biosystems Application Note	Monitoring for Reactive Gases	Date	1-1-2000
		Nº	AN2000-13
		By	Lars Boettern

Monitoring for Reactive Gases

1. Introduction

The purpose of this applications note is to provide end-users, and detector support personnel, with all of the information required to specify complete gas detection systems for monitoring reactive gases for worker safety and health applications.

Specifically this applications note discusses issues related to calibration and sampling the less often encountered "reactive" toxic gases of:

ammonia	(NH_3)
chlorine	(Cl_2)
chlorine dioxide	(ClO_2)
hydrogen chloride	(HCl)
nitrogen dioxide	(NO_2)
hydrogen cyanide	(HCN)

Phosphine (PH3), sulfur dioxide (SO2) and nitric oxide (NO) are excluded from this discussion since they can be monitored by use of standard detection equipment and methods.

1.1 Reactive Gas Definition

Before beginning our discussions on detection equipment, we need to define the term "reactive" toxic gas types. Reactive means that these gases are chemically more active than the more commonly encountered gases of CO, H2S and SO2. Because of their higher chemical activity,they are easily absorbed by the exposed surfaces of gas detection systems including detector housings, calibration adapters and remote sample draw accessories.

Because of their greater tendency to be depleted from a gas sample by the exposed surfaces of gas detection systems, special care must be taken to insure accurate monitoring results.

The principle danger is that failure to use compatible materials and proper calibration procedures can result in dangerously inaccurate (low) readings and increased response times.

2.0 Detector Selection

The following chart provides a quick summary of all of Biosystems current detector models - both fixed/wall mount and portables, that accept reactive gas sensor types and the range of monitoring available. An entry of N/A means "not available". Please note that there are exceptions to the availability of certain configurations. Two notable examples are that explosion-proof fixed system detector heads for Cl2 and ClO2 are not available, since the flame arrestor does not allow for the passage of these gases. Also alkaline battery model multi-sensor portable detectors (PhD Lite, PhD5, and PhD Ultra) should not be used with biased voltage sensors, in this case ammonia NH3. (and nitric oxide NO, which again, is not considered to be a reactive gas type). Brief Interruptions in the supply of power that can often occur with the use of alkaline battery model units can result in long sensor warm-up times.

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Biosystems Reactive Gas Detectors Sensors and Ranges

Portable Gas Detectors

	NH_3 ppm	Cl_2 ppm	ClO_2 ppm	NO_2 ppm	HCN ppm	HCl ppm
PhD 5	0-100	0-50	0-15	0-50	0-100	N/A
PhD Lite	0-100	0-50	0-15	0-50	0-100	N/A
PhD Ultra	0-100	0-50	0-15	0-50	0-100	N/A
PhD 2	0-100	0-6	N/A	0-6	0-100	1-100
Toxi Ultra	0-100	0-50	0-15	0-50	0-100	N/A
Toxilog	0-100	0-30	N/A	0-30	0-100	0-100

Fixed Gas Detectors

	NH_3 ppm	Cl_2 ppm	ClO_2 ppm	NO_2 ppm	HCN ppm	HCl ppm
ZoneGuard	N/A	0-20	0-10	0-20	N/A	N/A
GasChek	N/A	0-5	0-2	0-10	N/A	N/A

3.0 Calibration

Performing an accurate detector calibration is the first important step in achieving proper sampling of reactive gases in the field. Because of the special handling required of reactive gases, it is good to be aware of the factors that will insure this condition.

3.1 Calibration Gas

Biosystems provides accurate, stable nonrefillable (disposable) calibration gas cylinders containing the concentrations of reactive gases that work best with the sensors and calibration features of our detectors.

For reactive gases, we specify grades that are accurate to a tolerance of ±5- 10% of the value printed on the cylinder label. Certificates of analysis are kept on file for each gas mixture part number and lot number (printed on the cylinder) and are available upon request - preferably at time of order. Manufacture and mix analyses are done with standard weights and measures traceable to NIST.

All reactive gas mixtures are currently stored in aluminum cylinders. Any aluminum nonrefillable cylinders should be considered to contain a reactive gas component that has a definite shelf life. With current technology, these gas mixtures have a shelf life of 6 months to 1 year (please see the following table). Each cylinder label a "Best When Used By" date. This means that the contents of the cylinder are guaranteed to be at ±5-10% of the listed value within that timeframe. For use beyond the specified date, the active component will gradually be lost to the walls of the cylinder.

Gas Type	**Shelf Life**
Ammonia (NH_3	1 year
Chlorine (CO_2)	8 months
Chlorine Dioxide (ClO_2)	8 months
Hydrogen Chloride (HCl)	8 months
Nitrogen Dioxide (NO_2)	6 months
Hydrogen Cyanide (HCN)	1 year

Reactive gas cylinders are generally available in two sizes - 34 and 58 liters.

Please see Biosystems current Price List and Catalog - Calibration Gases & Regulators page for price and availability.

Shelf life and regulator type are not dependent on cylinder size. Therefore, a cylinder size should be selected depending on the number of times that the detector accuracy must be verified within the expected shelf life of a particular gas type. Reactive gas sensors generally require more gas volume to perform a calibration than standard toxic gas sensors. A good estimate is 2-3 liters for each calibration.

Chlorine Dioxide (ClO2) monitoring is normally done with a chlorine sensor. Because ClO2 is not stable in compressed gas cylinders, Biosystems recommends 5 ppm chlorine (Cl2) gas as the standard calibration surrogate for any ClO2 configured detector. In this case, the factory default calibration setpoint value is 1.7 ppm based on the sensor's relative response to ClO2 versus Cl2 (3:1).

An alternative for ClO2 calibration is use of a product known as an electrochemical gas generator. Electrochemical gas generators directly produce accurate ppm levels of ClO2. These are a perfectly acceptable substitute for surrogate chlorine cylinders, and may be more economical in the case of very frequent usage.

It is always prudent to verify, and adjust as necessary, the calibration setpoint in any Biosystems chlorine dioxide detector before doing an automatic calibration with a ClO2 generator. For direct calibration to ClO2 the automatic calibration setpoint value should be the direct output concentration of the generator.

3.2 Regulators

Biosystems has a standard fixed-flow regulator PN 12-023 for all reactive gases except ammonia NH3. Ammonia service requires a fixed-flow regulator PN 12-025 with nitrile rubber internal seals rather than the standard regulator with fluoro-elastomer seals to insure longevity of proper performance.

In the past, Biosystems had recommended a special regulator for chlorine Cl2 and hydrogen chloride HCl service. This has since been found to be unnecessary based on results from history of usage, with the low concentrations of these reactive gases.

Please note that either regulator may also be used for the balance of reactive and standard gas types for multi-gas detectors.

In all cases, Biosystems supplies fixed-flow regulators with no on/off knobs as standard. The major reason for this design preference is that it helps to insure the longest stability of reactive calibration gas mixtures in the field.

Best practice dictates that regulators be removed from cylinders when not in actual use as the cylinder/regulator connection is not a primary seal and therefore trace moisture and contamination may be introduced to the cylinder. Also when using a regulator with a shut-off knob, the knob should be opened before threading the regulator onto a gas cylinder. This simple step reduces the chance of introducing moisture and contamination into the cylinder through exchange of regulator dead volume with the cylinder contents.

Since repeated introduction of trace moisture and other contaminants into the gas cylinder accelerates the deterioration of gas mix stability. Regulators and cylinders should always be stored in a dry place.

3.3 Calibration Adapters

Calibration adapters are designed to transfer the flow of calibration gas from the regulator/cylinder to the detector's sensor face with minimal loss and in the most convenient manner.

The following table provides a summary of the detector type and the proper reactive gas calibration adapter. Please note that the proper calibration adapter (standard or reactive gas type) is always included as a standard accessory for any Biosystems detector.

Detector Model	Reactive Gas Cal. Adapter Part Number
PhD Lite	54-26-0405
PhD 5	54-05-A0409
PhD Ultra	54-05-A0409
PhD 2*	54-1860
Toxi Ultra	54-1861
Toxilog	54-1860
ZoneGuard	35-0136 & 35-0119
GasChek	35-0136 & 35-0119

* Detector also requires "rapid diffusion sensor cover" P/N 35-692

4.0 Gas Sampling Methods

Detection of reactive gases, and ambient atmospheric sampling in general, can be accomplished by two methods - through simple diffusion and through various sample draw methods.

Diffusion allows for sampling the atmosphere only in the immediate area of the detector. Random air currents serve to deliver the detected gas to the sensor face.

Sample draw methods give the enduser the ability to bring a gas sample from some remote location to the gas detector. This is accomplished through the use of a length of flexible tubing and a gas pumping mechanism - typically a one-way squeeze bulb (hand aspirator) or motorized sample draw pump. Draw methods, if done properly, are very advantageous since they allow the enduser the ability to sample an atmosphere, without being directly exposed to the full hazard that may be present at the remote location.

The greatest danger for any sampling method is that the atmosphere delivered to a detector, may not be representative of the true hazard. This results in under-reporting of the true hazard and a dangerous, false sense of security. Because of the special character of reactive gases, it is important to understand the proper sampling methods, materials/accessories and to realize the limitations of any sampling method.

4.1 Diffusion Sampling - General Limitations

For the diffusion sampling method, under-reporting may result if conditions are not uniform throughout a space. This can be overcome by sampling in all work areas and by leaving the detector on for the duration of work in potentially affected areas in the case where conditions may change.

4.1.1 Diffusion Sampling - Limitations for Reactive Gases

For certain highly reactive gases, diffusion methods can significantly underreport actual exposures. Specific examples are the very heavy and highly reactive gases of chlorine (Cl_2) and chlorine dioxide (ClO_2). Being very heavy compared to air, their rates of diffusion are very slow. Also being highly reactive, they are absorbed by any fresh surfaces they encounter. In stagnant air conditions, this can result in a poor initial response and significant delays in getting the true reading.

Given that reactive gases are easily absorbed by many surfaces, external water barrier membranes are not used in the detector sensor covers external to reactive gas sensors. This insures a completely unimpeded path to the sensor face.

4.2 Sample Draw - General Limitations

For sample draw methods, under-reporting of the true hazard can occur in a variety of ways. If the sampling system is not leak or flow checked, either a leak can dilute the stream of air resulting in a lower concentration delivered at the sensor face (higher for oxygen sensors when sampling depleted or inerted environments), or gas may not be flowing through the system at all.

For current model confined space entry detectors, (PhD Lite and PhD5) a leak check mode is enabled every time a motorized sample draw pump is attached to a detector. The system is designed to automatically sense the level of vacuum that builds when the end of the sample draw probe is plugged with a finger. Lack of sufficient vacuum level within a set period of time indicates a leak in the remote sample draw system. For handaspirated draw systems it is recommended to leak test by placing a finger over the end of the probe while the squeeze bulb is fully depressed. Rapid re-inflation of the bulb, upon release, indicates a leak in the system or a defective check valve in the squeeze bulb.

4.2.1 Sample Draw - Limitations for Reactive Gases

For reactive gases special attention needs to be taken for the working surfaces of the draw system. If these are not compatible with reactive gases, the active component may be rapidly depleted from the sampled gas stream - in extreme cases this can occur entirely.

There should be no unauthorized substitution of components used in remote sample draw systems. Use of unauthorized materials, or sampling through excessively long lengths of tubing may lead to erroneously low reported exposure values. A recommended maximum length of tubing for reactive gas sampling is 10 feet.

4.2.1.1 Remote Sampling - Compatible Components and Methods

Carbon black-filled rubber squeeze bulbs used in manual remote sample draw accessories are notoriously strong chemical absorbers for oxidizing gases such as chlorine (Cl2), chlorine dioxide (ClO2) and very reactive hydrogen chloride (HCl). Therefore a manual sample draw accessory should never be used for remote sampling these gases, as the in-line rubber bulb will remove them from the sampled stream.

Sample draw tubing normally presents the largest working surface to a sampled gas stream. Because of this, compatible materials selection is a very important consideration. Biosystems currently recommends two grades of flexible tubing for performing remote sampling of reactive gases, a poly(ester)urethane (PUR) and a stiffer FEP-lined polyethylene (with short PUR end-fittings to adapt to hose barb type connectors). Part numbers for standard 10-foot lengths and suitable gas types are listed below.

Description	P/N	Gases
Poly(ester)urethane (PUR)	53-002	All reactives except, Cl_2, ClO_2, & HCl
FEPilined Polyethylene (PUR end fittings)	35-0344	All reactives

Up until May 2000, Biosystems standard draw kit tubing was a grade of clear, flexible vinyl. Our current standard tubing is now a poly(ester)urethane (PUR) grade which is much more resistant to, and therefore compatible with, solvents, fuels and some reactive gases. PUR tubing can be distinguished from vinyl by its slight yellowish tinge and a much tougher, rugged feel.

Note as with vinyl, PUR tubing should not be used for remote sampling the highly reactive gas types of chlorine (Cl2), chlorine dioxide (ClO2) and hydrogen chloride (HCl). For these more reactive gas types, Biosystems recommends the highly inert FEP-lined polyethylene tubing.

Please note that in certain cases, Biosystems remote sampling systems can be field upgraded. The new grade of flexible PUR tubing can be fitted, by hand, to motorized sample draw components. However, it is normally applied to the larger metal end-fittings on manual aspirator (squeeze bulbs) by the use of a special "tubing spreader" tool. In order to facilitate the field upgrade of any manual aspirator remote sample draw kits we now offer a "manual draw tubing upgrade kit" consisting of the new tubing factory applied to the check valve end-fittings of squeeze bulbs.

Description	Part Number
Manual draw, tubing upgrade kit	35-382

Upon receipt of the upgraded tubing/check valve fitting assemblies provided in the kit, the old vinyl tubing and check valves can be detached from the rubber bulb and discarded. The new check valves can then be pushed into place in the original squeeze bulb. The immediate benefits are new check valves, and better sample draw tubing. Remember to always leak check the system before putting it back into service.

4.2.1.2 Importance of Filter and Sample Line Maintenance

The presence of aspirated dirt, soot and moisture on sample draw filters and tubing is an area of concern. These contaminants can serve to absorb reactive gases.

For example, moisture in the sampling line can very effectively absorb certain gases - such as ammonia (NH_3) and hydrogen chloride (HCl). Condensation of water can develop on draw surfaces if sampling from a warmer, more humid area, to a colder one. Condensation is most likely to occur when sampling below grade atmospheres during winter months, and in any case where the ambient air is significantly colder than the ground.

Biosystems uses clear sample draw tubing and probe/filter housings which allow for a quick visual check for the presence of contaminants in the sampling system. For trace reactive gas sampling, it is always good practice to make certain that filter elements are clean and dry and that the tubing is clear to allow for periodic visual inspection.

Biosystems provides two sizes of filter kits - the larger economy size allows for more economical replacement of filter elements.

Filter Kit*	Part Number
Filter Replacement Kit contains 10 ea. 61-046 particulate and 3 ea. 61-047 hydrophobic filters.	54-05-K0401
Economy Size Filter Replacement Kit contains 30 ea. 61-046 particulate and 10 ea. 61-047 hydrophobic filters.	54-05-K0403

*For current ribbed sample probe assembly type, part number 54-05-A0403

4.3 Reactive Gas Sampling Methods

The following table provides a summary of the currently approved methods for sampling reactive gases.

	Diffusion	Remote Manual	Remote Pump
Ammonia (NH_3)	Yes	Yes	Yes
Chlorine (Cl_2)	No	No	Yes
Chlorine Dioxide (ClO_2)	No	No	Yes
Hydrogen Chloride (HCL)	Yes	No	Yes
Nitrogen Dioxide (NO_2)	Yes	Yes	Yes
Hydrogen Cyanide (HCN)	Yes	Yes	Yes

4.4 Gas Detector Sample Draw Accessories for ReactiveGases

The table on the following page provides a summary of the sample draw accessories and part numbers associated with approved sampling methods for each model gas detector. The table is divided into the less reactive gas types, left three entries, and the highly reactive gas types, right three entries. For current price and availability, please contact Biosystems Customer Service Department.

For the most reactive gases, right three entries, best results are obtained if the length of tubing is strictly limited to 10 feet. Longer lengths will result in greater line losses and delays in equilibrium response. With current pumps for standard, non-reactive gas sampling, lengths up to 100' are permitted for field use. The associated delay in normal response time should be considered to be approximately 1 second per each foot of tubing.

5. Conclusion

Reactive gases can be monitored with properly calibrated and equipped gas detection systems. Extra care should be taken at the time of order to make sure that proper accessories are selected for use when it is anticipated that reactive gas sensors will be required for your gas monitoring application. For questions or concerns about reactive gas monitoring which are not addressed in this applications note, please contact Biosystems Gas Detection Applications Department at tel (800) 711-6776 or email us at

custserv@biosystems.com

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Gas Detector Sample Draw Accessories for Reactive Gases

	NH_3 Ammonia	NO_2 Nitrogen Dioxide	HCN Hydrgen Cyanide	Cl_2 Chlorine	ClO_2 Chlorine Dioxide	HCl Hydrogen Chloride
PhD Lite						
Manual Draw	54-26-0401			Not Recommended		
Pump Draw	54-26-0401			54-26-0101-C		
PhD 5						
Manual Draw	54-05-0401			Not Recommended		
Pump Draw (Slip-on)	54-27-0101			54-27-0101-C		
Pump Draw (Screw-on)	54-27-0102			54-27-0102-C		
PhD Ultra						
Manual Draw	54-05-A0401			Not Recommended		
Pump Draw	54-05-A0101			54-05-A0101-C		
PhD 2						
Manual Draw	54-1650			Not Recommended		
Pump Draw	54-1655A			54-1655A-C		
Toxi Ultra						
Manual Draw	54-09-A0101			Not Recommended		
Pump Draw	**Not Available**			**Not Available**		
Toxilog						
Manual Draw	54-1838			**Not Recommended**		
Pump Draw	**Not Available**					

Sample Draw Tubing for Reactive Gases

	NH_3 Ammonia	NO_2 Nitrogen Dioxide	HCN Hydrgen Cyanide	Cl_2 Chlorine	ClO_2 Chlorine Dioxide	HCl Hydrogen Chloride
Replacement Tubing	53-002 Poly(ester)urethane			35-0344 (53-0036 FEP-lined polyehylene with 53-002 PUR flexible end fittings)		