CHAPTER 5

Detector Selection Factors

To combat terrorism, we must anticipate what terrorists might do. Given that the CWAs are under tight controls, terrorists may resort to compounds that may be less toxic than the CWAs but that are easily accessible in large quantities such as the TICs discussed in Chapter 2. Thus, a single instrument (or small number of instruments) that can detect TICs as well as the more toxic CWAs is desirable.

In later chapters we discuss principles of operation and advantages and disadvantages of each type of detection technique. There is no perfect detector that could possibly satisfy all requirements, at least given current state-of-the-art technologies. We hope that our review will assist readers to select appropriate detection devices for their needs from the vast number of commercial off-the-shelf offerings.

Currently, available detectors vary in cost, performance, and reliability. To choose the correct device for an operation can be quite challenging. While cost may be a concern, choosing the best and most reliable detector for operational needs is more important. Although many existing detectors have been tested under diverse test programs, both governmental and industrial, many others have not been tested. Many detector manufacturers make claims based on their own testing. Some of those claims have not been thoroughly verified by third-party laboratories. Therefore, care must be taken in digesting available data on device performance and testing.

Many factors should be considered when selecting a detector, and we will discuss several important ones. There is no universal set of factors that will fit every objective. Depending on the specific application and circumstances, a detector that is ideal for one type of operation may not be appropriate or the best choice for another. For example, formaldehyde or other volatile organic compound (VOC) detectors may not be suitable for detection of nerve agents. A detector that is capable of detecting nerve agents may not be very useful for detecting certain TICs. To choose a suitable detector, knowing the target chemicals is important, as this information will help to determine what types of techniques are best for the application. In subsequent chapters, we explain several prominent detection techniques and the chemicals that they can detect.

Two types of factors should be considered in selecting a detector: detection capability (selectivity, sensitivity, response time, etc.) and performance (warm-up time, calibration requirements, portability, and power requirements) factors. These factors are discussed below.

5.1 SELECTIVITY

"Selectivity" is the term used to describe the ability of a detector to respond only to the targeted chemicals in the sample. When a detector is set to detect G-agents, it should only respond with G-agent detected in the sample, regardless of how many other chemicals are present. If, for example, pesticides in the sample interfere with G-agent detection, selectivity would be regarded as less than perfect. Depending on the techniques used, some detectors have better selectivity than others. For instance, flame photometric detectors respond only to phosphorus and/or sulfurous compounds through the use of specific light spectra, while flame ionization detectors are better equipped for detecting organic compounds. Given that most CWAs of interest contain either phosphorus (nerve agents) or sulfur (mustard gas), flame photometric detectors would serve well as a specific CWA detection device.

Colorimetric types of detectors are more specific to certain compounds through various chemical reactions. Therefore, they are highly specific detection devices and have higher selectivity, as they respond to a certain number of specific chemicals that they were designed to detect with little or no interference from other chemicals. Consequently, the potential for false responses/alarms is limited. More selective detectors are limited in terms of the number of compounds that could be added to their detection capability. Colorimetric detection devices would be a good choice for monitoring known chemicals in the air at a site where the specific chemical of interest may be present, such as monitoring the phosgene exposure level while personnel is working with phosgene in the laboratory. Because colorimetric detectors are highly selective, multiple colorimetric detectors would be required to detect different types of compounds. Consequently, the routine use of these types of detection devices for early and wide-spectrum warning is limited.

Other types of detectors are less selective and will respond to many chemicals. Flame ionization detectors respond to a large number of organic compounds without discrimination. Thus, they would not be suitable detection devices for CWAs or TICs in the field where the potential for exposure to specific toxins is unknown.

Photoionization detectors detect chemical compounds by ionizing them with UV light at certain electron volt energy levels. The only specificity of PID is that the substance with ionization potentials higher than the UV source will not be ionized and this will not cause a response signal. Similar to flame ionization detectors, photoionization detectors cannot distinguish among signals produced by different compounds. Their usefulness as CWA or TIC detectors in the field is limited because responses are derived from all substances that can be ionized, rather than only target compounds.

Technically speaking, any chemical that can be ionized by an ionization source will be detectable by the ion detectors. Some of these ion detectors can provide limited identification of diverse chemicals in an air sample. For instance, ion mobility spectroscopy devices, commonly referred to as IMS detectors, measure the time elapsed for the ionized species under atmospheric pressure to form the ion mobility spectrum. Thus, compounds can be identified through their respective characteristic mobility. However, because of the nondiscriminatory ionization process, IMS detectors are subject to potential interference by other compounds. It is necessary to provide means, such as limiting the number of peaks stored in the library or using more than one peak for substance identification, to improve the detectors identification capability and minimize false alarm potential.

Nonselective detectors are more suitable for field applications if only a broad-spectrum early-warning system is desired. A nonselective detector yields signals to various chemicals simultaneously, and thus could be useful in civilian arenas as an initial survey given that the chemicals used by terrorists in these scenarios are unpredictable. It would be necessary then to supplement the detection of certain compounds with more specific detection device(s) to identify potential CWAs and/or TICs.

It is important to recognize that there is no single detector that is absolutely selective or nonselective. A selective CWA detector may respond to other chemicals that possess similar properties. The number of chemicals a selective detector responds to is somewhat limited. Less-selective types of detectors can respond to more chemicals than selective detectors, but their responses cannot immediately be attributed to CWAs, TICs, or nontoxic substances. Therefore, a backup device with greater selectivity would still be required to assist in determining the precise nature of a given detected compound.

5.2 SENSITIVITY

Sensitivity of a detector or a method is a measure of its ability to discriminate between small differences in analyte concentration. The detector or method is more sensitive when a large change in signal intensity is observed for a small change in concentration. The instrument may also show a different degree of sensitivity toward low-concentration samples compared to high-concentration samples. Figure 5.1 is a generalized calibration curve observed for selected instruments. In the lower concentration range, the relative change of signal strength with the change in concentration (the slope of the curve) is greater than in the higher concentration range. Therefore, the detector is said to be more sensitive in the lower concentration range. When concentration increases out of the linear detection range of the instrument, the detector response starts to lose sensitivity and may reach a plateau (the output signal does not change as concentration increases).

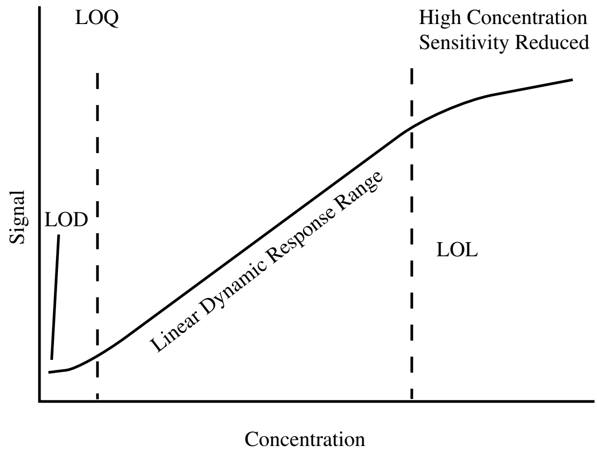

Figure 5.1 Response curve, limit of detection (LOD), limit of quantification (LOQ), and limit of linearity (LOL).

5.3 LIMIT OF DETECTION

A detector's limit of detection (LOD) is the lowest concentration level that it can identify with a certain degree of confidence. There are many definitions of LOD, such as the concentration at which the response signal generated is three times the instrument noise level. Here LOD is referred to as the minimum detection level (MDL) of concentration that will consistently cause the detector to alarm. It is affected by background noise and blank signals. The LOD of a detector may vary widely for different chemicals. Environmental and operational conditions could drastically affect the LOD. Manufacturers normally provide LOD information obtained under optimum conditions.

In general, detectors with lower LODs would be more suitable. As discussed in Chapter 4, the government has a set of exposure-level guidelines for numerous CWAs, TICs, and scenarios. A suitable detector should provide warning well before the IDLH level is reached to permit proper evacuation. Each type of operational scenario may require a different LOD.

5.4 RESPONSE DYNAMIC RANGE

After determining selectivity and sensitivity, dynamic range of the detection response is also a factor to be considered. Response dynamic range is the concentration range between the limit of quantification (LOQ) and the limit of linearity (LOL). The LOQ is the lowest concentration at which quantitative measurements can be made. The LOL represents the concentration level at which the calibration curve departs from linearity. LOD and LOQ are different in that the LOQ is usually somewhat higher than the LOD (Figure 5.1). Some contemporary detectors have large dynamic ranges of up to five or six orders of magnitude, while others have a dynamic range of only one or two orders of magnitude. When the concentration of a sample exceeds the LOL of the detector, the sensitivity of the detector is low. An increase in sample concentration may not be reflected in the observed or reported response. The smaller the dynamic range, the lower the sensitivity at lower concentration levels. The greater the dynamic range, the greater the sensitivity at lower concentration levels, and thus, the larger the concentration range in which a quantifiable response is generated.

For an analytical instrument, response dynamic range is crucial. However, for a field instrument, detecting the presence a toxic chemical in the air at a given concentration or higher is more important. Precise quantification of chemical composition is secondary provided that the detection level meets guidelines set by government agencies (for example) to identify hazardous substances.

5.5 QUANTITATIVE ANALYSIS CAPABILITY

Analysis performed using laboratory instruments can provide good quantitative results, because the laboratory environment is well controlled and calibration curves can be obtained with standard samples. Field instruments have to operate under harsh environmental conditions where temperature and humidity level can vary widely. Establishing standard calibration curves for an emergency situation is not practical. Field detectors can only be precalibrated in the laboratory for field applications, based on the assumption that the detector will perform the same or similarly under field conditions. Whether this assumption is valid depends on the relative ability of the detector to perform under field environmental conditions and stability of the detector after calibration. Many factors could affect the validity of this assumption. Environmental conditions such as humidity, dust, temperature, and potential interfering substances could affect quantitative or qualitative results.

Fortunately, in many situations precise quantitative analysis is not required. It is more important to know qualitatively and semiquantitatively whether the concentration of targeted chemicals surpasses certain levels. Therefore, semiquantitative analysis and qualitative analysis could satisfy such requirements. A semiquantitative detection result would indicate the approximate concentration range instead of an actual concentration level. Qualitative types of detectors only indicate whether targeted chemicals are detected at above-LOD levels, and do not display approximate concentrations.

5.6 FALSE ALARM RATE

False positive alarms and false negative alarms must be addressed when making decisions on appropriate detectors.

A false positive alarm occurs when the instrument reports that the sample contains targeted chemicals when in fact it does not. These alarms can be caused by various factors, depending on the specifics of techniques used. For example, phosphorus and sulfur compounds, such as pesticides, would generate a false positive

CWA alarm when a flame photometric detector is used for detection. This is because flame photometric detectors are made specifically to respond to chemicals containing phosphorus and sulfur. Detectors are always subject to yielding false positive alarms since no detector can be made 100% selective to only targeted chemicals. Most detection devices are made to detect multiple compounds. Therefore, a different technique may be necessary to serve as a backup to confirm alarms to reduce the potential for false positive alarms.

False negative alarms occur when instruments fail to respond to targeted chemicals that are present in a sample. These responses are viewed as more problematic than false positive alarms, because failure to produce a necessary alarm may lead to dangerous/disastrous situations. Causes of false negative alarms include changing environmental conditions; humidity effects; presence of interfering chemicals that mask normal detection capabilities; and detector malfunction, such as improper calibration and detection algorithm deviations.

5.7 RESPONSE TIME

Response time is the time required for the detector to respond to the targeted chemicals after an analysis cycle is started. The elapsed time for an alarm to occur after the detector is exposed to the targeted chemical at different concentration levels is another important factor. Response to higher-level concentrations must be fast and immediate, whereas somewhat slower response times for very low concentration levels may be acceptable.

Some detectors may require a certain amount of time before they can respond with an alarm. For example, detectors with a sample preconcentrator and/or a gas chromatography (GC) column in front of the sensor will require more time for analysis than detectors without such attachments. Response time is a function of vapor concentration for most direct-detection gross-level alarm devices.

Detectors that require thermal desorption, with or without GC column separation, will have a fixed response time. Therefore, regardless of the concentration level in the sample, response times for such devices will be approximately the same. The elapsed time necessary for analysis may be too long in some instances to permit warning in time for effective evacuation. For example, when a preconcentrator (which concentrates chemicals from vapor) is involved, response time will be that much longer than for a device without a preconcentrator.

Often, a GC column may be used to separate chemicals in a sample to provide specificity, and thus reduce the false alarm rate for nonselective detectors. Several minutes may be necessary for the process to complete. The cycle time depends on settings used for the GC elution. Consequently, detection by such instruments will require much longer response time than direct sampling types. Devices equipped with very low LODs with excessive response times may not be the best choices for a given operation because they lack the capacity for rapid warning in the event of high concentrations of the target compound. For postincident management scenarios, the more selective and sensitive types of instruments that include the use of sample concentration and GC separation would be useful.

In attempts to overcome the abovementioned risks, detector manufacturers have incorporated several functions to permit the choice between fast-response mode and high-sensitivity mode (preconcentration mode), or between the fast-response mode and the GC mode (less prone to false alarms).

5.8 RESISTANCE TO ENVIRONMENTAL CONDITIONS

Environmental conditions, including temperature, humidity level, dust concentration in the air, wind, and levels of contamination can affect the performance of a detector drastically. For military operations, temperatures in the field can range from –30°C to above 50°C with relative humidity levels ranging from less than 10% to 100%. It can also be very dusty, windy, and/or the air may contain diverse pollutants at varying levels. Ideally, a field detector must be operable under all environmental conditions, and should maintain its designated functions regardless of field conditions. However, all existing commercially available detectors are affected to one degree or another by environmental conditions. Operational temperature and humidity ranges are available from the manufacturers. Other factors that could affect their detection capabilities are not readily made available. Determining whether the detector can operate in the intended environment is crucial during the process of selecting detection devices.

5.9 SETUP AND WARMUP TIME

To respond to an emergency situation, it is desirable that a detector can be turned on and ready to operate within a short time. Setup time is the time needed to prepare the detector so that it can be powered up. Warm-up time is the time required for the detector to become ready for analysis after it has been turned on. For handheld detectors, the setup time is usually minimal because they are usually self-contained with only the necessary batteries as separate parts. Setup consists of inserting the battery pack. However, a period of warm-up time is normally required for any detector to reach operational status. This time could range from few seconds to half an hour or longer depending on the ambient temperature and relative operational parameters of the detector type. In general, the device goes through an internal self-check protocol to satisfy preset parameter requirements before it is ready for analysis functions.

5.10 CALIBRATION/VERIFICATION IN FIELD APPLICATIONS

Proper detector functioning will often require verification of capacity to perform upon each startup. For a chemical detector, the process is confirmed using known nontoxic chemicals as simulants of targeted compounds. Ideally, the proper operation of the detector can be verified with simple simulant checks that do not require complicated correlation calibration procedures before each use.

5.11 OTHER FACTORS

For a field detector, portability is another important factor to be considered. Portability, or whether the device can be transported, includes any support equipment required for operation. If transport and operation by a single person are considered important, then portability means a lightweight device. In situations where vehicle transport is acceptable or desirable, larger and heavier equipment (which in turn provide better detection and more refined analyses) carried by a vehicle are considered portable.

Field detectors must be transported from place to place by ground, rail, water, and air transport, and are subjected to extreme environmental conditions in storage. Rough handling in emergency situations is to be expected. Therefore, detector durability is another consideration.

In general, batteries are used to power handheld devices. Battery life is another logistical factor to be considered. Some detectors may require specially designed batteries, and thus finding replacements or recharging spent batteries in the field is difficult. Therefore, the chosen detector should ideally be operable through the use of two or more alternative power sources, and battery life must be sufficient to last through an entire mission. Fortunately, most modern handheld detectors are designed to permit the use of alternate power sources.

Operator training requirements are another factor to consider. Detector quality is only as good as an operator's understanding of instrument features and functions. Many modern instruments require a certain amount of special training to fully utilize their capabilities. Fortunately, most field detectors are designed to be user friendly; very little training is required to operate and maintain them.

However, a certain degree of data interpretation may be necessary to determine whether the data obtained from a given device is valid. Detailed knowledge of detector characteristics enables the operator to assess the likelihood of false positive response. Many field detectors do not directly display the concentration level of target chemicals that produce alarms. They may show bar graphs or other indicators on displays that show ranges of certain concentration levels. While knowing the exact concentration of the target agents may not be necessary, the ability to detect high concentration levels could prove to be vitally important. Operator training courses should emphasize result interpretation.

Operation costs should include equipment purchase, maintenance, and consumables costs. Cost comparisons should be based on the cost per analysis per chemical. For example, the purchase price of certain colorimetric detectors may seem relatively low but each analysis will incur additional consumables costs. Thus, the final cost of an operation could be relatively high compared to automatic continuous types of devices due to the cost of required consumables. Thus, although an automatic detector may cost tens of thousands of dollars initially, it does not require large amounts of consumables, it detects a number of chemicals at once, and it has a very long operational life.

There are other secondary concerns, such as the time required to clean the residual from the previous sample, waste generation, storage effects, maintenance frequency, whether the device can be easily decontaminated, and whether data can be saved for later analysis. The most important consideration is that the chosen detector must be able to provide the necessary reliability, sensitivity, and sufficient selectivity for a given operation scenario.

The perfect detector does not exist and no single detector possesses all the desirable features and functions. By weighing the factors mentioned above together with the operation scenario, it may be possible to find a detector that approaches meeting all or most requirements.