CHAPTER 10

Colorimetric Technology

Colorimetric detectors analyze the color change resulting from the reaction between the targeted chemical and reagents. This technique has been used in many different applications. Good examples of colorimetric detection are the use of litmus paper (or pH paper) to test the pH value of a solution, and the common water test kit used to analyze chlorine concentration in swimming pools. The litmus paper test is an example of a direct reading: the color is formed by the reaction with reagents impregnated on the paper, and no further manipulation occurs. As soon as the litmus paper is wetted with the solution, the pH of that solution causes the impregnated reagents to change color according to the solution's pH value. Chlorine content testing of swimming pool water is based on the addition of reagent o-Tolidine to the solution to form the visible orange color that can be used for quantitative determination. Color intensity is related to the relative concentration of chlorine in the water. Colorimetric detectors using different methods are all easy to use, low cost, and provide relatively fast responses.

Colorimetric detectors often take the form of badges and tubes where the signal (color change) is detected by the human eye instead of electronic devices. Therefore, most colorimetric detectors can be made small and simple, are less costly to produce, and do not use electric power for operation.

Most colorimetric detectors are designed to be selective because of carefully selected reagents. The reagents are selected to react only with a specific class of chemical compounds that produce the proper color change for detection purposes. The number of interferences for the specified detection is usually very limited. Typically, a single sensor is used to detect or monitor one class of chemicals. For example, a badge that is designed for monitoring phosgene will detect the presence of phosgene only and cannot be used for the detection of nerve gases. Thus, the advantage of this detector is its lower false alarm rate. On the other hand, it has the disadvantage of requiring many sensors for field applications.

To overcome the technique's major disadvantage, some detectors have incorporated several sensors for detecting specific classes of compounds. One badge contains several sensors, or several different detection tubes are used for each surveillance-monitoring task. For example, the military M18® detection kits are assembled with various sensor spots and tubes to detect CWAs. The later M256® Chemical Agent Detector Kit, using similar detection methodologies, combines all required reagents for various types of detection into a single sampler to detect CWAs.

Monitoring badges and detection tubes are mainly used for qualitative analysis or semiquantitative analysis, which uses human eyes as the signal (color) processors. The sensitivity of the human eye varies widely. Each person has slightly different color perception, and many people suffer from some degree of color-blindness. Environmental conditions and color formation media also affect colors and their interpretation. It is difficult to observe color in dim or bright light situations. These factors limit the effectiveness usage of detection badges and tubes as a reliable quantitative technique.

Since water can enhance or delay reactions, the moisture content of sensors, badge, tube, or paper-tape should be kept at a certain level. When manufacturing test kits, concerns for proper moisture level must be addressed. During use or storage of the kits, moisture may be lost from or absorbed by the sensor spots, which can affect the detection to become unreliable. Techniques to counter effects are usually incorporated when this methodology is employed.

10.1 PRINCIPLE OF OPERATION

The principle underlying the colorimetric method of detection is quite simple. Detectors are made with sorbent substrates, paper or paper tape, or glass tubes that are impregnated with colorimetric reagent(s), which react with a specific targeted chemical to form a particular color. Colorimetric tubes may consist of finely impregnated beads together with the necessary reagent ampoules. This arrangement enables the sample flow to contact the reagent-impregnated surface more effectively and homogenously.

Figure 10.1 is a block diagram showing the principle of operation. When the targeted chemical in the sample comes in contact with the chemically impregnated surface, whether through a passive or active sampling technique, the surface color changes due to specific chemical reactions. The change in color indicates the presence of the target chemical(s). Concentration of the targeted chemical in the sample can be estimated based on the intensity of the color (monitoring badge and paper tape) or the length of the stain (colorimetric tube) developed over the exposure time. Common types of colorimetric detectors are described below.

10.2 INSTRUMENTATION

The three common colorimetric-based detectors are badges, tubes, and paper tape. They can be very simple without any moving parts, that is, badges or paper

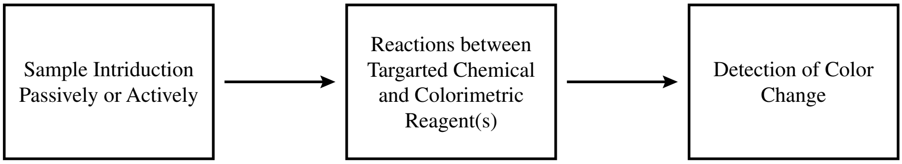

Figure 10.1 Block diagram of colorimetric detector analysis procedure.

spots. Some will use a sampling pump that can be powered by electricity or manually operated to draw sample into the detection tube. More advanced systems involve an automatically operated advancing tape, reagent injections, and colorimeter unit to detect color formation. Each type is designed for specific applications.

10.2.1 Badge Monitoring Kit and Paper Spot Detector

Colorimetric badges and paper spot detectors are based on papers that are impregnated with reagent before exposure to air. Both use a passive sampling technique, that is, the sensors are exposed to the air without any other means to force the air into contact with the sensor. Some sensors may require additional reagent and manipulation after exposure to form the color. This type of monitoring kit is inexpensive, lightweight, and easy to use. They can produce direct color development results without requiring a pump or any moving parts for sampling. Monitoring kits that are made as badges, used generally for personal exposure monitoring, are worn by individuals. They may also be used for area monitoring. Unlike other types of detectors, these kits are consumed after a single use. Monitoring results show only total exposure dose during the exposure time.

During the monitoring, the impregnated badge or paper spot is exposed to the air. Targeted chemicals, if any, diffuse onto the surface of the sensing area and react with the reagents. The reaction between the targeted chemical and the reagent changes the color of the badge/paper, which indicates presence of the target chemical. This type of monitoring kit is usually precalibrated to permit determination of the exposure level. The resultant color is compared to the standard color pallet similar to the function of a calibration curve. The results are, at best, semiquantitative.

10.2.2 Detection Tube

A detection tube can be made by coating the inner wall of a thin transparent tube with reagent. Similarly, fine impregnated beads of adsorbing materials may be packed inside of the tube (Figure 10.2). The turbulence created by the beads in the sample flow path enables a more complete reaction between the chemicals in the vapor and the reagent on the surface of the beads. Another type of colorimetric tube consists of adsorbent beds and reagent ampoules sealed within a glass tube. The reagent ampoules are broken to provide the necessary reactions that produce the color for detection. Although the monitoring badge and spot paper and the detection tube share similar colorimetric principles, there are important differences among them. Sample tubes require a suction pump to draw air samples, while the badge

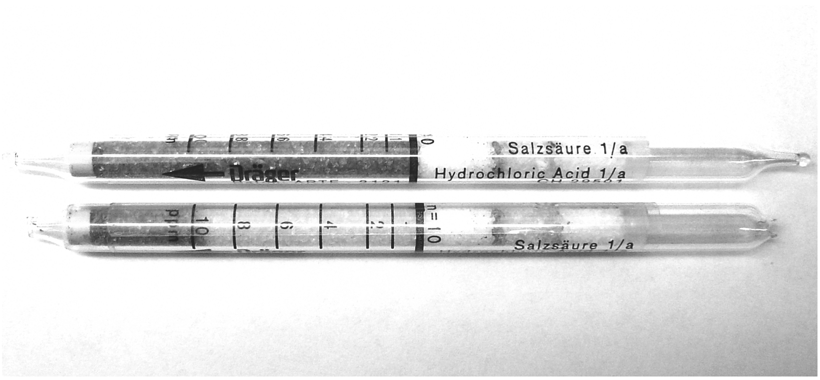

Figure 10.2 Colorimetric tube.

and spot paper is passively exposed to the air. The tube is not designed for continuous monitoring. It is used as a means to detect the presence of targeted chemicals at test time. In general, tubes can perform detection with greater sensitivity in shorter time.

The tubes are sealed until ready for detection to avoid any potential contamination. At the time of detection, both ends of the tube are opened and the tube is connected to the special pump (Figure 10.3). The pump can be a manually operated suction pump or a battery-operated pump that draws air at a certain flow rate. The coated reagents will react with the targeted substances to produce the stain on the sensing surface in direct-reading types of detectors (Figure 10.2). Normally, a colorimetric tube requires a fixed volume of sample for quantitative analysis.

Figure 10.3 Colorimetric tube with sampling pump.

The targeted chemical reacts with the colorimetric reagent first in the area closest to the inlet of the tube; thus, the most intense color is developed at that end. When more of the targeted chemical is drawn in, the reagent near the inlet may become mostly consumed by the target chemical, so more of the target chemical is available to penetrate farther into the bed and produce the stain there. Thus, the length of the colored stain increases. This type of colorimetric tube is usually precalibrated with marks at different positions on the tube to indicate the approximate concentration of the target chemical in the air. The reading from the tube after detection is related to total targeted chemical dosage. Sampling time and flow rate are considered when calculating estimated vapor sample concentration.

Sensitivity of the colorimetric tube varies with the sampling volume and is generally in the parts-per-billion (ppm) to parts-per-million (ppm) level. For less concentrated vapor, a larger sampling volume introduces more of the chemical for the reaction, therefore, sensitivity increases. The dynamic range of a tube is usually limited with respect to the total amount of targeted chemical that it is exposed to. The operating procedure provided by the manufacturer is usually chosen to achieve the intended detection thresholds for which the tubes are designed. Different tube types may use a different number of strokes.

Another type of colorimetric detection tube uses solid adsorbent to adsorb the incoming targeted chemicals either with or without first being impregnated with reagents contained in an ampoule. Another reagent is added after the sample is adsorbed to the dry adsorbent or absorbed to the reagent-wetted adsorbent material to form the color. Depending on the reaction mechanism, appearance or disappearance of a given color is used to denote detection.

10.2.3 Advancing Tape–Based Colorimetric Detector

These colorimetric devices use tape impregnated with chemical reagents as a platform for detection. The tape is commonly about a half-inch wide and made of paper or cloth. Unlike the monitoring badges discussed above that are exposed to the air and take samples passively through diffusion, the advancing tape instruments draw samples through the reagent-impregnated tape using a pump at certain flow rate. After the predetermined sampling time, the tape is advanced to the next stop where a color-developing reagent is added and the color development is monitored by a colorimeter. The rate or intensity of the color developed or the fading of a developed color determines the concentration of the target chemical.

Major components of an advancing tape–based colorimetric detector include colorimetric tape, sample pump, and colorimeter (Figure 10.4). The tape that is or will be impregnated with the reagent serves as a base to generate the color signal. The tape must be isolated from exposure to the sample air except for a small spot that is used as the detection sensor. The tape is advanced at a predetermined time. This allows a new "sensor" spot to be exposed to another sample. The air pump draws the sample vapor through the tape at the spot that has been impregnated with the reagent from the dispenser so that the targeted chemical reacts with the impregnated reagents during the sampling cycle. If the sampled air contains the targeted chemical, reactions between the reagent and the targeted chemical will

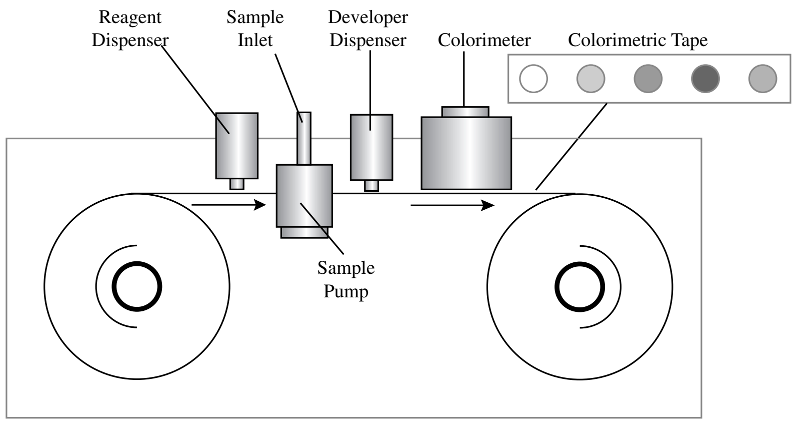

Figure 10.4 Schematic diagram of tape-based colorimetric detector.

change the color of the spot. For some chemicals, the color spot must be developed by adding another reagent. The spot will then be monitored by the colorimeter to record the color observation. This results in one sample observation per tape advancement period thereafter. The sample cycle is dependent on the time required for each step to ensure sufficient time for reaction and color development. Therefore, the cycle time would be the longest time required by one of the steps.

An electronic device called a colorimeter that measures the color intensity is used to determine the intensity of the color that can be related to concentration. This colorimeter measures the light reflected from the exposed stain as well as the light reflected from an unstained area as the reference. The difference between the two signals is used to determine detection. Alternatively, the rate of color formation or color fading could also be used. The instrument can first measure the color at the time the developer reagent is added as compared to the subsequent color intensity after a time interval. This type of instrument usually includes temperature controls that accelerate the rate of reaction.

Another method that monitors the color change rate instead of color intensity at the end of each sampling period is also used. An intensity threshold is preset, and stain intensity is continually monitored. An alarm is triggered as soon as the stain reaches its preset threshold. This rate of change is relative to concentration of the targeted gas in the sample; thus, it can be used to estimate sample concentration. At higher concentrations, the stain intensity reaches the defined threshold in a shorter time than at lower concentrations (Figure 10.5). The advantage of this method is that when high concentrations of the targeted substance are detected, the device quickly delivers a response, thereby speeding up the alarm time.

This colorimetric tape method provides much faster detection of low-concentration samples than badges or tubes could provide. Its LOD can be as low as parts per billion. More importantly, this method provides continuous detection capability that tubes or badges lack. It also records exposure history.

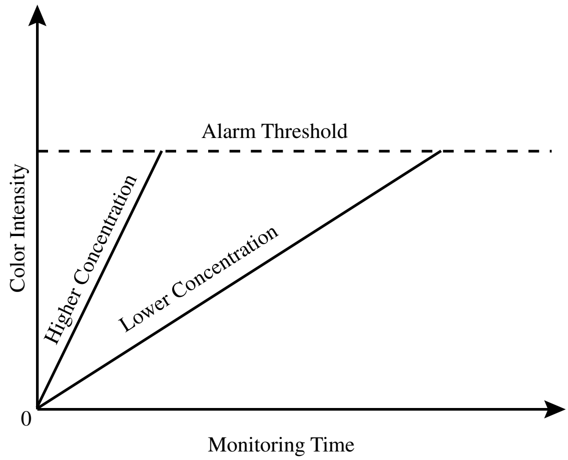

Figure 10.5 Detection based on change rate of color intensity.

In conclusion, the colorimetric detection technique is, in general, very selective and sensitive. Three different types of colorimetric detectors — badges, tubes and papers, and moving tape — use a similar chemical reaction process but with different procedures. Badges are typically used to monitor total exposure levels (dose monitoring), called dosimeters. Tubes or paper spots are used as point sampling detectors that could provide approximate concentrations. Moving tapes are used in detectors designed for continuous monitoring. By combining several different tubes or paper spots, a colorimetric detector can detect multiple chemicals.

10.3 APPLICATIONS

The most well-known colorimetric detectors for CWA detection are the M8® Chemical Agent Detector paper (Figure 10.6), M9® Chemical Agent Detector paper, and the M256A1® Chemical Agent Detector Kit. The M8 and M9 papers each contain a dye that produces a color when dissolved via contact with liquid chemical agent droplets. The M9 paper shows generic red spots, while the M8 paper distinguishes among three classes of agents. M8 paper is used to test suspect droplets of liquid on a surface. The paper will turn yellow when in contact with a G-type nerve agent, red when in contact with mustard agents, and dark green when in contact with a V-type agent. The use of M9 paper is limited to showing red dots in contact with an agent aerosol, warning of potential exposure to a CWA attack. Unfortunately, such M9 detection per se would not protect the individual from harm by the target agent. Both M8 and M9 CWA detector papers are examples of direct colorimetric detection.

The M256A1 Chemical Agent Detector Kit (Figure 10.7) includes M8 paper and a vapor sampler that uses colorimetric detection technology in different ways. It consists of paper spots that are impregnated with reagents (or the spots are impregnated prior to exposure to the air) for simultaneously detecting the presence

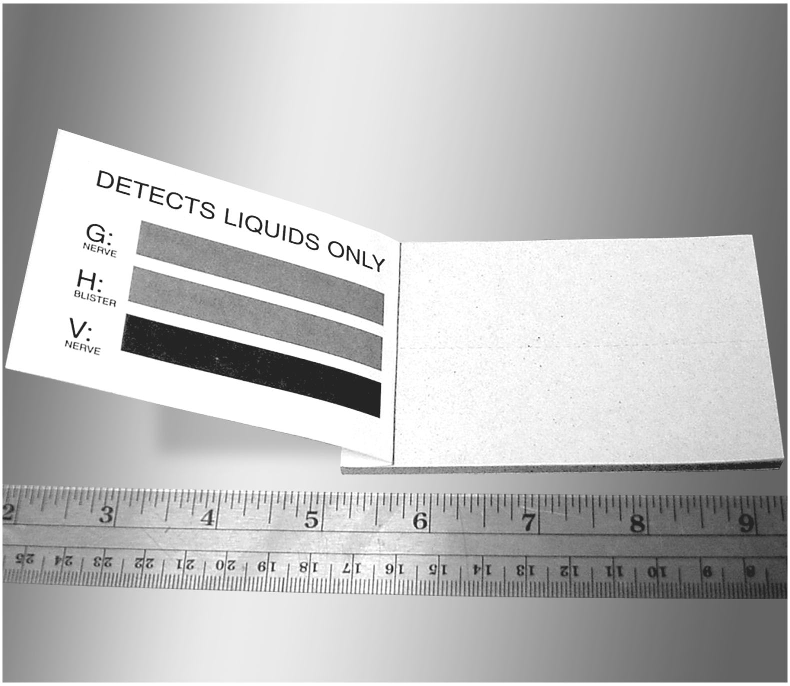

Figure 10.6 M8 paper detector.

of multiple CWAs. All required reagents are encapsulated in sealed ampoules arranged in order according to reaction requirements. The ticket can detect nerve, blood, and blister agents from a single exposure. Two components produce a direct color development without further manipulation after the exposure. The other two spots require the addition of color development reagents to produce colors after exposure.

The M256A1 Chemical Agent Detector Kit is generally used for postincident monitoring to determine the level of CWA presence (and thus when it is no longer a threat) because of its ability to detect very low concentrations of nerve agents. Nerve agents are detected using an enzyme reaction with the anticholinesterase effect that is characteristic of these agents. The M256A1 Kit is also used to verify the presence of CWAs when one or more other generic CWA detectors indicate their potential presence. Because of the lengthy time period required for detection using the M256A1 Chemical Agent Detector Kit, it is not a suitable device for early warning of CWA exposure.

The well-known M18A1® Kit, Draeger tubes (Figure 10.2 and Figure 10.3), and detection tubes from manufacturers such as the Mines Safety Appliances (MSA), among others, consist of sealed glass tubes that contain the required reagents and support beds to test for the presence of targeted classes of substances. Numerous detector tubes are available, covering the range of most TICs as well as CWAs.

Figure 10.7 M256A1 Kit. Photo courtesy of K. Y. Ong.

The Domestic Preparedness Program has tested two types of these tubes for CWA detection ability. For example, the thioether tubes can detect HD, and phosphoric acid ester tubes can detect nerve agents at very low concentrations.

The use of moving-tape instruments to develop the color that can be monitored with an electronic colorimeter can be best illustrated by the Russian enzymatic detector used by the Aum Shinrikyo group that produced the sarin gas in the Tokyo subway incident in 1995. That instrument is an automatic nerve agent detector; acetylcholine or acetylthiocholine is hydrolyzed and then reacts with a color developer to form the color in the absence of a nerve agent. The instrument utilizes a moving tape methodology in which the sampling spot is first impregnated with an enzyme solution before the sample air is passed through the spot. After a sampling period, the cloth tape is advanced to move the exposed spot to the next stop where the reagent containing the color developer that reacts with the hydrolyzed enzyme and acetylcholine or acetylthiocholine product to form the color. In the presence of a nerve agent, the anticholinesterase effect of the nerve agent inhibits the cholinesterase enzyme such that the reaction with the acetylcholine or acetylthiocholine is deterred. Consequently, less color results.

The U.S. military has also used similar enzyme detection techniques, but does not depend on moving tape for CWA detection, which was known as the real-time monitor in the 1970s. This is another example of how colorimetric detectors can be used in CWA detection. The system was developed for safety monitoring of workplaces where nerve agents were being disposed of to support the CWA demilitarization program. The system uses a moving solution system. An air sample is drawn through a scrubber concentrator that is wetted with a pH-adjusted aqueous solution. A portion of the sampled solution is pumped into the tubing via the moving solution system where it encounters an injection of cholinesterase enzyme solution. The presence of nerve gas will inhibit the enzyme as it moves along the tubing; color intensity varies according to nerve agent concentration. By comparing the baseline color (without nerve agent) and the resultant color (after exposure to nerve agent), the relative concentration can be calculated, unless the concentration is so high that the enzyme was totally inhibited.

Colorimetric detectors are usually specifically developed for certain groups of compounds that undergo similar chemical reactions. Therefore, they are usually less prone to interference compared to other types of generic detection technologies. The downside is that reactions require time and manipulation, and different reactions are required to detect different types of compounds. Therefore, colorimetric detectors are best used to supplement other types of devices that could provide more effective real-time detection of CWA or TIC presence.

10.4 FACT SHEETS ON SELECTED COLORIMETRIC TECHNIQUE–BASED DETECTORS

Detector Name

Chemical Agent Liquid Detectors, 3 Way, and M8 and M9 Paper

Manufacturer/Distributor and Contact Information

Tradeways Ltd.
184 Duke of Gloucester Street
Annapolis, MD 21401
Tel: 410-295-0813

Technique Description

This M8 is designed to detect the presence of chemical agent liquid droplets via colorimetric reactions. Provides rapid identification of the three major groups of CWAs, V, G, or H. M9 contains dye that is dissolved when hit with agent aerosol to show red dots as an indication of an exposure to aerosol.

Chemical Detection Capability and Performance

The M8 paper turns green upon exposure to V-agents, yellow when G-agents are present, and red when exposed to H. The M9 paper does not differentiate among the three agent types. Liquid agent droplets dissolve the impregnated dye into red dots for detection purposes.

Other Feature

Not suitable for CWA vapor detection. M9 paper is worn by soldiers intended to detect an aerosol exposure only. M8 is used as a wipe to identify liquid droplets as V, G, or H agent-class.

Detector Name

Chemical Agent Water Test Kit: M272®

Manufacturer/Distributor and Contact Information

Tradeways Ltd.
184 Duke of Gloucester Street
Annapolis, MD 21401
Tel: 410-295-0813

Technique Description

The Chemical Agent Water Test Kit M272 consists of colorimetric detector tubes and enzyme impregnated detection tickets for nerve agent detection. The kit is designed to detect the presence of chemical agents in water samples.

Chemical Detection Capability and Performance

The detector sets are designed to serve as postincident management monitoring of CWAs or TICs. Sensitivity is expected to meet current drinking standard requirements. Processing time varies according to the number of manipulations and the required reaction time for color development from each sample. The time required for the process to complete is quite lengthy. Sensitivity is limited by the ability of the Alka Seltzer®–type tablets to drive agent vapor out of the solution.

Other Feature

Visual indication of detection through the color development by human vision.

Detector Name

M18A3 and M256A1 Chemical Agent Detector Kits

Manufacturer/Distributor and Contact Information

Tradeways Ltd.
184 Duke of Gloucester Street
Annapolis, MD 21401
Tel: 410-295-0813

Technique Description

These kits detect CWA vapors through the use of colorimetric reactions on reactant-impregnated paper or in detection tubes. They are designed to detect the presence of chemical agents in the air through the use of colorimetric reactions. Similar techniques are employed in both kits for detection of nerve, blister, blood, and choking agents. The M256A1 Kit permits simultaneous multiagent detection, whereas the M18A3 Kit requires separate use of tubes or paper tickets for each class of agent.

Chemical Detection Capability and Performance

Papers are designed to rapidly detect the existence of CWA agents in liquid. The kits are sometimes used to determine when the concentration of a given CWA is low enough to permit removal of protective facemasks after an incident or during a decontamination operation.

Other Features

Not suitable for gross-level CWA vapor detection due to time required for determination, as the process requires approximately 15 min to complete.

Detector Name

Simultaneous Test Sets from Draeger Safety

Manufacturer/Distributor and Contact Information

AFC International, Inc.
715 SW Almond Street, Suite C
DeMotte, IN 46310
Tel: 800-952-3293

Technique Description

These products are available in several different sets of colorimetric detector tubes. Each set is designed for detection of specific TICs, TIMs, or CWAs at or below IDLH or close to AEL levels.

Chemical Detection Capability and Performance

The detector sets are designed to serve as postincident management monitoring of CWAs or TICs. Sensitivity is expected to meet/exceed current IDLH requirements. Several tubes can be used to simultaneously draw samples. Processing time varies according to number of manipulations and required reaction time for color development. These tubes are not suitable for gross-level detection due to the lengthy time required for the process to complete. Sensitivity can be increased through longer sampling times or increasing the number of pump strokes.

Other Features

Multicompound detection capability varies according to the number of tubes used. Kits are available to meet Homeland Defense needs for TIC or CWA detection.