyzer monitors.
Amperometric	Electrolytic type sensor which uses counter and sensing electrodes to detect chlorine gas.
Breathing Zone	The height above a walking surface that personnel in the area would obtain their air to breathe.
CAER	Community Awareness and Emergency Response Program.
Calibration	Procedure by which monitor is set for a known concentration to enable meaningful results.
Chlorine	Chlorine as Cl_2 and its oxyacid species; HOCl, ClO_2, etc.
Chlorine Monitoring	Spring 1989 survey distributed to Chlorine Institute

Equipment Survey	official correspondents.
Colorimetric	Method of analysis utilizing a colorimeter as the detector.
Coulometric	Methodology which utilizes an initially fixed potential applied across electrodes in contact with a supporting electrolyte to detect chlorine gas.
Current	Flow of electrons.
Daisy Chained	A way of connecting transmitter or monitor wires which is similar to series wiring.
Diffusion	Movement of gas through a membrane, electrolyte, filter or other supporting medium.
Dispersion Modeling	Technique used to determine desired locations of chlorine sensors.
Distributive Control System	Computer system which uses outputs from monitors to perform another function such as activate alarms, perform concentration calculations, etc.
Electrochemical	Methodology which uses an electrolyte and electrodes for the detection of chlorine.
Electrolyte	Usually a saturated KBr, KCl, $CaBr_2$ or KI solution in which electrodes are placed.
EHC	Environment and Health Committee of the Chlorine Institute
EPA	United States Environmental Protection Agency
EPCRA	Emergency Planning and Comments Right to Know Act, Title III - Superfund Amendments and Reauthorization Act (40 CFR355).
Fixed Point Monitor	Chlorine monitor used to identify releases of chlorine gas at a predetermined location.
Fluid Filled Sensor	Electrochemical type sensor using liquid electrolyte.
Fugitive Emission	Release of gas from a non-specific source such as a flange.
Gel Filled Sensor	Electrochemical type sensor using gel electrolyte.
Leak Detection	The identification of a chlorine emission.

Microprocessor	A computer which evaluates outputs of chlorine monitors and performs additional tasks with the output such as a volume calculation.
Monitoring Network	A system of sensors tied to a computer which may include atmospheric monitoring device inputs, automatic concentration calculation outputs, etc.
NCASI	The National Council of the Paper Industry for Air and Stream Improvement, Inc.
Negative Interference	An unwanted response of a chlorine monitor that causes the result to be lower than the actual value.
Ohm's Law	Voltage = current x resistance.
Oxidation	Loss of electrons.
Oxidant	Pertaining to chlorine monitors: ozone, chlorine dioxide, fluorine, bromine, iodine, nitrogen oxide, nitrogen dioxide.
OSHA	United States Occupational Safety and Health Administration.
PPM	Parts per million.
Perimeter Chlorine Monitor	Chlorine detecting monitor with sensors located surrounding a portion of or all of an operating plant.
Personnel Monitor	Personnel Monitor Badge or pump type chlorine monitor worn on a person to detect chlorine.
Photoelectric	Method of analysis utilizing a photoelectric detector.
POSC	Plant Operations and Safety Committee of the Chlorine Institute.
Point Source	Term used to describe a potential leak source which is being monitored.
Positive Interference	An unwanted response of a chlorine monitor that causes the result to be higher than the actual value.
Potentiometric	Methodology in which an electrode potential is developed between ion sensitive electrodes.
Precision	Repeatability of the chlorine monitor response to the same concentration of chlorine gas.

Preventive Maintenance	Maintenance performed on a routine schedule to increase performance of a monitoring system.
PAS	Properties, Analysis and Specification Support Group of The Chlorine Institute.
Qualitative Calibration	A test performed to ensure that the monitor responds to chlorine gas.
Quantitative Calibration	A procedure to relate the monitor response to chlorine gas concentration.
Reduction	Gain of electrons.
Reductant	A chemical reagent capable of reducing chlorine, e.g., hydrogen sulfide, hydrogen chloride and sulfur dioxide.
Relative Humidity	The ratio of the actual amount of water vapor present in air to the maximum amount possible at the same temperature.
Reliability	The relative amount of time that a monitor operates without needing maintenance or calibration.
Resistance	That property of a material that opposes the flow of electric current.
Sample Point	Monitoring location of chlorine sensor.
Self Checking	Option which allows monitor to verify its operation.
Semiconductor	Notably a proprietary metal oxide compound used in solid state chlorine sensors.
Sensor	Probe or device which detects chlorine.
Solid State	A type of metal-oxide semiconductor used for the detection of chlorine.
Source Chlorine Monitor	Chlorine monitor used to identify releases of chlorine gas from a particular source such as a valve, vent stack, etc.
Spectrometric	Methodology utilizing a spectrometer as the detector.
Speed of Response	The time in which the sensor is first exposed to chlorine until it reaches 90% of its increase in response.

Stack Gas Monitor	A monitor used to detect chlorine concentrations in a vent stack.
Survey Monitor	A portable instrument used to check chlorine concentrations at specific locations.
Transmitter	Device which sends an output to another device where it may be monitored.
VAC	Volts Alternating Current.
Voltammetric	Methodology which utilizes an applied fixed potential across two electrodes within an electrolyte for the detection of chlorine.
4-20 mA	4 to 20 milliamp output from a chlorine monitor.

3. SYSTEM DESIGN

3.1 Objective

Ambient chlorine monitoring systems, as used by Chlorine Institute member companies, are designed for the detection of leaks from fugitive emissions and point sources. Ambient chlorine detectors can identify releases to help protect operating personnel and the community from chlorine exposure. Fixed area detectors are not intended to monitor personnel exposure nor to quantify leaks in the absence of other input.

3.2 Sensor Distribution

Ambient chlorine detectors may be utilized either for perimeter monitoring or for monitoring at point sources. Many applications involve a combination of perimeter monitors and source monitors. Perimeter monitors may be located using several methods which are detailed in section 5.4. The sensors are normally distributed around sources with the highest potential for emissions such as loading/unloading areas, compressors, or scrubbers. Perimeter monitors can give an indication of likely emission source locations when combined with meteorological information about wind speed and direction. Ambient chlorine detectors are not ordinarily utilized for in-stack monitoring, although some sensors may be suitable for this type of application.

3.3 Operator Interface

A chlorine monitoring system serves as an early warning device to facilitate decisions concerning leaks. It is not intended to, or even capable of, providing exact chlorine concentrations during an incident. Although chlorine leaks often can be detected due to odor, plant workers may not always be immediately present in the area of a leak, and the odor threshold for people can vary greatly. A continuous monitoring system can assist operating personnel by helping to identify an incident sooner.

Virtually all ambient chlorine monitoring systems set off alarms at control panels, indicators or distributive control system displays. Detected concentrations are ordinarily displayed for each sensor. The indication of gas concentration may be as simple as a sequencer and multi-point indicator or may involve a separate indicator for each point. Microprocessors are available that interface the sensor controllers to transmit video signals to color display monitors. Controller outputs can also be transmitted to printers or chart recorders. Complete microprocessor controlled continuous measurement systems are available which can record, alarm, time stamp and store data from each system. Indication and storage requirements should be studied to select a system to meet present needs and future expansion.

Several plants input monitoring data into a computer with dispersion modeling capabilities. Based on the chlorine concentrations and known meteorological data, the model can estimate the size of the release and predict the downwind impact. It is extremely important for users to understand the limitations and assumptions of the model. Some dispersion modeling systems can be designed to provide backup capabilities for detection systems. An example output from a dispersion modeling system is presented in Figure 1.

Clearly defined operator responses to problem identification are an important part of an effective chlorine monitoring system. Monitoring program responsibilities are frequently divided among operating, management, and security personnel. The appropriate level of information must be available to each group to allow informed and coordinated action. An action plan and training is an important consideration.

3.4 Other Considerations

Other relevant design considerations such as accessibility, ease of maintenance and calibration, environmental conditions, specificity to chlorine, cost, and expansion potential are discussed elsewhere in this pamphlet.

4. CHLORINE MONITOR SELECTION

4.1 Requirements/Capabilities

The chlorine industry needs a low maintenance chlorine monitor that will provide a repeatable and reliable indication of the presence of chlorine in ambient air. The ideal chlorine monitor would have the following features:

a. highly specific to chlorine

b. detects chlorine in nuisance ranges as well as indicates magnitude of large excursions

c. quick response and recovery time

d. accurate and stable readings

e. works in variable environmental conditions

f. self checking with minimal maintenance requirements

g. easily calibrated

h. reasonable cost

At the present time, The Chlorine Institute ideal chlorine monitor does not exist for use in the plant environment. A continuous field monitor must operate in a wide variety of environmental conditions. Because of the large number of different applications and requirements, manufacturers must make compromises in the development of chlorine monitors. The chlorine industry must evaluate the effects of these compromises in specific applications. The number of unsuccessful installations serves as a warning to those who would proceed without adequate planning. Consider the following examples:

a. The non-specific monitor

When demonstrated in the office, this monitor responded to chlorine. However, when installed in the field, the monitor also responded to interferences and the operators soon lost confidence in the system and disregarded alarms.

b. The high-maintenance monitor

In this case there was a commitment to a chlorine monitor and the system was installed. Because calibration and maintenance were expensive and time consuming, the system was neglected and became unreliable.

c. The no-maintenance monitor

This system was not supposed to require maintenance. However, this system was never tested. The system indicated no leaks, received no maintenance and did not give false alarms. Unfortunately, the system also did not detect chlorine.

It is encouraging to note the number of successful ambient chlorine monitoring installations within the industry as indicated by the results of the chlorine monitoring survey. A successful system reliably detects and approximates the concentration of a chlorine emission. It also assists in the estimation of the duration of the emission. Combined with information from meteorological instruments, these data allow the rapid identification of the source of the chlorine release.

Chlorine monitoring installations are successful where the personnel responsible have adequately defined their requirements and completed their evaluation. To completely define the system requirements they should consider the accuracy required, the potential interferences, the ambient environment, the required reliability, and the means of calibration in making their selection. Maintenance technicians input should be included in the testing phases whenever possible. An adequate level of testing and maintenance insures the continuing successful operation of the system.

4.2 Monitor Types

Four types of monitors are commonly used to detect chlorine in ambient air; the personnel monitor, the survey monitor, the fixed point monitor, and the stack gas monitor. These are briefly discussed below.

4.2.1 Personnel Monitor

The personnel monitor is designed to monitor an individual's exposure to chlorine during the course of a day. It is often worn with a shoulder strap or belt or even carried in a shirt pocket. This type of equipment is beyond the scope of this pamphlet.

4.2.2 Survey Monitor

The survey monitor is designed to be a portable instrument to check specific locations for the presence of chlorine. The survey monitor could be used on a semi-permanent basis as a single point monitor during a specific task. This type of instrument is not suitable for a fixed point system and is not considered in this pamphlet.

4.2.3 Fixed Point Monitor

The fixed point monitor is the primary choice for perimeter monitoring. It is designed to be permanently located where ambient chlorine monitoring/alarming is desired. Fixed point monitors are available in single point and multi-point configurations and in alarm only and concentration indicating types.

The alarm only monitor is used to detect the presence of chlorine and activate an alarm if the concentration exceeds a preset limit. These units provide no indication of the concentration of chlorine present, only that it exceeds the set point. This type of device is quite common in single point installations and at user facilities with a small amount of chlorine handling equipment. Alarm only monitors have limited value in a multi-point perimeter monitoring application as they give no indication about the concentration of chlorine present.

The fixed point monitor type is the most commonly used for source and perimeter monitoring of chlorine. This monitor transmits an output proportional to the concentration of chlorine detected.

4.2.4 Stack Gas Monitor

The stack gas monitor is used in stack gas applications. Due to the wide variety of stack conditions, these types of monitors are very application-specific. Many times an ambient air monitor may be used in this service, but a detailed evaluation is required.

4.3 <u>Sensor Technology</u>

Chlorine sensor technology has been advancing on several fronts. The methodology used by the sensors can be solid state, colorimetric, and electrochemical.

4.3.1 Solid State Sensors

Solid state sensor technology uses a solid-state, continuous, diffusion type element. A proprietary metal oxide semiconductor is located in the sensor circuit and acts as a resistor. When chlorine diffuses into the sensor, it is absorbed on the semiconductor causing its electrical resistance to increase. This resistance change is proportional to the chlorine concentration. When the chlorine disappears, the sensor returns to its original resistance level.

This technology has been especially troubled by interfering gases, slow time to clear after exposure and the need to recalibrate after a significant dose of chlorine. Since the solid state sensor relies on the electrical characteristics of the metal oxide semiconductor, exposure to high concentrations of chlorine will corrode or permanently modify the semiconductor, therefore requiring recalibration for the new characteristics of the metal oxide semiconductor.

This solid state sensor technology holds the promise of being a very effective monitor if the problems can be solved. The low maintenance requirements and long sensor lifetime are advantages of this sensor. At the present time, its use for detecting chlorine has been very limited. Respondent companies to The Chlorine Institute survey are not currently using solid state sensors.

4.3.2 Colorimetric Sensor

The colorimetric technology uses a proprietary reagent which is exposed to chlorine. As a result of this exposure, a stain or color change develops which is proportional to the concentration. This color change may be determined visually, photoelectrically or spectrometrically. This technology has limited usefulness in ambient chlorine source or perimeter monitoring because of the complexity of the hardware. It could be applied by using a central instrument which would draw samples from many different locations within a facility. This would not give real time information or a continuous indication at each point.

4.3.3 Electrochemical Sensor

Electrochemical chlorine monitors are the most widely used and accepted of the available technologies. This technology uses various forms of fluid filled or gel filled electrochemical sensors. Electrochemical gas sensors are differentiated according to which parameter of Ohm's law is the dependent variable. Electrochemical sensors can be described as amperometric or potentiometric.

The amperometric sensor utilizes an electrolyte solution or gel electrolyte with counter and sensing electrodes to detect chlorine gas. The electrolyte contains species capable of being oxidized by chlorine ($CaBr_2$, KC1, KBr or KI). A fixed potential (voltammetric) or an initially fixed potential (coulometric) is applied across the electrodes in contact with the electrolyte.

When chlorine is present, it is reduced at the cathode and a current is generated. The quantity of current is related to the concentration of oxidized species formed, and also to the chlorine gas concentration. This technique is termed amperometric, in that the amperage necessary to reduce species oxidized by the anolyte constitutes the analytical signal.

In potentiometric sensors, an electrode potential is developed between ion selective electrodes. The potential is a linear function of the concentration of the ions or species formed by oxidation of the electrolyte and is related to the concentration of oxidizing gases in the sample.

The technology for the above methods is proprietary. Because of the lack of specific design information, it is impossible to assign performance characteristics (response times, linearity, reaction to interference gases, etc.) to different electrochemical design categories. Field testing and evaluation of the actual sensor design using the procedure presented in Section 8 is advised.

4.4 Precision and Accuracy

In the evaluation of perimeter chlorine monitors, it is important to remember that the goal is to find a monitor suitable for atmospheric monitoring. The precision specifications for the various chlorine monitors are in the range of +/-2% to 3% of full scale. The accuracy is a function of both the method of analysis used and the validity of the calibration technique. It would not be unreasonable to expect a precision of +/-1 ppm with a 0-10 ppm chlorine range (+ 10%) to be acceptable in the field. Lower personnel exposure limits for chlorine may require more precise sensors. They would also require more accurate calibration methods.

Precision is also a function of the sensing range of the sensor. The majority of manufacturers offer sensors with chlorine ranges of 0-5 ppm or 0-10 ppm, which would be satisfactory for perimeter monitoring uses. A few of the sensors have a maximum range of 0-3 ppm. This range may limit the useful data collection if the monitors are to be used to supplement computerized gas dispersion modeling systems. On the other hand, a low range may be desirable for area monitoring if the alarm concentrations are intended to be 0.5 to 1.0 ppm.

In a study conducted by The National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI) (9.4), it was observed that, with few exceptions, there were no significant differences in the performance of the chlorine monitors tested. They concluded, "The zero and span drift performance of all of the instruments tested was similar, and none of the instruments showed zero or span drift performance which would be considered excessive in light of the anticipated use of these instruments (9.4; page 75)."

The NCASI study also found no major differences in the stability of the monitors over the study period. This implies that the differences among sensors used for the accurate determination of chlorine become evident in areas of chemical interferences, speed of response and memory effect.

4.4.1 Chemical Interferences

Each plant is unique in its siting and potential airborne interferences. To be of value the monitor must be highly specific to chlorine. All chlorine monitors are subject to interferences from other gases. Since most sensors respond to oxidants or reductants, strongly oxidizing gases such as ozone, chlorine dioxide, fluorine, bromine, iodine, nitrogen oxide, nitrogen dioxide, and others, may be a positive interference (causing errors on the high side), while reducing gases such as hydrogen sulfide, hydrogen chloride and sulfur dioxide may be a negative interference (causing errors on the low side). For example, chlorine dioxide has sufficient oxidation potential to produce reactions on some monitors as much as 10 times higher than chlorine at the same concentration. Also, interferents may react in the sensor itself. In sensors using a reducing electrolyte, choice of the reducing ion may avoid some interference.

Manufacturers commonly provide a table of known chemical interferences and levels. However, site specific testing is highly recommended. Species not normally listed but known to cause a problem include: paint fumes, car exhaust and solvents.

4.4.2 Speed of Response and Memory Effect

An important feature of the chlorine monitor is the ability to quickly indicate the presence of chlorine. In fact, in many applications, the speed of response is more important than the absolute accuracy. For example, it may be more important that the operator be advised that a significant amount of chlorine is present in the area within 20 seconds of its release than to know that exactly 4.7 to 5.3 ppm of chlorine is present after a delay of 3 minutes. Many of the available sensors differ in the speed of response and this should be a criterion in selecting a unit. The NCASI study uncovered differences in response times as a function of how frequently the sensor is exposed to chlorine. Several units exhibited a greatly extended response time after having been exposed to clean air alone for a 24 hour period. Another factor involved in speed of response is the velocity of the sample past the sensor. The diffusion type sensor requires air movement in order to provide a representative air sample. If the sensor is situated in still air or in a confined location there may be a local depletion of chlorine, due to the sensor reaction. This problem may be alleviated through the use of a sample pump.

The sample pump insures that a representative sample continues to flow past the sensor. Sample pumps also allow the sensor to quickly clear or return to normal after a chlorine exposure.

4.5 Ambient Environment

The respondents to the chlorine monitoring equipment survey covered a wide range of geographic locations and therefore a wide range of ambient temperature extremes. Temperatures vary from the -40 degrees Fahrenheit range in northern locations, to the low 100's in the south. At the same time, humidity and corrosive conditions also vary among the plants. A monitor suitable for installation in Louisiana may not be suitable for Canada.

4.5.1 Temperature

Temperature changes affect the diffusion rate and reactivity of chlorine to some extent in all monitors. Temperature induced span drifts of 10 to 20% with a 1 ppm chlorine sample are not unusual with diffusion type sensors.

Recognizing the need for low temperature service, manufacturers have modified their sensors to increase the operating temperature range. This is achieved through using different strength electrolytes, anti-freeze agents or an added heater. The use of anti-freeze agents or different strength electrolytes may affect the characteristics of the sensor.

4.5.2 Humidity

The effect of humidity varied among the various monitors. The relative humidity appears to have some effect on all electrochemical sensors. Most sensors are suitable for a relative humidity range of 20% to 90%. Sensors using a liquid electrolyte experience accelerated electrolyte evaporation at low humidity conditions. The result is sensors will have to be refilled more often. One manufacturer suggests a weekly electrolyte check when the relative humidity falls below 45%. High humidity conditions can also affect liquid electrolyte. One manufacturer advised that the electrolyte may drip from the sensor in high humidity conditions.

Humidity can also affect the gel-filled sensors. Although the chemistry is not completely understood, the response of some sensors decreases dramatically with reduced humidity. Some lose response completely when relative humidity drops below 20%. This loss of response is important to consider when using electrochemical sensors and when calibrating the instruments. Sensors intended for more humid installations should use a calibration technique involving moist air rather than a dry gas.

4.5.3 Electrical Effects

Sensors and associated electronic equipment may be affected by electrical interference. If monitoring equipment will be operated under conditions of strong radio frequency interference or will be exposed to strong electrical fields (i.e., chlorine cell rooms), appropriate investigation and supplier consultation is necessary.

4.6 Reliability

Often the best way to evaluate a system's reliability is to gain operating experience with the unit. Several of the monitoring systems have already been installed at member plants within The Chlorine Institute. The experience of these plants has been summarized in the member survey, which is presented in Appendix 10.1.

Some features of the monitors have been designed to increase their reliability. Modifications are made to improve the performance of the instrument but sometimes with added complexity. Some of these features are discussed below:

4.6.1 Self-Checking

Reliability is an important factor in selecting a perimeter monitor. The monitor is not something that is going to be exposed to chlorine every day. But it must work when it is required. When an electrochemical probe wears out or fails it becomes unresponsive. The failure may not show up until the sensor is calibrated or tested. Some manufacturers have recognized the need for a self-test to verify operation and this becomes a major selling point.

There are differences between the way sensors are tested or self-checked. Some manufacturers use a "live zero", where the signal from the sensor should always be above a baseline. If the reading drops below this baseline the probe needs electrolyte or some type of maintenance. Another manufacturer manually subjects the sensor to a 2 volt jolt via a test button to simulate a chlorine reaction. This is used to test the sensor and the electronics. Another manufacturer has gone so far as to include a gas generator in the sensor head which automatically comes on every 12 or 24 hours. Several manufacturers offer an electronic test. This checks the sensor line and the system electronics. It does not indicate whether the sensor is responsive or not. This has limited value unless the electronics are quite complicated. Other systems offer what they describe as self-diagnostics. Self-diagnostics may be misleading because they do not identify all the types of failures. Most sensors based on a two- wire 4-20 mA signal have no self testing. The testing must be accomplished manually by a technician.

4.6.2 Sensor Design Enhancements

As with many facets of the ambient chlorine monitor, the sensor design is a compromise between many elements. Membranes are added to electrochemical sensors to reduce the evaporation rate of the electrolyte and to increase the selectivity of the sensor to chlorine. The gel-fill probe was developed to eliminate electrolyte replacement. The trend away from electrolyte replacement should mean an improvement in reliability because this is one less item of concern for the maintenance personnel. Sample pumps were added to insure sample flow in still air, and to reduce the effects of ambient conditions on probe response. Sample pumps are an additional maintenance item, but they have been used in a lot of analytical equipment. They do become a problem in cold weather, as a heater is required more for the pump than for the sensor.

5. INSTALLATION

5.1 Signal Types

Chlorine monitors/sensors are available using many types of signal transmission. The most common are 4-20 mA analog current loops, digital data, low level analog voltage signals specific to individual manufactures sensors, and VHF/UHF radio transmissions. Separate sensors and electronics are used to keep delicate electronics out of the field. Some important characteristics of each type are outlined below.

5.1.1 4-20 mA Current Loop

This system uses a two wire (industry standard) 4-20 mA analog signal. This may allow maximum inter-changeability between different manufacturers systems. Sensor calibration can be done by a technician in the field or in the shop. Systems can be interfaced to multiplexers and DCS systems. Changing ambient conditions can effect readings. Both self test and checking capability are limited. This system type requires careful planning when cable lengths are long.

5.1.2 Digital Data

Digital data allows many system parameters (alarms, set points, etc) to be transferred. Self checks of system conditions and data integrity are possible. Systems may be "daisy-chained" together to minimize wiring installation. Data protocol is usually manufacturer specific, limiting inter-changeability. This type of data transmission often requires special cable and usually requires 120 volt AC in the field. With non-redundant systems, the complete system may be lost with a single component failure.

5.1.3 Radio Transmission

Radio transmission signals tend to be cost effective for large installations and over long distances. Large amounts of digital data can be transmitted in a short time. Radio transmissions are very reliable if quality radios/modems are used. Power is required at each transmission site.

5.2 Wiring and Power Supply

The type system selected determines the types of wiring required. Digital or low level voltage signals often require special cables and cable support. Most systems are affected by power line spikes and surges as well as both direct and indirect lightning strikes. Precautions such as power supply filtering and noise suppression should be used on all power supplies. Field mounted systems, in open areas, should be protected by recommended electrical code lightning rods and grounding systems.

Systems with separate electronics often require 120 volt AC if located in a control room. Battery backup systems may be utilized. Two wire, field mounted sensors/systems are powered through the signal lines by 24 - 50 volts DC. Other systems requiring field power require 24 volt DC or 120 volt AC/DC power may be difficult to supply over long distances. A solution may be to supply 120 volt AC at the field site, converting to DC as needed.

Recent technology enhancements allow for the use of stand-alone sensors that utilize solar power with battery backup. Such sensors eliminate the need for a source of electrical power supply.

5.3 Environmental Considerations

Chlor-Alkali facilities are by nature corrosive environments. This corrosive environment is hard on electronic equipment. In fixed-area installations, centralized equipment can be placed in a controlled environment. However, sensors and transmitters must be at the sample points and are therefore subject to corrosive conditions and extremes of temperature and humidity. Most sensors with integral electronics are furnished with enclosures designed to protect against such exposure.

Exposed chlorine sensing equipment should be constructed of corrosion resistant materials. Plastics such as PVC, CPVC, etc. are recommended. Avoid the use of aluminum, especially for small details like conduit or cable connectors which are often overlooked by manufacturers. Particular attention should be given to the sensor signal/power connections. Metal connections that are used by most sensor manufacturers should be given to the sensor signal/power connections. Metal connections that are used by most sensor manufacturers should be waterproofed and painted to prevent corrosion. A good method of protecting the sensor signal connections is to use a silicon dielectric compound, such as Dow Corning DC-4, to "pot" the cable connectors. The sensors can be protected from water, dirt and breakage by fabricating covers/housings from plastic or fiberglass reinforced plastic piping. The determination of appropriate materials of construction in the selection stage of acquiring chlorine monitors can greatly reduce future maintenance requirements.

An additional concern is electrical classification. Review the electrical classification of the sensor location. Sensors are available in explosion proof or intrinsically safe construction for use in electrically hazardous areas.

5.4 Sensor Placement

The prevailing wind direction is often considered when determining sensor locations. Another method that can be used to locate perimeter sensors is dispersion modeling. Dispersion modeling may also be used to evaluate the effectiveness of the selected locations and heights for the detection of chlorine emissions from various sources. Atmospheric conditions, wind speed, and direction, building locations, and release rates at specified sources are input into commonly employed dispersion models. The possibility that a given release could go undetected at the selected sensor locations may be assessed by dispersion modeling. Dispersion model results may suggest additional sensors or the relocation of sensors to detect a given release. One needs to study the process area and adjacent environment to determine the optimum sensor location. Factors such as: 1) distance from source; 2) gas density; 3) plan and elevation details; 4) ventilation; 5) wind speed and direction; and 6) neighboring facilities and populations should all be considered when selecting a location for the sensors. The following guidelines should be considered when determining sensor location.

a. Place the sensor in the breathing zone.

b. Locate the sensor where prevailing air currents contain the maximum concentration of gas.

c. Locate sensors close to the potential sources of escaping gas.

d. Sensors have ambient temperature limitations. Install the sensor in a location which will remain within the specified range.

e. Avoid vibration when locating the sensor.

f. Insure that the sensors are accessible for calibration and maintenance.

g. Protect sensors from immersion or direct contact with water.

h. Provide dust covers for sensors in dusty environments.

i. Insure that the applicable codes are followed when installing sensors and cabling.

6. MAINTENANCE

The maintenance requirements of ambient chlorine monitors vary considerably. A logical conclusion may be made that more complex systems require more maintenance. However, this is not necessarily the case with chlorine monitors. NCASI conducted a study of different types of chlorine monitors and concluded, "the sample draw instruments did not necessarily require more maintenance than the diffusion sensor based instruments (9.4; page 76). The kind of maintenance required by a monitor is dependent on the principle of operation. For example, sample draw instruments require pump maintenance, sensors require cleaning of sensor surfaces, and wet chemical instruments require replenishment of reagents.

The level of training that technicians receive on the operation of chlorine monitors will directly affect the quality of maintenance that a system receives. In most cases, the manufacturer of the monitor is capable of providing technical and practical training for maintenance technicians. It also is helpful to include technicians during monitor testing phases in order to obtain their input. Contracted maintenance services are available from some manufacturers. One survey respondent uses a contractor to perform quarterly calibrations on its analyzers.

Preventive maintenance should be performed to ensure the reliability and proper operation of the chlorine monitors. Manufacturer's guidelines should be followed for preventive maintenance. The manufacturer can often advise on the spare parts inventory that should be stocked.

7. CALIBRATION

The calibration of chlorine monitors is a very important factor in overall system performance. The objective of calibrating the monitor is to provide meaningful results about ambient chlorine levels in a given area. In theory, the calibration is simple: chlorine is measured by the monitor and by a corresponding standard test. In practice, however, it is rarely simple to calibrate a chlorine monitor correctly and accurately. The biggest problem in calibration is the generation of the chlorine standard.

Many problems relate to the dependence of the sensor response to moisture. Also, temperature can affect the sensor response. For these reasons, both quantitative and qualitative methods are widely used for the calibration of ambient chlorine monitors, although the qualitative test is used more frequently.

Qualitative calibrations are performed to ensure that the monitor responds to chlorine gas. Qualitative calibrations verify the fact that a monitor responds to chlorine gas but fails to validate the accuracy of the responses. A qualitative calibration may be accomplished by exposing the monitor to chlorine gas generated when hypochlorite solution (bleach) is carefully mixed with acid. Chlorine ampules are also available for use as a qualitative test. Monitors equipped with self-calibration circuits are popular. A calibration mode is initiated from the control module and the monitor is calibrated electronically. This feature is not available on all monitors. Until more experience is acquired with self-calibration, this should be considered a qualitative test.

Quantitative calibrations are performed to determine the concentration of chlorine in air. These methods determine the accuracy, or absolute correctness, of the response of a monitor to chlorine. The quantitative calibration methods include the use of prepared standard gas cylinders, the chlorine ampule and bag technique, self-calibrating monitors, portable electrolytic chlorine generators and chlorine permeation devices. These methods are listed in order of popularity of use as reported in the recent survey results on ambient chlorine monitoring equipment. A discussion of each calibration method and its limitations follows.

The standardized gas cylinder is the most widely used method. A specially-lined cylinder is prepared to contain chlorine in the concentration range of 0-10 ppm with nitrogen as the balance. The sensing portion of the monitor is exposed to the chlorine and the span of the monitor is set to equal the concentration of gas in the cylinder. This calibration is most often performed in a laboratory or maintenance shop since the cylinders are not easily transported in the field. This method also assumes that environmental conditions and interferences have no affect on monitor response, which may or may not be so. Some respondents purge the standard chlorine gas through acidic water prior to exposure to the sensor in an attempt to correct for humidity effects.

Another calibration technique uses an ampule which contains chlorine and a gas sampling bag. The contents of the ampule are emptied into the bag and the resulting gas mixture equals some known concentration. This technique may be used in the field and has the advantage of allowing the gas to which the sensor is normally exposed to be used in the preparation of the standard gas. Although this method has been reported to be awkward and slow by some survey respondents, others believe that it is more accurate than the gas cylinder method.

A product that has been recently introduced to the market is the portable electrolytic chlorine generator. This device operates like a miniature chlorine cell to generate chlorine gas. Since it has only recently become available, information on its successful use is limited. One respondent company has had a high degree of experience and success with this method.

Chlorine permeation devices are also used to calibrate chlorine monitors. Liquid chlorine, sealed in a permeation tube, is heated to a constant temperature. It permeates the walls of the tube at a constant rate. A known concentration of chlorine is prepared by passing a predetermined flow of gas past the tube. This technique is most often performed in a laboratory or maintenance shop although portable permeation devices are available. The time required for equilibration of the permeation tube and the necessity of maintaining a constant flow and temperature are limitations of this method.

According to survey respondents, the frequency of calibration ranges from daily qualitative checks and weekly quantitative tests to not calibrating at all. The majority of users of chlorine monitors calibrate monthly. They use both the quantitative and qualitative techniques mentioned above to calibrate their monitors.

There is much room for improvement in the area of calibration of chlorine monitors. There is an overwhelming request from respondents of the survey for the development of improved calibration techniques. Some monitors require two technicians to perform the calibration, one at the remote sensor and one near the electronics. Problems due to environmental conditions arise when monitors are calibrated under laboratory conditions and then are installed in the field. It is difficult to simulate field conditions in a chlorine standard. Difficulties are encountered when trying to prepare a chlorine standard in the field.

8. RECOMMENDED EVALUATION PROCEDURE

The actual selection of a suitable ambient chlorine monitor for a facility will be based on a number of criteria. Probably one of the most influential will be the previous successful operating experience in similar facilities. Contacting other users of promising systems to determine what was done to make the system successful is highly beneficial. Perform a pilot test at a single point or a small number of points at your facility before committing to a complete system. With the rapidly changing technology, there could be a better one tomorrow.

8.1 Considerations

The following considerations will significantly affect the choice of sensor manufacturer:

a. Will the sensors stand alone, report to a central control panel, or directly to a computerized system? Will the system be dedicated to chlorine or will sensors be provided for additional gases?

b. Is the facility located in a rural, industrial or residential area?

c. What are the expected ambient temperature and humidity extremes?

d. What maintenance resources are available at the facility that can be dedicated to the upkeep of this system?

e. Does the potential supplier have local representatives with stocking and repair facilities?

8.2 Selection Criteria

The following criteria should be considered when evaluating and selecting a potential chlorine monitoring system:

a. The monitor should have a demonstrated level of reliability based on previous installations.

b. The monitor should be highly specific to chlorine, with a minimum of interferents.

c. The monitor should have a fast response and clearing time.

d. The monitor should operate within anticipated temperature and humidity ranges.

e. The ideal monitor should require a minimum of maintenance.

f. The monitor should be easy to calibrate and maintain.

g. The monitoring system should be easy to install.

h. The ease of interface to a computer system may need to be considered.

Additional criteria may be developed in order to meet the requirements of each specific application. Each criterion could be assigned a priority and each potential system evaluated against their criteria. In this manner, a suitable monitoring system can be selected.

9. REFERENCES AND ADDITIONAL SOURCE DOCUMENTS

9.1 The United States Environmental Protection Agency, "Review of Emergency Systems; Report to Congress, Section 305(b) Title III Superfund Amendments and Reauthorization Act of 1986," Washington, DC, June, 1988.

9.2 Code of Federal Regulations. Title 29, Section 1910.119. Process Safety Management of Highly Hazardous Chemicals.

9.3 Code of Federal Regulations. Title 40, Part 68. Accidental Release Prevention Requirement; Risk Management Program Under the Clean Air Act.

9.4 NCASI Technical Bulletin 485, "Laboratory and Field Examination of Several Area, Survey and Personal Workplace Atmosphere Chlorine Monitors". The National Council of the Paper Industry for Air and Stream Improvements, Inc., New York, NY, March 1986.

9.5 *Estimating the Area Affected by a Chlorine Release*, ed. 3; Pamphlet 74, The Chlorine Institute, Arlington, VA, 1997.

10 APPENDICES

10.1 2002 CHLORINE MONITORING EQUIPMENT SURVEY

In mid 2002 the Chlorine Institute surveyed its members to determine what, if any, chlorine monitors had been installed since 2002 and are currently in use. The purpose of this survey was to identify additional chlorine monitor equipment venders to include in Appendix 10.2.

Chlorine Production Facilities

Twenty nine facilities reported that 39 new installations have occurred since July 1, 1996. Some facilities have had more than one installation.

Manufacturer	No. of Installations Since July 1, 1996
Scott Bacharach (includes Enterra and EIT(Exidyne))	11
Draeger (all models)	8
Gastronics (includes Gas Detection Systems)	5
Analytical Technology	4
Mil-ram	2
PPM Industries	2
BW Research	1
Compur (includes Statox)	1
Detcon	1
General Monitors	1
MDA	1
MSA	1
Safenet System	1

Chlorine Repackager Facilities

Nineteen facilities reported that new installations have occurred since July 1, 1996.

Manufacturer	No. of Installations Since July 1, 1996
Scott Bacharach (includes Enterra and EIT(Exidyne))	8
Analytical Technology	4
Sensidyne	3
Draeger	1
Gas Tech	1
Mil-ram	1
RC Systems	1

Chlorine Use Facilities

Forty five facilities reported that 72 new installations have occurred since July 1, 1996. Some facilities have had more than one installation.

Manufacturer	No. of Installations Since July 1, 1996
Scott Bacharach (includes Enterra and EIT (Exidyne))	30
Sensidyne	14
Draeger	5
Analytical Technology	4
Mil-ram	3
MSA	3
Rosemount	3
Gastronics (includes Gas Detection Systems)	2
Wallace & Tiernan	2
Analytical Technologies	1
BW Research	1
Detco	1
MDI	1
Nova	1
Compur (includes Statox)	1

10.2 2002 - 2003 CHLORINE MONITORING EQUIPMENT MANUFACTURERS SURVEY

The Chlorine Institute contacted known vendors of chlorine monitoring equipment between August 2002 and January 2003. The original intent was to compile the information received into a standard format as was done in the prior edition of this pamphlet. However, several vendors did not respond or did not provide the requested information. Because the information can readily be provided through direct contact to the vendor, primarily via the Internet, it has been decided to provide only vendor address information in this edition.

Any manufacturer who is not listed below or is listed incorrectly and wishes to be listed/correctly listed is requested to provide the full name and address including phone, fax, and web address to the Secretary of the Institute. CI will include such additions/corrections as an addendum to be included with the pamphlet.

- Analytical Technology

  Analytical Technology, Inc. (ATI)
  6 Iron Bridge Drive
  Collegeville, PA19426
  Phone: 1.610.917.0991
  Fax: 1.610.917.0992
  Web address: www.analyticaltechnology.com

- BW Research

  Davis Inotek Instruments
  4701 Mount Hope Drive
  Baltimore, MD 21215
  Phone: 1.410-358-3900
  Fax: 1.410-258-0252
  Web address: www.davisontheweb.com

- Compur Monitors

  Compur Monitors
  Weissenseestrade 101
  D-81539 Munchen
  Germany
  Phone:49(0)89.62038.268
  Fax: 49(0)89.62038.184
  Web address: www.compur.com

- Detco

  No information found

- Detcon

  Detcon Inc.
  P.O. Box 8067
  The Woodlands, TX 77387
  Phone: 1.281.367.4100
  Fax: 1.281.292.2860
  Web address: www.detcon.com

- Draeger

  Draeger Safety, Inc.
  P. O. Box 120
  Pittsburgh, PA15230
  Phone: 1.412.787.8383
  Fax: 1.412.787.8383
  Web address: www.draeger.com

- Exidyne

  See Scott Bacharach

- Gas Detection Systems

  See Gastronics
  .

- Gas Tech

  Gas Tech, Inc.
  8407 Central Avenue
  Newark, CA 94560
  Phone: 1.510.745.8700
  Fax: 1.510.794.6201
  Web address: www.gastech.com

- Gastronics

  Gastronics, Inc.
  23660 Miles Road, Suite 110
  Bedford Heights, OH 44128
  Phone: 1.216.662.4899
  Fax: 1.216.662.4999
  Web address: www.gastronics.com

- General Monitors

  General Monitors
  26776 Simpatica Circle
  Lake Forest, CA 92630
  Phone: 1.919.581.4464
  Fax: none provided
  Web address: www.generalmonitors.com

- MDA

  No information found

- MDI

  No information found

- Mil-Ram
  Mil-Ram Technology, Inc.
  5423 Central Avenue, suitres1
  Newark, CA 94560
  Phone: 1.510.818.0200
  Fax: 1.510.818.0300
  Web address: www.mil-ram.com

- MSA

  Mine Safety Appliances Company
  P.O. Box 426
  Pittsburgh, PA 15230
  Phone: 1.412.967.3000
  Fax: 1.412.967.3451
  Web address: www.msanet.com

- Nova

  Nova Analytical Systems, Inc.
  1925 Pine Avenue
  Niagara Falls, NY 14301
  Phone:1.716.285.3771
  Fax: 1.716.282.2937
  Web address: www.nova-gas.com

- PPM Industries

  PPM Technology
  Unit 34
  Cibyn Ind. Est
  Caernarfon
  LL55 2BD
  United Kingdom
  Phone:44.1248.671717
  Fax: 44.1248.671582
  Web address: www.ppm-technology.com

- RC Systems

  RC Systems Co. Inc.
  2513 Hwy.646
  Santa Fe, TX 77510
  Phone: 1.409.925.7808
  Fax: 1-409.925.1078
  Web address: www.rcsystemsco.com

- Rosemount

  Rosemount Analytical
  Process Analytic Division
  1200 North Main Street
  Orrville, OH44667
  Phone: 1.800.433.6076
  Fax: 1.330.684.4434
  Web address: www.emersonprocess.com/proanalytic

- Safenet System

  No information found

- Scott Bacharach (all models including Enterra and EIT, Exidyne Instrumentation Technologies))

  Scott Technologies, Inc.
  251 Welsh Pool Road
  Exton, PA 19341
  Phone: 1.610.363.5450
  Fax: 1.610.363.0167
  Web address: www.scottinstruments.com

- Sensidyne

  Sensidyne
  16333 Bay Vista Drive
  Clearwater, FL 33760
  Phone: 1.727.530.3602
  Fax: 1.727.539.0550
  Web address: www.sensidyne.com

- Statox

  See Compur Monitors

- Wallace & Tiernan

  USFilter / Wallace & Tiernan Products
  1901 West Garden Road
  Vineland, NJ 08360
  Phone: 1.856.507.9000
  Fax: 1.856.507.4125
  Website address: www.usfwt.com

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