

# Surface Acoustic Wave and Electrochemical Techniques

Surface acoustic wave (SAW) technology utilizes the production, control, transmission, and reception of acoustic waves formed on the surface of a piezoelectric substance. It has been used in telecommunications applications for over 50 years. SAW devices are used in mobile cellular phones and base stations as band-pass filters, and also serve as sensors for many other applications such as torque, pressure, temperature, humidity, and chemical sensors.

The first chemical agent sensor using SAW technology was reported in 1979 by Wohltjen and Dessy. Currently, many variations of SAW-based chemical sensors are under development around the world. For example, the current Joint Chemical Agent Detector (JCAD), under development by the U.S. military, uses SAW technology. SAW devices as viable future CWA detectors are being aggressively developed. The race is on to produce detection devices that meet JCAD requirements.

The heart of a SAW device is a piezoelectric crystal plate. When an electrical field is applied to the crystal, a surface acoustic wave is generated and propagates on the surface of the piezoelectric substrate. Any changes in characteristics of the propagation path affect the wave frequency. For example, additional deposits of substances on a surface change the surface characteristics, and thus affect the wave propagation frequency. This change in frequency is monitored and can be correlated to the corresponding quantity of deposit being measured. Consequently, the amount of CWA loaded on the piezoelectric substrate surface upon exposure to a vapor sample can be detected.

SAW devices have some advantages over other technologies. The device can be manufactured at relatively low cost but with good detection sensitivity. It responds rapidly to chemicals deposited on its surface and can be miniaturized easily. Its reliability as a viable CWA detector is steadily being improved through aggressive research and development efforts.

Since both HAZMATCAD and JCAD employ electrochemical (EC) sensors to detect blood agents and other TICs, discussion of this topic is also included in this chapter.

## 9.1 PRINCIPLE OF OPERATION OF SAW DEVICES

Two major processes contribute to detection with a SAW device: generation and change of surface waves on a piezoelectric plate, and the sorption/desorption of chemicals on the surface.

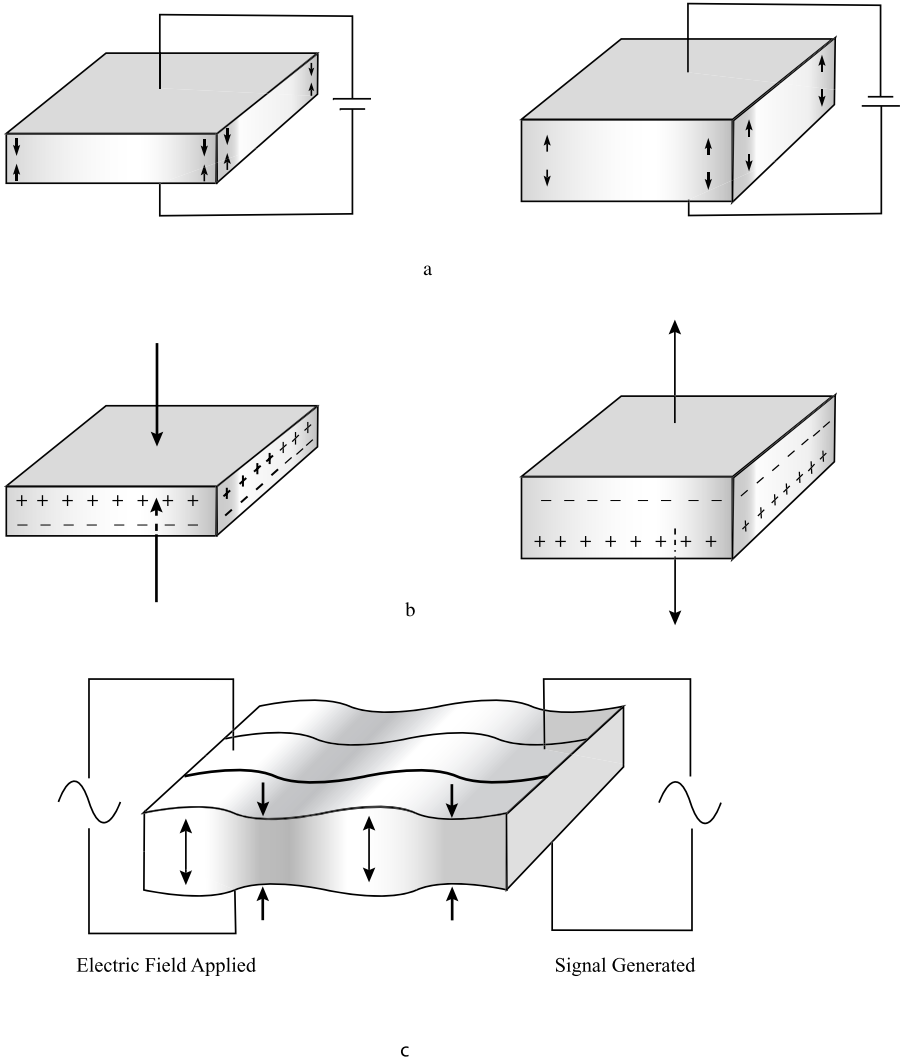
### 9.1.1 Piezoelectric Effect

Figure 9.1 illustrates the piezoelectric effect. Piezoelectric plates are made of natural crystals (e.g., quartz) that do not possess center symmetry. When piezoelectric crystals are subjected to an external voltage, the crystals will expand or contract accordingly (Figure 9.1a). When the crystals are subjected to a mechanical strain (tension or compression), an electric voltage is generated (Figure 9.1b). This is called the piezoelectric effect, discovered by Pierre Curie (1859–1906) in 1880. When an AC field is applied at one end of the piezoelectric crystal plate, this end of the plate will expand and contract accordingly. This movement propagates through the crystal, or along the surface of the crystal, toward the other end of the plate. Electric voltage is generated by this expansion and contraction because of the piezoelectric effect (Figure 9.1c).

### 9.1.2 Surface Acoustic Waves

Applying an electric field to a piezoelectric crystal causes vibration resonance in several different ways, including flexure, lengthwise, area, radial, thickness-shear, thickness-trapped, and SAW, among others. Direction of vibration varies from one type to another.

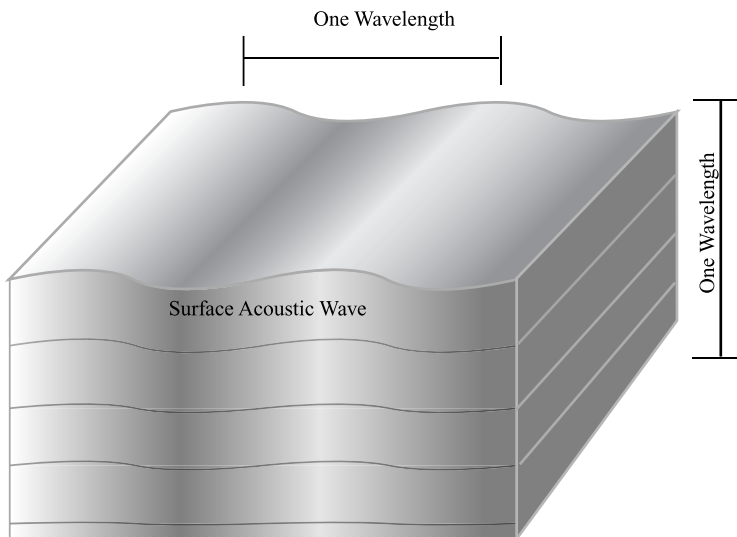
Many chemical detection sensors are based on the SAW effect. In Figure 9.2, SAW occurs on a piezoelectric crystal plate with all the acoustic energy confined within one wavelength thickness of the surface. Since the wave propagates along the surface, the SAW sensor directly senses any mass change with associated changes in frequency and wave attenuation. SAW frequency may range from 25 MHz to 500 MHz or even higher. In general, frequencies greater than 50 MHz are used. Sensitivity is a function of the square of the vibration frequency; therefore, higher operational frequency enables increased sensitivity of the device to monitor surface perturbations. Because the wave propagates only along the surface of one side of the crystal, the other side can be bonded to a support base without interference in the detection process.



**Figure 9.1** Piezoelectric effect.

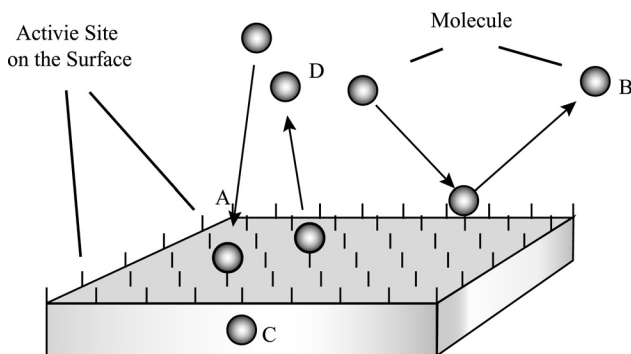
**9.1.3 Surface Sorption**

To use the SAW device to detect chemicals, the targeted chemicals must be sorbed onto its surface to change the acoustic wave’s propagation path property. The piezoelectric crystal does not itself have the desirable sorption ability to attract target chemicals. A thin layer of polymer substrate on the piezoelectric material is used to provide selective sorption of the targeted chemical from the vapor sample.



**Figure 9.2** Surface acoustic wave.

A polymer can be comprised of a natural or a synthetic compound, consisting of millions of small, simple molecules called monomers. Each monomer is a link in the long-chained polymer molecule. Polymers have many free, active sorption sites that can effectively sorb the incoming chemical molecules (Figure 9.3). When a sample vapor enters the SAW detector, molecules in the vapor come in contact with the polymer surface at a certain rate depending on the vapor flow. When a chemical agent molecule hits the surface, it will be either bonded to the active sorption sites on the surface of the polymer (A in Figure 9.3) or deflected by the surface (B in Figure 9.3). The surface sorbs the molecules when they are captured on the active sites of the polymer. Adsorption occurs when the molecule (adsorbate) remains on the surface of the polymer (adsorbent).



**Figure 9.3** Surface sorption.

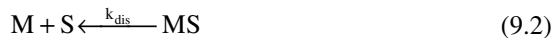
Absorption occurs when the molecule soaks into the coating rather than remaining on the surface (C in Figure 9.3). The difference between adsorption and absorption is adsorption occurs when the particle remains on the surface while absorption occurs when the substance enters the substrate. Sorption occurs when both happen simultaneously. Adsorption can reach equilibrium much faster than the absorption process. Consequently, the adsorption process requires a much shorter recovery time.

The simplest way to explain a sorption process is to describe it as a first-order reaction between the sorbate (S) and the sorbent (M):



where  $k_{\text{ads}}$  is the sorption rate constant.

Disassociation occurs at the same time at a different rate:



where  $k_{\text{dis}}$  is the desorption rate constant.

In the following, the sorption coefficient,  $K$ , represents the affinity between the sorbate and the sorbent, is the ratio of the two constants:

$$K = \frac{k_{\text{ads}}}{k_{\text{dis}}} \quad (9.3)$$

When adsorption equilibrium is reached,  $K$  equals

$$K = \frac{[MS]}{[M][S]} \quad (9.4)$$

The number of molecules that can be sorbed on the surface depends on several factors: the sorption coefficient ( $K$ ) of the polymer to the chemical, the number of available sorption sites on the sensor's surface ( $M$ ), and the concentration or vapor pressure of the sorbate in the vapor sample ( $S$ ).

A high sorption coefficient means that the substance has strong affinity to the polymer, such that it can be sorbed to the sorbent effectively and rapidly. As expressed in Equation 9.4, a higher sorbed concentration ( $MS$ ) at lower chemical concentrations yields a higher  $K$  value of the vapor at equilibrium. Chemicals with high  $K$  values will be sorbed more readily than those with low  $K$  values, as they compete for the available sorption sites. Therefore, chemicals with high  $K$  values are selectively sorbed on the polymer coating surface on the detector's SAW sensors.

The sorption coefficient decreases with temperature. The potential energy of a molecule is higher at higher temperatures. When the temperature reaches a certain level, the bond between the sorbent and the sorbate will break, resulting in release of the sorbed molecules from the polymer (D in Figure 9.3). This increases the dissociation coefficient ( $k_{dis}$ ) and reduces the sorption coefficient (K). Therefore, the sorption ability of the polymer is reduced at higher temperatures. Effective release of the sorbed chemical from the SAW sensor surfaces can be induced with similar effect by heating the sensors to a higher temperature. This method is used to release the sorbed chemicals from the SAW sensors after each sample analysis.

The limit of detection (LOD) for various chemicals is determined by respective sorption coefficient values. The sensor polymer can attract more of the chemicals with higher K values from vapor onto its surface to produce a higher MS. Therefore, the given sensor is said to have a better limit of detection toward a compound that has a high sorption coefficient value. Thus, the detector can identify the higher K-value chemicals at lower concentrations.

The available active sorption sites M in a unit of surface area, and the vapor pressure or concentration of the chemical in the vapor that governs S are factors that determine how much adsorbate can be sorbed. Equation 9.4 can be rearranged to

$$[MS] = K[M][S] \quad (9.5)$$

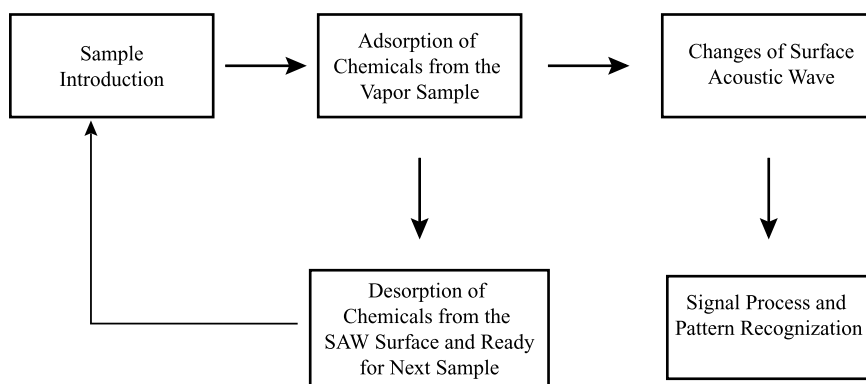
Since K is a constant at a certain temperature, the increase of either M or S will increase the sorbed concentration on the surface, MS. For a SAW sensor, the surface area of the polymer coating is a constant. Thus, M can be considered as a constant also. Therefore, the responses of the detector are directly related to the concentration of the chemicals in the sample.

Equation 9.4 also suggests that decreasing the sample concentration in the vapor reduces the sorbed chemical on the surface. Therefore, the effective way to clean the SAW device after an analysis is the use of heat to reduce the sorption coefficient while using a clean carrier gas to flush the released sorbates out of the detector.

The above discussion is based on the establishment of sorption equilibrium. The equilibrium between the vapor and the surface is essential for quantitative analysis. Unless sorption equilibrium is reached, it is difficult, if not impossible, to determine vapor concentration. Fortunately, such sorption equilibrium can be reached within seconds.

#### 9.1.4 SAW Chemical Sensor

Figure 9.4 shows a block diagram of a SAW chemical detector. The sample is introduced and chemicals in the sample are sorbed onto the surface. This results in changing the acoustic wave frequency that propagates through the surface. Almost all SAW chemical sensors rely on mass sensitivity of the device. Since the polymer coats the surface of the piezoelectric substrate to adsorb molecules from the vapor, any sorption of chemicals on the polymer will change surface wave propagation on the substrate surface. Wave frequency change and its attenuation are used to



**Figure 9.4** Block diagram of SAW analysis procedure.

determine the amount of substance deposited on the device. The signals are processed to identify chemicals sorbed from the sample. Flash heat is then applied to the SAW device to release the sorbed chemicals from the sites. The sensors are ready for the next sample analysis. By assuming that sorption equilibrium is reached, concentration of the chemical in the vapor can be determined.

## 9.2 INSTRUMENTATION

Chemical detectors using SAW technology are under aggressive development by many different practitioners. As a result, these detectors may be very different from each other. In general, an array of SAW sensors coated with various polymers is used to minimize interference and increase selectivity. A typical SAW detector may have three, four, or more sensors. One of the sensors is isolated from the sample flow path for compensation of temperature-induced effects. The other sensors, coated with specific polymers that are selective to target chemicals, will have different response characteristics when exposed to the sample vapor to detect different types of compounds. A pattern of responses from these sensors can be monitored and an algorithm developed to identify the chemicals sorbed. When the pattern matches the criteria stored in the algorithm, the detector will indicate the presence of the targeted chemical. The array is housed within a package that has a pathway for vapor to flow over all sensors. This package can be temperature controlled to reduce temperature effects and optimize sensitivity.

### 9.2.1 Sample Input

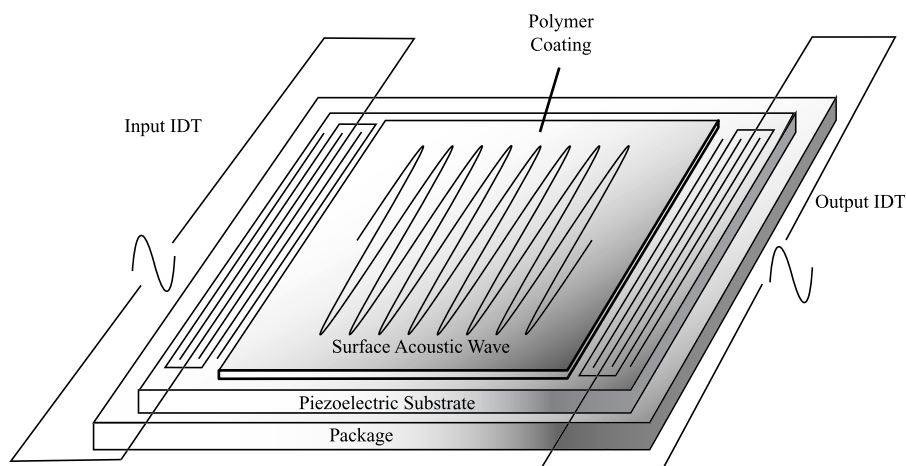
SAW-based detectors can draw vapor directly or through a sample concentrator before analysis by the sensor array. Sample concentrators are substances with high surface areas to sorb large amounts of incoming molecules from an air sample. Charcoal is commonly used to sorb targeted chemicals from the vapor stream. Charcoal sorbs CWAs and TICs strongly, stripping them from the air and, thus,

concentrates them on its surface. This concentration technique before the sample is presented to the sensors by heat desorption, is very helpful for achieving better sensitivity and improving the instrument's minimum detectable level (MDL). It not only permits detection of low-concentration samples, but also reduces certain undesirable features of direct-sample detectors. The sample preconcentrator acts as a buffer to reduce effects from moisture and interference chemicals that the SAW sensors are quite sensitive to. The sampling time and rate are controlled so that the concentration can be calculated for detection optimization. Some devices use a gas chromatograph (GC) column in front of the sensors to further reduce interference with targeted chemicals to enhance selectivity. The use of a preconcentrator and GC column increases the sensitivity and selectivity of the detector and further minimizes the abovementioned adverse effects.

The preconcentrator, after sorbing chemicals from the sampled air during the sampling period, is then heated to release the sorbed chemicals. A flow of carrier gas sweeps the released chemicals into the GC column for separation of components prior to reaching the SAW sensor array for detection/identification. Relative elution times for each of component can serve as a means of identification. The relative strength of signals can be related to concentrations of the substance in the sampled air.

### 9.2.2 SAW Device

A typical SAW device includes two sets of interdigital transducers (IDTs) made by a photolithographic process on the surface of a piezoelectric substrate (Figure 9.5). An electrical field is applied to one of the IDTs to form an acoustic wave on the surface of the sensor. The wave propagates through the substrate to the other IDT where the mechanical energy of the acoustic wave is converted back to electricity.



**Figure 9.5** Schematic diagram of a SAW device.



To selectively detect targeted chemicals, the propagation path of the acoustic wave is coated with a selected polymer substance. One important requirement for the coating is that the sorption of targeted chemicals must be totally reversible after an analysis. All sorbed substances must be released totally without residue after an analysis so that the detector can be used to analyze the next sample. The sorption coefficient of the coating with respect to the specific type of chemicals should possess high  $K$  value to achieve good sensitivity and selectivity. Fast recovery time is also a required characteristic of the polymer.

Practically, it is impossible for a polymer coating on a SAW sensor to be made to only sorb one chemical. A single polymer may sorb several chemicals from a gas mixture. This opens the door for potential false alarms. Similarly, chemicals contained in the gas mixture can be sorbed by more than one polymer sensor in the array with various sorption coefficient values. Each of the sensors in the array is coated with a specific kind of polymer intended for selective sorption of a targeted group of chemicals. The presence of a targeted chemical generates a specific response pattern. Based on the pattern generated, the chemical in the vapor can be identified. Many different sensors having various coatings could be used in a detector to increase its detection reliability.

### 9.2.3 Temperature Effect and Compensation

The surrounding temperature affects the performance of a SAW device in two ways. Temperature changes the crystalline structure of the piezoelectric substrate that in turn affects the propagation property of the SAW. Temperature changes also affect the sorption and desorption property of the coating film. The effect that affects the property of the piezoelectric crystal can be reduced through installation of a reference SAW sensor that is isolated from the sample vapor. Temperature fluctuation affects not only the SAW sensors for the detection but also the reference sensor. Therefore, the temperature effect on the sensors could be compensated for by negating the similar effect experienced by the reference sensor.

Temperature changes the sorption coefficient of the polymer coating film. The polymer has stronger sorption ability to chemicals at lower temperatures. Consequently, the sensors theoretically should have better detection sensitivity at lower temperatures than those at higher temperatures. However, at low temperatures, much more energy and time are required for effective total release of sorbed chemicals before the next analysis cycle. It is also possible that the sorbed chemicals cannot be totally released at low temperatures, which means that sensors malfunction. In addition, the polymer may become very rigid at extremely cold temperatures and lose its adsorption ability, which also causes the detector to fail.

When temperature rises, the energy of molecules in the vapor becomes higher as the bonding strength between the molecules and polymer becomes weaker. The bonding strength of the polymer may not be strong enough to retain the sorbed molecules striking its surface. This reduces the ability of the sensor to sorb effectively, resulting in a higher minimum detectable level (MDL). This characteristic proves to be a necessary and desirable trait, as it provides a means for fast clearing

of sorbed chemicals from the polymer surface after each analysis. The sensors are heated, together with a flow to clear the surface.

For both stationary and handheld detectors, it is possible and desirable to maintain a constant temperature on the sensors during the analysis. Heating the sensor cavity to a temperature above the ambient temperature reduces the effect of ambient temperature fluctuations that are known to influence detection characteristics. Unfortunately, higher-than-ambient temperatures will tend to worsen the sensors' LOD. Therefore, a compromise setting must be chosen to provide the best detection results.

### 9.3 ANALYSIS PROCESSES

An internal pump draws the sample into the sample preconcentrator where the targeted chemicals are sorbed. After the sampling period — a few seconds to several minutes — the preconcentrator is heated to release the sorbed chemicals. In the absence of a GC column, the carrier gas then sweeps the released chemicals into the sensor cavity where the vapor is evenly distributed onto each of the SAW sensors in the array. The concentration released from the preconcentrator as a slug is much higher than the concentration in the air sample. Chemicals in the released vapor are selectively sorbed onto the SAW sensors in the array and detection occurs. With the help of calibration curves, quantitative or semiquantitative results can be obtained. After the analysis, heat is again applied to the SAW sensors to clear sorbed chemicals. The analysis cycle is repeated. Choosing the proper timing sequences, each of the heating and cooling processes will occur in tandem.

### 9.4 TECHNICAL SPECIFICATIONS

#### 9.4.1 Selectivity

Because polymers cannot be made specific to only sorb a single chemical, false positive alarms may occur when various unknown chemicals are being sorbed onto polymer. To minimize this false alarm problem, multiple SAW sensors with different polymer coatings are used in a single detector. The combined response patterns can improve detection reliability. For each chemical of interest, the response pattern is established via comparison with standardized samples. The pattern recognition is based on comparison between the output signals and the established response pattern stored in the detector's databases.

In field applications, many unknown components are common. It is very possible that the targeted chemicals found in the field may be mixed with various substances that cause them to behave differently from standard samples used in the laboratory to construct the database. Therefore, false alarms, both positive and negative, are still possible. Hopefully, continued experimentation made by researchers and manufacturers can and will overcome some of these problems.

### 9.4.2 Sensitivity, MDL, and Response Dynamic Range

SAW detectors can be very sensitive. Sensors may detect chemicals in vapor at the parts-per-billion level. Controlling factors affecting sensitivity are SAW device frequency, polymer properties, and respective targeted chemicals. SAW device using higher frequencies are more sensitive to the change of mass on the polymer coating. As discussed above, polymers with higher adsorption coefficients can sense lower concentrations of chemicals in vapor. It is noteworthy that moisture level in a sample may drastically affect sensor sensitivity. Polymers can sorb water easily. Because water concentration in an air sample can be much higher than the concentration of targeted chemicals, water molecules may occupy many of the active sorption sites of the polymer and effectively reduce sorption ability of the polymer to adsorb targeted chemical molecules. This will significantly reduce detector sensitivity. A preconcentrator, water trap, or GC column helps to minimize or remove water content before the chemical sample reaches the SAW sensors.

The response dynamic range of the typical SAW sensor is very broad and could be up to six orders of magnitude. The sensor reaches its saturation point only when the target chemical in the sample is sufficiently concentrated to occupy most or all active sorption sites available on the polymer-coated surface.

### 9.4.3 Response Time

Once the chemical vapor comes into contact with the SAW sensors, a response is developed within seconds. A complete analysis cycle for a SAW-based detector includes sampling time, desorption time from the preconcentrator, analysis time by the sensors, and recovery time to clear the sorbed chemicals from the polymer. Additional elution time is added when a GC column is incorporated. Analysis time is only a very small portion of the entire cycle. Detection speed depends on sampling time, especially when a preconcentrator or GC column is used for low-concentration samples. While it is possible to bypass the preconcentrator to reduce the analysis cycle time, the probability of false responses by the sensors significantly increases. Recovery time depends on the quantity of chemicals sorbed, strength of the bond between the sorbed molecules and sorption polymer, and the temperature necessary for releasing sorbed chemicals. Recovery time ranges from a few seconds to several minutes.

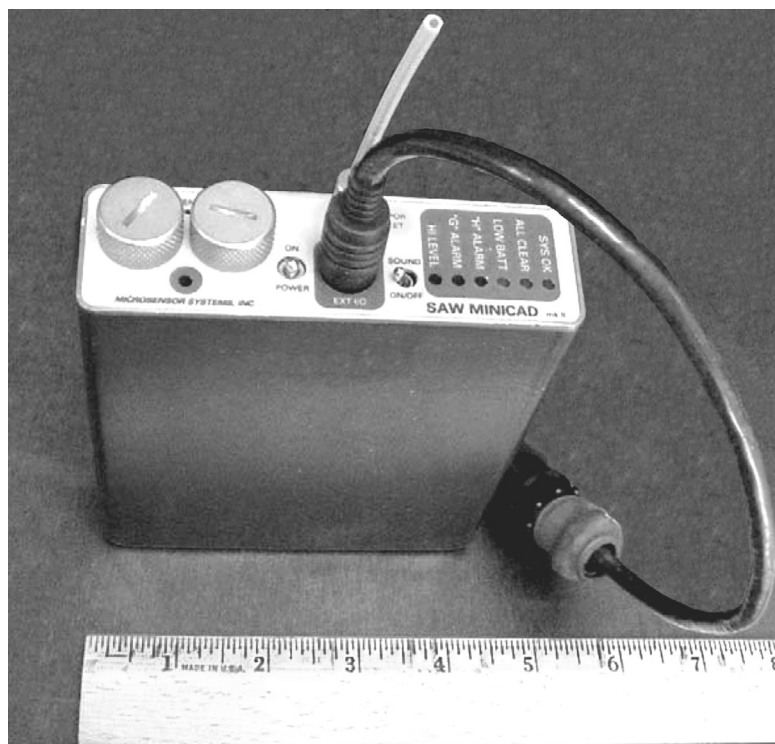
In summary, SAW-based chemical sensors have the potential to provide fast and sensitive detection of chemicals. Sensors can be miniaturized and made economically. Therefore, SAW-based detectors can be made into small, lightweight packages. For low-concentration vapor, a preconcentrator alone or a preconcentrator connected in tandem with a GC column is used to increase sensitivity and improve selectivity. Selectivity also depends on the polymer coating on the surface of the piezoelectric substrate together with using an array of several sensors. The current Joint Chemical Agent Detector (JCAD), under development by the U.S. military, is a SAW-based detector. The JCAD intends to replace the current Automatic Chemical Agent Detection Alarm (ACADA), which is a device based on ion mobility spectroscopy.

## 9.5 APPLICATIONS

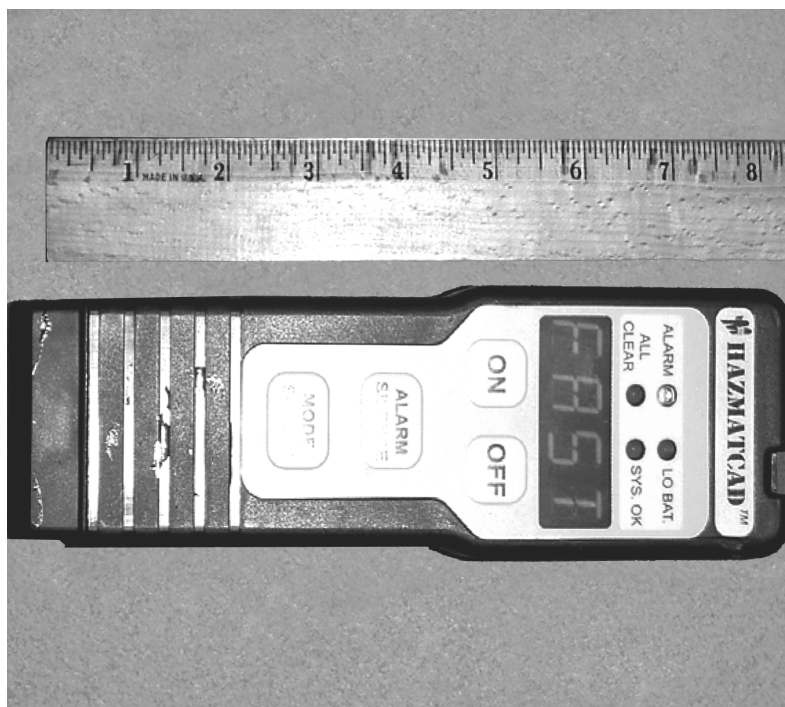
A few devices using the SAW technology are described below. The SAW MiniCAD® (Figure 9.6) is a commercially available, handheld, pocket-sized detector that can monitor for trace levels of sulfur mustard and G-type nerve agents with specificity. The instrument is equipped with a sampling pump and a sample concentrator that can be heat desorbed to provide an enriched sample concentration for the two microsensors to analyze. More details are included in the fact sheet on this device at the end of the chapter.

The HAZMATCAD® (Figure 9.7) was developed subsequent to the SAW MiniCAD. The HAZMATCAD measures 2.3 in. × 2.5 in. × 7.8 in. and weighs approximately 1.5 lb. It detects sulfur mustard and G-type nerve agents using micro-SAW sensors, as well as TICs or blood agents (AC, CG, and CK) by including an EC cell for this purpose. This device's operational temperature ranges from  $-10^{\circ}\text{C}$  to  $50^{\circ}\text{C}$  at all levels of humidity. The time required for the device to warm up (to a specified temperature) before detection is approximately 30 sec. A fact sheet on this device at the end of the chapter provides more details.

The HAZMATCAD has two modes of detection. The “Fast” mode requires 20 sec per sample cycle. The “High Sens” mode requires 120 sec per cycle of sample and purging. This mode can be used to monitor low-concentration situations. During



**Figure 9.6** MiniCAD detector. Photo courtesy of K. Y. Ong.



**Figure 9.7** HAZMATCAD detector. Photo courtesy of K. Y. Ong.

operation in the high-sensitivity mode, the detector draws its sample for a longer period so that more of the targeted compound is concentrated for the sensors to detect. The instrument does not use a GC column to aid in separating sample components. The use of a heat-desorbed sample concentrator permits the instrument to operate at various humidity levels without significant adverse effects.

Testing conducted under the Domestic Preparedness Program has confirmed that the SAW sensor can detect and differentiate the HD and the G nerve agents. Results indicated that sensitivity toward the more volatile GB is lower than that of the less volatile GA. Humidity effects on detection were avoided with the use of a preconcentrator. Temperature affected some of the detection algorithms due to the insufficient size of the heater used.

The HAZMATCAD technology has further been incorporated in the development of the CW Sentry<sup>®</sup> system that is used for monitoring buildings or subway systems where the unit can operate continuously around the clock 7 days a week. The SAW sensors fit well in this application because it requires very minimal maintenance and practically no consumables except for an occasional dust filter change.

Another detector, still under development for the U.S. military by BAE Corporation, is the JCAD, which uses SAW techniques to detect nerve, blister, and blood agents, and assorted TIC compounds. When fully developed, it should have the ability to report on concentrations of respective agents. The detector will be lightweight, and handheld or carried in a small pouch. It will be powered by rechargeable

batteries that provide more than 12 hr of continuous operation. The JCAD is expected to be operational from  $-32^{\circ}\text{C}$  to  $49^{\circ}\text{C}$  at all humidity levels.

The Micro-Chem Lab<sup>®</sup> detector, developed by Sandia National Laboratories, incorporates a micro-GC column after the sample concentrator to separate sample components before reaching the SAW sensor array for detection and identification. While the elution components are sensed with generic types of SAW sensors, the GC's elution time required for a detected component could provide identification. This system is also lightweight. As of this writing, this detector was undergoing numerous tests.

Different versions of SAW-based detectors are continuously being developed, as SAW devices can be manufactured at relatively low cost as compared to other technologies. The polymer coating can be refined to provide greater selectivity and/or higher sensitivity. The sensors can be easily miniaturized, and more sensitive models are emerging. Methods to harvest response signals are becoming more mature and sophisticated through aggressive research efforts. It is hoped that a highly reliable CWA and TIC detector based on SAW technology that fits JCAD requirements will be available soon.

## 9.6 ELECTROCHEMICAL SENSORS

Both HAZMATCAD and JCAD employ EC sensors for detecting blood agents and other TICs. Sensors based on EC techniques or EC sensors have been used to measure toxic gases at the parts-per-million level for many years. This technique is based on the electric current generated by the oxidation or reduction reactions. Electrochemical sensors have properties that make them attractive for long-term monitoring, real-time measurement, process control, and safety applications. Many different gases, such as  $\text{CO}$ ,  $\text{O}_2$ , and  $\text{H}_2\text{S}$ , can be detected and monitored in real time with EC sensors. In fact, any gas that undergoes oxidation–reduction reactions can be detected with EC sensors. Since sensor structure is very simple, it can be made very small and requires little power for personal monitoring applications.

### 9.6.1 Oxidation–Reduction Reactions

EC sensors utilize the electric current generated by oxidation or reduction reactions between chemicals in the air and the electrolyte residing in the sensor. The reaction involves the exchange of electrons. As an example, a simple oxidation–reduction reaction is illustrated through the burning of hydrogen gas in air. When hydrogen burns, it reacts with oxygen in the air to form water molecules.



This reaction can be rewritten in its ionic format that shows the exchange of electrons between the hydrogen and oxygen molecules:



Each hydrogen atom donates its single electron and forms a positively charged ion,



while each oxygen atom gains two electrons and forms a negatively charged ion:



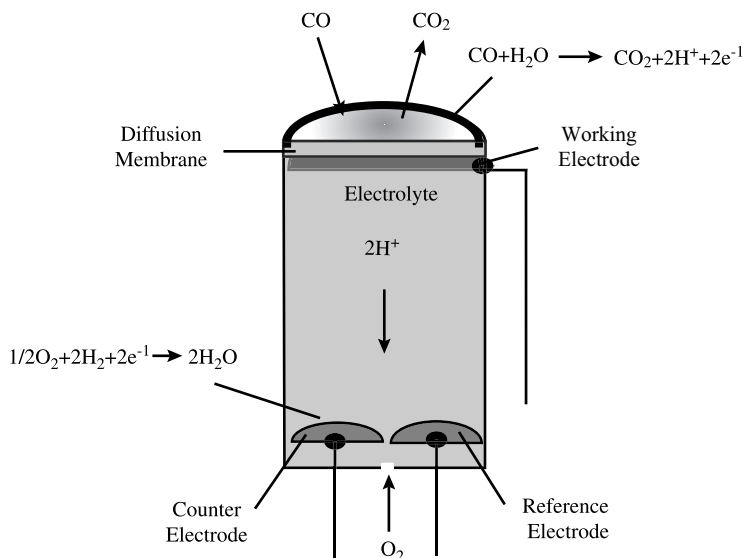
The lost electron from the hydrogen atom flows to the oxygen atom. Thus, the oxygen in this reaction is the “oxidizing agent” or “oxidant” that oxidizes the hydrogen. The hydrogen loses its electron, and thus is a “reducing agent” or “reductant.” In this oxidation–reduction reaction process, the “oxidizing agent” (oxygen) is reduced to a lower valence by the “reducing agent” (hydrogen). Oxidation and reduction always occur simultaneously. A common application relying on oxidation–reduction reactions is to generate electric power in a car battery.

An EC sensor is similar to an electric generator. The oxidation or reduction of the electroactive gases with the residing reagent generates a measurable electric current in the sensor. This generated electric current, instead of being used to produce power, is measured as a detection signal.

## 9.6.2 The Sensor

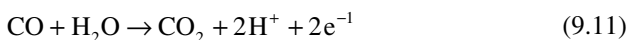
Figure 9.8 shows the structure of a typical EC sensor that consists of three electrodes. Although EC sensor types are numerous, their basic structures and principles are similar. Basically, three electrodes — working electrode (WE), counter electrode (CE), and reference electrode (RE) — are immersed in an electrolyte, such as  $\text{H}_2\text{SO}_4$  solution in car batteries. Solid-state electrolytes are also used. The electrodes and the electrolyte are included in a small (e.g., plastic) container. The WE, also called the sensing electrode, consists of a porous polymer membrane that coats a small gold or platinum plate, which in turn is connected to an external electric source at a certain electric potential. The oxidation or reduction of the targeted chemicals occurs when the chemicals are in contact with the electrode. The reaction that occurs here is only half of the oxidation–reduction reaction. The other half occurs on the CE that is used to balance the reaction on the WE. The RE is used to control the electric potential of the WE through a feedback mechanism.

When the sensor is exposed to the sample vapor, molecules diffuse through the porous membrane and come into contact with the WE. Both the membrane and electrode are immersed in the electrolyte. The porous membrane is saturated with the electrolyte. The reaction takes place on the surface of the working electrode where the incoming molecules become oxidized or reduced by the electrolyte. The gold or platinum plate itself serves as the catalyst for the reaction. The reaction generates an electric current that is measured for detection purposes.

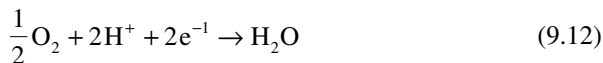


**Figure 9.8** Schematic diagram of EC sensor.

As an illustration, we will use the carbon monoxide oxidation and reduction reaction. When CO is in contact with the WE, the CO molecules will be oxidized:



The oxidation of CO is half of the reaction. The produced  $\text{CO}_2$  is released back to the air while  $\text{H}^+$  stays in the electrolyte and migrates toward the CE where the other half of the oxidation–reduction occurs as follows:



The function of the CE is to complete the oxidation–reduction reaction. Thus, the overall EC reaction is



The electric current generated by this oxidation–reduction reaction is measured for determining the CO concentration in the sample.

To accurately measure a chemical concentration in the air, the relative voltage between the WE and CE should remain constant. The  $\text{H}^+$  ion produced from the WE dissolved in the electrolyte changes the electrical potential of the electrolyte and, therefore, the voltage of the WE relative to the CE. To compensate for this voltage



fluctuation due to the change of ion concentration in the electrolyte, a third (reference) electrode is used. The RE is made with material that is non-conductive and stable in the electrolyte. It measures the electric potential of the electrolyte during the analysis and feeds the information back to the WE so that the relative potential difference is adjusted accordingly.

When an EC detector is used for monitoring or detection, the sample flows over the sensor and contacts the surface. The molecules in the vapor sample diffuse through the porous polymer on top of the gold or platinum plate where the oxidation–reduction occurs. This diffusion through the polymer is the controlling factor for detection, and serves to prevent the sensor from becoming saturated by the targeted chemicals. This will ensure that the response is proportional to the concentration of the target chemicals in the sample. The reaction is catalyzed by the gold or platinum surface of the plate. The generated electric current is sent to the processor for signal analysis.

### 9.6.3 Operation, Sensitivity, and Selectivity

Electrochemical detection of CWAs can be illustrated with an example involving the reaction of a cholinesterase with nerve agents. A solution of cholinesterase enzyme is contained within the cell. When a nerve agent comes into contact with the enzyme solution as it diffuses through the membrane, a certain amount of the enzyme will be inhibited while the uninhibited enzyme reacts with another reagent to form an electrochemically active product that can be measured. Given that the initial amount of enzyme is known, the amount of inhibited enzyme as derived from measurement of the uninhibited enzyme can be related to the concentration of the detected nerve agent.

Other EC sensors measure the change in resistance upon absorbing targeted chemical agents into the thin-film polymer coating on a gold substrate. The swelling or contraction of the film as the agent is absorbed into or released from the polymer causes differentials in resistance measurements for a given applied potential.

EC sensors are relatively sensitive, as they react to chemical vapor concentrations at the low parts-per-million level. However, EC sensors are not as selective as colorimetric detectors (see [Chapter 10](#)). They may respond to various chemicals simultaneously without differentiation capability. This is because the oxidation–reduction reaction between the chemicals in the sample and the electrolyte controls the detection. Any chemicals contained in the sample that will react with the electrolyte on the working electrode surface will generate electrical current and are detected together with those from targeted chemicals. Using a chemical filter may reduce or eliminate some of the chemical interference potential. The use of a second working electrode that responds to different sets of chemicals from the first working electrode within the same sensor may also lead to better selectivity.

Several factors may affect the performance of EC sensors. Environmental conditions are major concerns. During operation in high-humidity conditions, the cell electrolyte may absorb water from the air. In contrast, while operating in low-humidity conditions, the cell electrolyte may lose water. This gain and loss of water

will change the concentration and volume of the electrolyte within the sensor and affect sensor sensitivity.

Sensor lifetime can be reasonably long. However, its sensitivity may vary due to loss of electrolyte and contamination of the catalytic surface.

The first chemical agent detector that was developed by the U.S. military, the M43, is an EC detector that senses the reaction of a nerve agent with an oxime solution. The electrical signal generated is measured through the use of platinum and silver electrodes.

Another example of chemical agent detection using an EC cell is the Individual Chemical Agent Detector<sup>®</sup>. The ICAD can detect both nerve and mustard agents simultaneously through the use of two sensor cells.

## 9.7 FACT SHEETS FOR SELECTED SAW AND/OR ELECTROCHEMICAL DETECTORS

### Detector Name

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HAZMATCAD and HAZMATCAD/Plus

### Manufacturer/Distributor and Contact Information

Microsensor Systems  
62 Corporate Court  
Bowling Green, KY 42103  
Tel: 270-745-0099  
Fax: 270-745-0095

### Technique Description

This instrument is a handheld SAW-based detector that uses the change in SAW frequency caused by adsorption of substances on the surface of polymeric sensors. The detector has two sensitivity modes: fast mode has a detection cycle of 20 sec per analysis; and high-sensitivity mode requires 1 min per analysis. The detector automatically recycles after each analysis cycle. It can detect nerve, blister, and blood agents. TICs and blood agents are detected via EC sensors.

### Chemical Detection Capability and Performance

The detector is designed to detect nerve, blister, choking, and blood agents, together with a list of TICs. Sensitivity is expected to approximate current JSOR requirements. It includes a sample preconcentrator to increase sensitivity and stability.

### Other Features

Interface for network connection. The HAZMATCAD/Plus uses four EC sensors to detect blood and choking agents as well as some TICs.

### Domestic Preparedness Test Report

Domestic Preparedness Program Testing of HAZMATCAD Detectors Against Chemical Warfare Agents Summary Report, February 2002  
(<http://hld.sbcom.army.mil/ip/reports.htm#detectors>)

**Detector Name**

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Individual Chemical Agent Detector (ICAD®)

**Manufacturer/Distributor and Contact Information**

Smiths Detection  
2202 Lakeside Blvd.  
Edgewood, MD 21040  
Tel: 410-510-9100

**Technique Description**

This instrument is a miniature chemical agent detector, approximately the size of a cigarette pack weighing about 8 oz, that can detect and alarm to nerve, blister, and blood agents. It may be used as a point detector that is worn by individuals, and may be connected to a network. The chemical agent concentrations in the electrolyte are measured by multiple-electrode EC sensor systems that trigger an alarm when a preset threshold level is reached.

**Chemical Detection Capability and Performance**

The detector has two EC sensors covered by a thin diffusion membrane. One sensor detects GA, GB, GD, AC, and CG, and the other detects H and L agents.

**Other Features**

Visual and auditory alarms. Interface for network connection. Operational life of approximately 4 months depending on temperature during use. EC cells can be replaced in the field.

**Detector Name**

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JCAD Joint Chemical Agent Detector

**Manufacturer/Distributor and Contact Information**

BAE Systems  
6500 Tracor Lane  
Austin, TX 78725  
Tel: 512-929-4753

**Technique Description**

Instrument is a handheld detector using change in SAW frequency caused by adsorption of substances on surface of polymeric sensors. Electrochemical sensors are used to detect TICs.

**Chemical Detection Capability and Performance**

Instrument is designed to detect nerve, blister, and blood agents together with a list of TICs. Sensitivity is expected to meet current JSOR requirements. It will include sample preconcentrator to increase sensitivity to parts-per-billion level.

**Other Features**

Interface for network connection. This device is being developed by the U.S. Joint Services as a future detector to replace/complement the ACADA.

### Detector Name

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MiniCAD SAW MK

### Manufacturer/Distributor and Contact Information

Microsensor Systems  
62 Corporate Court  
Bowling Green, KY 42103  
Tel: 270-745-0099  
Fax: 270-745-0095

### Technique Description

This instrument is a pocket-sized detector that uses the change in SAW frequency caused by adsorption of substances on the surface of polymeric sensors. The detector has two sensitivity modes: fast mode has a detection cycle of 20 sec per analysis; and high-sensitivity mode requires 1 min per analysis. The detector automatically recycles after each analysis. It can detect nerve, blister, and blood agents. Blood agent detection is done via EC sensors.

### Chemical Detection Capability and Performance

This detector is designed to detect nerve and blister agents. Sensitivity is expected to be around the IDLH region. Sample preconcentrator is included to increase sensitivity and stability.

### Domestic Preparedness Test Report

Domestic Preparedness Program: Testing of SAW MiniCAD MKI Detector Against Chemical Warfare Agents Summary Report, September 2001  
(<http://hld.sbcom.army.mil/ip/reports.htm#detectors>).