CHAPTER 1

CHEMICAL SENSING

RONALD L. WOODFIN
Sandia National Laboratories (retired)

We do a lot of chemical sensing. Mostly we do it without special equipment. But, whether it is the pleasant notification of tortillas toasting or bread baking or the jarring realization of a skunk or a cigar on the golf course, sensing, analyzing, and cataloging chemical signals are a part of our daily lives. We also use other means for chemical sensing. When we travel, we judge the local water hardness by the amount of soap we need to wash or shampoo. We use test kits to measure the chemistry of a swimming pool or a flower bed. In this chapter we will examine some basic ideas of chemical sensing as they apply to finding explosives.

1.1 WHAT IS CHEMICAL SENSING?

When we speak here of *chemical sensing* we mean the direct sensing of chemicals, rather than sensing of something else by means of chemicals. By that choice we will not consider those techniques often called "wet chemistry." We then have a fairly clear idea that we mean to search for a specific chemical or suite of chemicals. Sometimes the search is for single chemicals like chemical warfare agents such as mustard or sarin. At other times combinations of chemicals, such as found in marijuana, are the object of the search. A short digression to consider the broader range of techniques and targets is appropriate in order to limit more precisely the scope of this book to the specific type of search indicated by its title. We broadly classify the possible types of sensing system according to activity and according to focus.

1.2 TYPES OF SENSING SYSTEMS

First, we may class sensors according to the activity required of the sensing system. Hence a system may be passive, active, or semiactive. Passive sensors

---

Trace Chemical Sensing of Explosives, Edited by Ronald L. Woodfin

do not produce any emanations directed toward the target; they are based on sensing something emanated or released by the target without stimulation by the sensing system. Conversely, active sensors need no emanation or release of anything from the target; they provide some sort of emission that interacts with the target. The active sensor then senses the alteration in its emission by the target. Semiactive sensors operate in yet another way. They provide a stimulation that produces some sensible emission or emanation from the target, which they then sense in the manner of a passive sensor.

1.3 SENSING POSSIBILITIES

1.3.1 Bulk Sensors

There are two basic ways to look for explosive material. They differ in their point of focus. Some sensors seek the mass of explosive material within a device. These are particularly useful when the device is well sealed and its surface is well cleaned of stray explosive molecules, or when the explosive being used is nonaromatic, that is, it does not readily release molecules from its bulk. We will refer to these as *bulk sensors*. They include X-ray techniques, both transmission and backscatter; neutron activation in several techniques; γ-ray excitation, in either transmission or backscatter modes; and nuclear resonance techniques, either nuclear magnetic resonance (NMR) or nuclear quadrupole resonance (NQR). Bruschini [1] has described these thoroughly. They are also described by the staff of the Jet Propulsion Laboratory [2]. The following forms a very brief synopsis.

1.3.1.1 X-ray Techniques X-ray techniques are familiar because of their use in medical diagnosis. The basic concept is that material of different densities or chemical compositions absorb and scatter X-rays differently. When the X-rays pass through the materials and strike the film or detector, they form a gray-scale image. After proper calibration a bulk charge of explosive may be inferred from this image.

In many applications, such as seeking buried munitions, it is not possible to place the X-ray source and the detector on opposite sides of the objects being investigated. In this case techniques have been developed to form images from the X-rays that are scattered back toward the source, or *backscattered*.

1.3.1.2 Neutron or γ Sensors Neutron- or γ-based sensors are similar in concept to the X-ray sensors. They use different forms of excitation and different detectors, but the basic forms of transmission or backscatter follow the pattern described above. Both normally rely on extensive computation for signal processing called computed tomography, where the detector signals are combined to synthesize an image of the irradiated object.

1.3.1.3 Electromagnetic Techniques Sensors based on the related principles of NMR and NQR have been successfully developed. These are active techniques that excite the electromagnetic interactions between the atomic nuclei by means of an external magnetic field. In NMR the magnetic field is a dc, or fixed, field, whereas in NQR it is an oscillating, or ac, field. The detector is tuned to respond to resonant frequency of a molecule of interest, such as RDX [3]. Both portable and fixed systems have been demonstrated.

It may be possible that ground-penetrating radar (GPR) could be tuned to preferentially indicate masses of particular chemicals, but such work is not known to have been reported.

1.3.1.4 Bulk Sensor Targets All the bulk sensor technologies have a common thread. They seek to find a mass of material with certain physical properties and to distinguish its shape when other materials obscure it. The object may be buried in the ground or contained within a vehicle, a structure, or container such as a crate or luggage. Potential targets are mines, unexploded ordnance (UXO), improvised explosive devices (IEDs), or drug caches. We are perhaps most familiar with the medical search for tumors or foreign objects within a body using computer-aided tomography, or CAT scan, and magnetic resonance imaging (MRI).

1.3.2 Trace Sensors

Bulk sensors certainly have a role in chemical sensing of explosives, but the subject of this book is the other basic type sensor, one that seeks molecules released from the bulk of the explosive material in an object. We will refer to these as *trace chemical sensors*. They are sometimes called *vapor sensors*, but that seems a less accurate description when they are applied to explosive molecules, which may not always be found in a vapor state. As we shall see in Chapter 5, that requires us to understand where and how to look for these molecules. It will become apparent upon a little reflection that the two types of sensors are complementary and are best used in different situations. Furthermore, even when trace sensors are used, in some situations sampling of particles of soil or vegetation or sampling from surfaces may prove to be more productive that vapor sampling. For underwater sources the term *vapor sensing* is also inappropriate.

In fact, with the very recent addition of differential reflection spectroscopy (DRS) to the suite of applicable technologies, as described in Chapter 15, we now have the possibility of sensing trace quantities of explosives where they are most often found in the environment, adsorbed to solid surfaces. Technologies that can, like DRS, locate these traces in situ offer a very different way to approach the problem. There have been several recent attempts to do this in situ detection from some distance away. To date the DRS seems the most successful. It has demonstrated detection at a range of a few meters.

The marked advantage of an in situ detection system is that it does not ingest the molecules; hence it does not disturb the area, does not require as close approach to an explosive device, and it should produce a faster response time than ingesting systems. The disadvantage of in situ systems is also that they do not ingest the molecules; hence they have no means of concentrating the sample for sensing. Thus they must have greater direct sensitivities in order to produce comparable results.

This book was in press before the first publication of the DRS results. Therefore, the following chapters were written with the expectation that most sensor systems would require ingesting samples. This condition is expected to continue, since in situ sensors will most likely supplement, not replace, ingesting sensors. Nevertheless, the discussion applies to the in situ systems by recognizing the high proportion of molecules that are normally adsorbed to surfaces, such as dust, plants, manmade objects, and the like. These form the target for the in situ systems. Trying to apply in situ systems like DRS to vapors and plumes is unlikely to lead to success; but, when vapors and plumes strike solid objects, there is a marked tendency for the entrained molecules to adsorb to the surface, producing opportunity for the in situ sensor.

1.4 AROMAS

The ability to recognize, locate, or distinguish among specific materials by their characteristic aromas can be useful in a variety of applications. Our first warning of a fire is frequently the smell of smoke. Wine and tea tasters regularly use their sense of smell to assist in quality control of these food items. Similarly, when we buy fruits such as peaches, we often sniff them to judge quality. We become aware of poor water quality before tasting the water because it “smells bad.” It is well known by medical personnel that certain diseases and conditions can be diagnosed quickly from the patient’s aroma. Farmers sometimes judge when to harvest from the aroma of the produce.

We often see television news reports of trained dogs searching for contraband illegal drugs. Trained soldiers can recognize some chemical agent attacks from the first whiff of the agent, hopefully in time to protect themselves. Dogs and other animals are being effectively used in searching for hidden explosives in a variety of situations, including humanitarian demining and antiterrorist patrols.

In each of these situations, sensing the aroma, which, for the purposes of this book, we will consider to consist of a specific molecule or suite of molecules that is uniquely produced by its source, provides the means of identification and/or location of the source. In each of these examples the user would gain significant advantage if a very sensitive and specifically “tuned” electronic sensor, which could accurately and reliably identify the characteristic aroma for that application, were available.

1.4.1 Biosensors

The historical use of the biologically based sensors mentioned above might lead us to the conclusion that finding hidden sources of explosives simply means training some kind of animal. Indeed, that conclusion has merit, and a great deal of success has been recorded in that way. This is discussed somewhat more fully in Chapter 8. There are, of course, disadvantages to this technique. The possibilities of biosensors have certainly not been exhausted in the search for explosives or other trace chemicals.

As an aside, designed to pique a hope of even broader application for technologies developed primarily to search for explosives, consider a recent finding by researchers at Amersham Hospital in the United Kingdom. [4] They report success in using dogs to detect cancers. For centuries people, particularly nurses, have been aware that certain conditions, for example, gangrene, could be detected and diagnosed by smell. This latest finding offers hope that research will make us able to apply electronic vapor sensing to medical diagnosis as well as our immediate objective of finding hidden explosives.

There have been efforts directed toward using bacteria in the search for explosives[1] [5]. Whether this approach offers a potential for developing practical sensing systems based on bacteria is an open question.

1.4.1.1 Mammals

Perhaps because we have a long history of domesticating mammals for various tasks, the preponderance of explosive search to date has been by mammals, mostly dogs [6, pp. 165–174], though some work has been done using rats [6, pp. 175–193] and pigs [7]. There have been two principal approaches used, which may be characterized as direct and indirect search. These techniques are discussed in detail in McLean [6].

Direct Mammalian Search In the direct search technique the animal, usually a dog, is brought to the suspected location of the hidden explosive. The animal is trained to go to the strongest scent of the aromas presented during training. The animal is trained to adopt a particular behavior when nearest the source. With dogs, this is usually to sit near the source. This technique has the advantage of immediate results; hence it is the method most often adopted by military personnel or police forces when the threat is immediate. This direct approach has several distinct disadvantages as well. When animals such as dogs are used in a field environment, they become subject to the hazards of that environment. Approaching an explosive device puts both animal and handler in the danger zone. Of course, in such a zone there are often related dangers. Also, because of the danger, the animal is restrained, usually by training, from actual contact with the source. Hence there is always an area of uncertainty surrounding the actual location of the source, particularly a buried one.

Animals find a multitude of interesting distractions in a field environment. Since they operate in a world of aromas undetectable to us, it is hard to realize how many distractions there may be. Certainly food aromas and sexual stimulation aromas are present. Animals are subject to physical ailments, just as we are. A dog with the equivalent of a “head cold” is not as effective in search. Providing proper care for the animal in such locations often becomes difficult and expensive. Training is also time consuming and expensive. In spite of all

---

[1] http://www.ornl.gov/info/ornlreview/meas_tech/threat.htm and http://eerc.ra.utk.edu/insites/ins54.htm#critters. Both sites visited 9/28/05.

these difficulties, the use of dogs in direct search for hidden explosives remains one of the most effective, arguably the most effective, method for finding hidden explosives.

The limit of detection[2] (LOD) for explosive searching dogs has been a subject for active debate for years. Chapter 8 includes some discussion on this matter. One report [8] attempts, with partial success, to quantify this LOD.

Indirect Mammalian Search In the indirect method, called in general terms the REST concept, for remote explosive scent tracking [6, pp. 53–107, 9], samples of chemicals in air are trapped in special filter cartridges by passing large volumes of air from the search area through them. In principle, the concept could be extended to water also. The filter cartridges are then taken to a laboratory, or other protected area, where they are offered to trained mammals, sometimes dogs and sometimes rats, for sniffing. When the animal detects the aroma for which it has been trained, it gives the proper response. The sample is correlated with its collection location so that more detailed sampling or direct search can be initiated. This technique was first developed in the late 1980s in South Africa, largely through the work of Dr. Vernon Joynt and colleagues at Mechem Consultants, a division of Denel (Pty) Ltd. They called it MEDDS (Mechem Explosives and Drug Detection System). The technique has been called EVD (Explosives Vapour Detection) by Norwegian People’s Aid (NPA) and Checkmate elsewhere. The term REST is now applied generically.

REST was conceived for solving the most pressing question in Humanitarian Demining, or in any postconflict ordnance cleanup operation: “Where are there no explosives?” The most immediate need is always to identify those areas that are free of explosives, so that they can quickly be returned to normal activity, such as agriculture and transportation. Then the detailed search and removal efforts can be concentrated on the areas that actually contain explosives. REST has been used with success in several postconflict areas, especially in Africa.

A typical REST application mounts an apparatus on a vehicle that can move safely through the suspect area. The apparatus has a vacuum pump that pulls air through the removable filter cartridge. A material for which explosive materials have an affinity is chosen for the filter. That is a material on whose surface the explosive molecules tend to tightly adhere. Most often, that tendency is a function of temperature, so the molecules adhere more tenaciously at lower temperatures and release as the temperature is increased. This characteristic is one often exploited in electronic sensing systems as well. When a certain region, say a predetermined length of a particular road, has been sampled, the filter cartridge is removed and stored. A new filter cartridge is inserted and the next area sampled. Filter cartridges are then offered to the trained mammal in a controlled environment. This technique is essentially similar to the one used with the

---

[2] We can conveniently refer to the smallest quantity of any given compound that an animal or a technology can detect as its LOD.

cancer seeking dogs [4]. Large areas can be surveyed quickly, safely, and inexpensively. REST has also been effective in searching for contraband at border crossings.

REST need not necessarily involve any animals at all. If electronic sensors of adequate sensitivity are developed, they can replace the animals. Certainly, the history of electronic instrument development shows that the earlier generations of any device are more suited for laboratory than field use, and that laboratory units can normally be expected to show better performance than portable ones. Calibration of an electronic instrument, which corresponds to training of a mammal, should become more precise and dependable than that training.

1.4.1.2 Insects

It has long been recognized that many insects may have a more acute sense of smell than any mammal. A consensus found in articles by many researchers seems to indicate that only a few molecules are required for odor detection by some insects. We have little experience in domesticating insects. Usually, we simply gather the ones we deem useful, mostly bees and silkworms (the larvae of an insect, the *Bombycid* moth, *Bombyx mori*), to a convenient location and let them do their normal activity. We then take their produce when it is available. Even within this limited process we can find ways to use them for chemical search. Researchers have found that bees can be trained to seek out sources of explosive molecules by the simple expedient of feeding them sugar-water laced with the target molecules [10]. Training bees is thus much simpler and quicker than training mammals.

Bees have an obvious advantage when entering a minefield or similar danger area. They are too small to actuate any sort of mine, so they are completely safe. Thus, they have one of the most desirable characteristics for sensing systems. They do not put the searchers at risk. With an appropriate method for tracking the bees and geographically fixing the points where a concentration of foraging bees indicates a source of explosive molecules, a minefield can be mapped for efficient search and removal. Such techniques have been offered [10]. After discovering that bees tend to forage along a particular vector from the hive, the researchers found it possible to “aim” the bees in a general direction and track them with a LIDAR[3] system developed at Sandia National Laboratories [11].

Recently, wasps, *Microplitis croceipes*, have been conditioned to detect explosives [12]. Training is similar to that of the bees, but instead of allowing the wasps to range freely, a handheld, air-ingesting sensor has been developed with the wasps as the sensing element, with a video system for monitoring behavioral indications of detection [13]. The device, called Wasp Hound, was developed originally for other purposes, primarily agricultural, but has been successfully demonstrated in detecting 2,4 DNT. No detailed information on filed LOD for explosive compounds is yet available, but comparison with one commercial electronic sensor, Cyranose 320, [14] seems to indicate somewhat better LODs for some chemicals. Thus, Wasp Hound can be classified as a hybrid sensor, part biological and part electronic.

---

[3] LIDAR: light detection and ranging.

1.4.2 Electronic Sensors

The term *electronic* is used here in the most generic sense. Since the objective is to find and identify small quantities of explosive molecules by extracting them from their environment, the problem is analogous to many solved with electronic devices. Common examples include radio and television receivers and electronic instruments for measuring physical quantities such as weight, acceleration, or temperature. The principal difference here lies in the sensing modules that form part of the systems we will consider. Of course, it is conceivable that a system can be developed that uses no electronics, perhaps using color changes, or something else, but the systems discussed herein all use some electronic modules to enable the observer to know when explosive molecules have been located.

Whatever system may be developed, the basic objective is the same. Different technologies may be employed, but the reason for the system is always to locate and identify explosive molecules in air, water or soil, or on a surface, in order to pinpoint the source of these molecules. Ideally, the source is located before it can be actuated in a harmful way. Consequently, every system developed for this purpose will have some characteristics in common with any other developed for the same purpose. Therefore, it is valuable to consider those common elements in a general way.

We are faced with locating molecules that are sparse within the environment, hence the term *trace*. There are several basic steps that are necessary, independent of the design of the specific system or the technology being incorporated. Table 1.1 lists those steps and correlates them with more common electronic instrumentation nomenclature. Some of the *actions* will involve

TABLE 1.1 Common Processes in Locating and Identifying Explosive Molecules within the Environment

Step	Action	Electrical Analog
Sample	Introduce a quantity of explosive-bearing medium into the system	Receiver or transducer
Separate	Pass the sample through some process that preferentially selects the explosive molecules	Tuner
Concentrate	Collect the separated molecules while additional sampling and separation continues	Filter/amplifier
Identify and quantify	Apply some signal processing procedure or algorithm to infer the in situ concentration of explosive molecules in the samples	Signal processor
Present	Organize the results in a form that can be interpreted by an operator or that can be used to guide further activities in autonomous devices	Display

physical processes, such as pumping air or water past a collector. Some may use chemical processes, such as tagging the explosive molecules with other molecules that can be sensed more easily or sensitively. Some will use electronic processing; some may use radiation, such as ultraviolet light. The variety of possibilities has not yet been fully explored.

Several types of systems have been, or are being, developed. The following descriptions are presented as a brief summary. Detailed descriptions will be found in the chapters devoted to each technology.

1.4.2.1 Spectrometry

"Spectroscopy[4] is basically an experimental subject and is concerned with the adsorption, emission or scattering of electromagnetic radiation by atoms or molecules" [15, p. 1]. A wide variety of applications of this concept have been applied in analyzing many substances. In the particular case of explosive molecules the most prominent are several forms of mass spectrometry and ion mobility spectrometry. Each has certain advantages and disadvantages. Each is discussed in detail in a later chapter. The former is most often used in fixed applications; the latter, in both fixed and portable applications.

1.4.2.2 Surface Effect Sensors

Surface effect sensors have been offered in several forms. In each design they rely on using a substrate, often a microstructure, coated with a material having an affinity for adsorbing specific molecules. When the molecules adhere to it, they alter some property of the substrate. Depending on the particular concept the property exploited may be physical or electrical. Some designs measure altered resistance; some, altered capacitance. Some designs measure alterations in physical effects, such as the frequency of vibration of a microcantilever or the frequency or amplitude of an induced surface acoustic wave (SAW) [16].

Sensors of this type tend to be very good at identifying a broad range of chemicals, particularly complex aromas that contain suites of compounds. They have been used to sort fruits for ripeness and can distinguish among fruits. These sensors use an array of sensing elements, each coated with a different material, to adsorb different molecules. They then form signature patterns for different aromas in a calibration process not completely unlike a dog's training. Signal processing algorithms then match patterns of sampled aromas to known patterns for identification.

Acoustic wave devices have been used, primarily as electronic bandpass filters, for more than 60 years, but the first reported use as a chemical sensor appeared in 1979 [16, p7].

A form of surface effect sensor that exploits altered surface resistance, or chemiresistors, forms the surface from a mixture of tailored polymers and a finely divided conductive material, such as carbon black, as a thin film on a substrate. They use a number of polymers, 32 in one implementation, with different properties to form an array of chemiresistors. When a vapor is passed over the array,

---

[4] Spectroscopy uses photographic means to record the spectrum; spectrometry uses photoelectric recording [15, p. 67].

the film swells. Each film swells differently. The pattern of altered resistances forms a signature for that vapor. Sophisticated signal processing matches these signatures to known aromas, much as fingerprints are matched. Chemiresistors have been successfully employed to detect undesirable odors in food packaging materials and to distinguish among five varieties of diesel fuel [17].

When the design focus becomes this kind of specificity among aromas, the sensitivity for simple compounds such as explosives may be reduced. A design focused directly on explosive molecules will likely prove more adaptable to the search for hidden explosives. Chapter 12 describes one of these sensors in detail. To date none of these sensors has produced an LOD adequate for field search for explosives.

1.4.2.3 Amplifying Fluorescence Polymers (AFPs) The development of materials that fluoresce intensely in the presence of ultraviolet light when no nitroaromatic explosive compounds are present, but are prevented from fluorescing when those compounds are introduced, has led to the development of a new class of sensors. Upon encountering a nitroaromatic molecule, the tailored fluorescing polymer binds with it. The bound pair no longer fluoresces when struck by a photon. This behavior is exhibited by a class of polymer compounds called chemophores, each having an affinity for a particular class of analytes.

The characteristic that distinguishes AFPs from other chemophores is their forming of long chains with as many binding sites as molecules forming the chain. A single explosive molecule, binding at any one of these sites, is sufficient to induce quenching of the fluorescence along the entire chain; thus, the appellation of “amplifying.” The intensity of the quenching produced by the binding of one explosive molecule is thus multiplied many times. Very low concentrations of explosive molecules are thus detectable. Chapter 9 describes the way AFPs have been incorporated into a family of fielded sensing systems. Chapter 6 examines the experience gained in using one of this family in an unmanned underwater vehicle (UUV) called *SeaDog*. Chapter 7 describes field experience with AFPs in air, as implemented in the Fido® sensor.

1.4.3 Other Indirect Methods (Switch of Molecules)

Methods similar to AFPs in that they introduce other molecules have been suggested. The concept is that molecules that are easier to detect than explosive molecules, but only when the target molecules are present, can be introduced to increase the sensitivity of the detector system. With the introduction of AFPs that concept is clearly proven. Other adaptations are to be expected in the future.

1.4.4 Target Possibilities

When we consider possible targets in the context of system design we may group them into three broad classes, all of which may be considered as unexploded ordnance, UXO. Classes 1 and 2, and sometimes all three, are termed explosive remnants of war, ERW by the United Nations, UN.

TABLE 1.2 Possibility Space for System Indication of Detected Explosive

System Indication	Actual Condition	
	Explosive Present	No Explosive Present
Explosive	True Positive	False Positive
No Explosive	False Negative	True Negative

Class 1 includes any munition, whether standard or IED, that is deployed with the intent of causing damage to an opponent during a belligerency of any nature. These form two subclasses, those that are "fresh" and those that are abandoned. Clearly, those fresh ones constitute the most urgent targets. Those that are abandoned may be functional, as with mines, or malfunctioning units. These "duds" may still constitute an immediate danger, depending on the reason for their malfunction.

Class 2 includes those munitions that have become lost or discarded during military operations or transport. Major quantities of ordnance are lost when ships are sunk or blow up. When munition storage areas are attacked, some munitions are ejected to substantial distances. These munitions may be fully assembled and functional, as when an aircraft ejects them. Others may be incomplete, likely unfuzed.

Class 3 includes those ordnance items that are intentionally buried, dumped at sea, or otherwise disposed of either in an intact or in a partially assembled condition. It also includes military or civilian storage and military practice ranges.

Each class has distinct characteristics that should be considered in optimizing a system design. The level of urgency varies greatly. The consequences of false negatives also vary greatly. The mention of false negatives begs a bit of explanation. During a search for hidden explosives the sensing system continually operates within a two-by-two space of possibilities, as diagrammed in Table 1.2. When the system provides the correct indication, whether positive or negative, it is functioning properly. However, there are two different error conditions that can be realized. These are indicated by the shaded blocks. A false negative means a missed target. Obviously, that can lead to immediate danger for the operator or others. A false positive induces a different kind of danger, deferred danger, due to loss of operator confidence in the system.

1.4.5 Sensitivity and the Problem of False Positives

One of the primary characteristics of any sensor is its sensitivity. In principle, increased sensitivity should lead to increased performance, that is, a greater likelihood of finding the object being sought. However, increasing the sensitivity in a cluttered environment often leads instead to an increase in "false positive." A false positive occurs when the sensor system correctly detects an item of the class it is designed to detect, but an item that is not the item being sought. For example, when a metal detector is used to search for buried landmines, it also detects odd bits of metallic debris in addition to the mines. This can greatly impede the search for the mines. It produces deferred danger when the operator, having encountered several false positives, becomes skeptical of a true positive. One solution is to reduce the sensitivity of the sensor. Such a reduction in sensitivity may also reduce the probability of detecting the mines. Therefore, in any search the probability of detection, P_{D}, must be balanced against the probability of false positive, P_{FA}. This is discussed in a little more depth in Chapter 11. For some sensors seeking explosive molecules, an increase in sensitivity can lead to the detection of molecules other than explosives. These can be interpreted as false positives.

Clearly, if there is unburned explosive material present in an area of interest, then the trace chemical sensor will register a false positive. Similarly, some bulk chemical sensors may provide false positives when they encounter a mass of nitrogen-rich material, such as fertilizer or feces. In either case the rate of false positives is still likely to be less that the false-positive rate of a metal detector.

Adjusting the sensor sensitivity is usually only partially successful. There is another way to overcome the problem of false positives. A suite of sensors that are "orthogonal in principle" can be used together.

1.4.5.1 Orthogonality In geometry lines or planes are called orthogonal when they meet at a right angle. Values or conditions on one are therefore independent of those on the other. We consider two sensors to be orthogonal when they depend on different principles of chemistry or physics. In that sense, a chemical sensor is clearly orthogonal to a metal detector. When searching for hidden, explosive-bearing objects, false positives can be dangerous, as finding too many can cause an operator to lose concentration. Therefore, when one needs to identify an object detected by any sensor, that means that indications from two or more sensors, each of which exploits a different physical or chemical property of the target, need to be compared before identification can be considered definitive. For example, a set of three sensors that are orthogonal in this sense is illustrated in Figure 1.1.

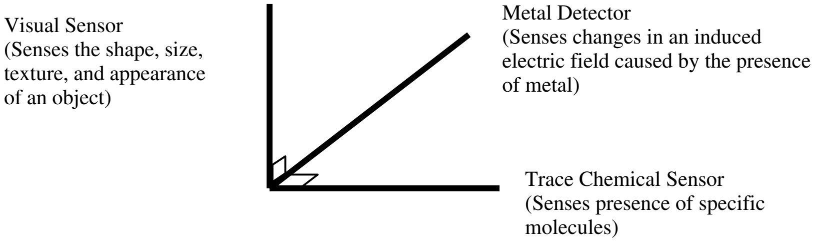

Figure 1.1 Orthogonal sensor suite.

It is normally advisable to adhere to the principal of orthogonality in some way. In the above example the three sensors could be independently applied, not necessarily part of a single package or system, especially if the object in question is where it can be seen directly.

1.5 CONFIGURING AN ELECTRONIC TRACE SENSOR

Before anyone begins development of a sensor system, the first task is to determine what is being sought. That is not necessarily the procedure when developing a sensing technology. Thus, it is common for a technology to find its most effective application in systems that were not originally envisioned. Perhaps the most apparent need that led to the development of some of the trace chemical sensing technologies was the need for a method of warning troops, or populations, when they were being attacked with chemical weapons. While this still forms a major application of these technologies we will consider one that was not as apparent originally.

The original need that led to development of trace chemical sensors for explosives was the need to restore land that had been abandoned to public or private use. This land was abandoned because of the presence of, or perception of the presence of, mines or unexploded ordnance, often called UXO. These potentially lethal items could be the result of some earlier armed conflict. In that case it is now common to refer to them as explosive remnants of war, or ERW. In some cases the war that left its remnants was concluded many years ago. Dangerous ERW are still found on World War I battlefields, and occasionally on U.S. Civil War battlefields, though the latter munitions are usually deteriorated beyond holding any dangerous explosive residue. UXO are also found on former military training facilities, such as Ft. Ord, California, or Kahoolawe, Hawaii. Both these sites have undergone restoration in recent years.

Since September 11, 2001, the realization that explosive devices might be deposited almost anywhere by terrorists or other malefactors has added a new group of devices to the list of targets. These are improvised explosive devices, or IEDs. An IED may take any form, subject only to the imagination of its fabricator. Many contain traditional munitions but are constructed to permit delivery and/or actuation in nonstandard, or improvised, ways. Examples are “dud” artillery shells or aviation bombs that have been salvaged and equipped with a fuze for use as a mine or booby trap. Car bombs are also common examples of IEDs. When IEDs are constructed using salvaged munitions, they will naturally include conventional explosives; hence they may be appropriate targets for trace chemical sensors. However, IEDs are not always made in this way. Chapter 3 discusses a variety of nontraditional explosives that are being discovered in IEDs.

In this book we will focus our attention on applications that require portable sensors, sensors that must be transported to the vicinity of the target. These applications include mine and UXO removal and the search for and identification of IEDs. Chapter 11 forms a notable exception to this focus, where fixed screening of airport portals is the principal application to date. Fixed sensing stations are considered more fully by Oxley [18]. Our focus is due to the very different conditions in the two applications. We will devote a chapter, Chapter 4, to the peculiar subject of the environment fate and transport, or EF&T, of that elusive quarry, the free explosive molecule. These free molecules are the trace chemicals that we are trying to sense. We will explore how they become free, the environmental factors that affect their mobility, and where we may expect to find them in sufficient concentration to be detectable.

1.5.1 Required Elements

There are some common elements that any trace chemical sensing system must have. Each system will have a defined purpose and be subject to specific size, weight, power, mobility, performance, and cost constraints. These, along with the imagination of the system designer, will steer the designs of different systems in individual ways, but the basic elements will remain, though their forms may be very different among a group of systems. The terminology used here is that commonly used in electronic instrumentation, but in some cases the element may have no electronic components. The elements are described in sequential order. In each case, except as noted, the function of each follows that of the preceding one. Conceptually, one samples, then concentrates, then senses, and so forth. No inference about the movement of material from one stage to the next is implied. That movement is a unique property of the system design.

1.5.1.1 Sampling Unit Since we are seeking the free molecules that form a trace chemical “signal,” we must have a unit that collects them from their environment. For some systems that environment is air, for others water or soil. For some, it may be a surface, such as a parcel, a vehicle, a leaf, or a wall. It will be necessary for the system designer to devise a way to collect the molecules from that environment of interest. While most of the system elements are more or less independent of the search environment, the sampling unit is entirely dependent on it.

Sampling units may be as simple as a piece of chemically treated paper used to “swipe” a surface or one with multiple parts such as pumps, valves, scoops, and heating units. It may be physically integrated into the rest of the system or operated separately, as in the case of the swipe paper.

The sampling unit will always be required to accept some of the environment along with the quarry molecules. Because these bits of the environment obscure the trace signal, it is necessary to sort through the sample in some way to collect as many as possible of the quarry molecules together while excluding as much as possible of the environment. This process is the function of the concentrating unit. In many practical systems the sampling unit and the concentrating unit may be so integrated as to be physically inseparable. Nevertheless, their functions remain conceptually distinct.

1.5.1.2 Concentrating Unit As described in the preceding paragraph, the concentrating unit sorts through the sample taken by the sampling unit to extract the molecules of interest. Sections 1.6.2 to 1.6.4 discuss some of the considerations that determine the design of a sampling unit and a concentrating unit.

Concentrator materials of choice are often polymers. Polydimethylsiloxane (PDMS), or a polydimethylsiloxane/divinylbenzene copolymer (PDMS/DVB) are favored choices for explosive molecules. PDMS are often used in the form of solid-phase microextraction (SPME) fibers. PDMS/DVB is often used in the form of microspheres with diameters in the 50- to 75-μm range. Detailed considerations for use of SPME fibers is given on a website maintained by the University of Western England [19]. It references a more complete treatise [20]. Other geometries, such as stacked spheres, have also been used successfully [21].

Some concentrating units use chemical solvents; some use mechanical methods, sometimes coating a surface with a material for which the quarry molecules have a distinct affinity. One of the most convenient characteristics of explosive molecules is the way temperature affects their adhesion to surfaces. They adhere readily to cool surfaces but are easily released by a modest rise in temperature. Concentrating units often exploit this characteristic by alternately chilling and warming a collection surface. The surface is chilled while sampling and warmed for sensing.

1.5.1.3 Sensing Unit The heart of the sensor system is the sensing unit. It is here that the wide variety of sensing technologies discussed in Chapters 8 through 14 are employed in different systems. As systems are designed and integrated, the various units may be merged physically, but the sensing unit is where the quarry molecules are identified as present or not in a concentrated sample. The success of the entire system is determined by the performance of the sensing unit, but does not function without the other units.

We often associate the overall performance of the system with the sensitivity of the sensing unit. Design of the other units can either enhance or degrade that overall performance by large factors. Nevertheless, the search for more sensitive sensing technologies is ongoing and needed. Along with sensitivity, the other dominant characteristic of a sensing technology is specificity. A technology that is very sensitive but lacks specificity leads to many false positives, or a high probability of false positive (sometimes called false alarms), P_{FA}; one that lacks sensitivity provides a lower probability of detection, P_{D}.

False positives cause the search to become diverted in an attempt to positively identify each one. They slow the search and can become dangerous if they obscure the real target or lull an operator into complacency. A low P_{D} becomes dangerous when a potential hazard, such as a mine, is left undetected. A design that maximizes the P_{D} while minimizing P_{FA} is the goal for sensing technologies.

1.5.1.4 Amplifier Some systems may use an amplifier. This unit may use a process of chemical replacement or reaction to produce secondary molecules from the few quarry molecules collected. These molecules may be more numerous, easier to detect, or exhibit a characteristic that permits a different principle of detection to be employed. This kind of amplifier may precede the sensing unit. Another kind of amplifier may be used, one that simply increases the intensity of the sensing unit output when a quarry molecule is detected. This type amplifier will follow the sensing unit.

1.5.1.5 Signal Processor Electronic instruments normally employ signal processing of some form. Sometimes the calculations are quite extensive and complex. Often the object is to extract a signal from its background. In our case, that is also the function of the concentrating unit. However, it may be possible to further improve the system performance by some form of signal processing at this stage. This process is sometimes termed chemometrics.

1.5.1.6 Output and/or Display Unit Finally, the results of the process to this point must be formatted in a manner appropriate to the purpose of the system, so that some action can be taken. If the system has a human operator the display may be presented in any number of visual and/or audible forms. The operator, upon recognizing the message of the display, decides on his next course of action. If the system is a part of an unmanned or robotic vehicle, the output may be in the form of a digital value or a flag, depending on whether the decision algorithms are contained within the vehicle or are part of the signal processing of the sensor system.

1.5.2 Integration and Packaging

There are always practical considerations when designing a system. Some of these relate to optimizing its performance, and some derive from its anticipated field service environment. In many instruments increased sensitivity to the target often corresponds to increased sensitivity to environmental effects such as temperature, humidity, electromagnetic interference, shock, and vibration. It sometimes requires heroic measures to mitigate these effects. Systems can become large or clumsy. The systems we are principally considering, portable, field-operable trace chemical sensing systems, have some common constraints.

Portable systems must operate on a portable power source. Often this simply means batteries. When heating becomes a part of the operating sequence, batteries can be consumed quickly. A well-defined energy budget is necessary early in the design process.

Portable systems are often introduced into small spaces in search of the quarry. They also tend to be handled rather roughly by their operators. Current trends in microminiaturization offer relief to the system designer in both these areas.

1.6 ISSUE OF CONCENTRATION

1.6.1 Nomenclature

In this book we will often consider very small quantities of materials. In an effort to ensure understanding, Table 1.3 presents the notation used for mass.

TABLE 1.3 Mass Nomenclature

Abbreviation	Name	Scientific Notation	Decimal Notation
g	gram	10^0 g	1 g
mg	milligram	10^{-3} g	0.001 g
μg	microgram	10^{-6} g	0.000001 g
ng	nanogram	10^{-9} g	0.000000001 g
pg	picogram	10^{-12} g	0.000000000001 g
fg	femtogram	10^{-15} g	0.000000000000001 g
ag	attogram	10^{-18} g	0.000000000000000001 g

1.6.1.1 Concentration Most often these mass terms will be used to describe concentration of the chemical of interest in some medium, usually air, water, or soil. When we talk of concentration, we have in mind some sort of normalization, so instead of describing an absolute quantity we describe the quantity of the chemical of interest contained in a fixed quantity of the containing medium. When that medium is air or water, we most frequently use a specified volume; when it is soil, we use a specified mass. Thus we will use terms like *ng/L* (nanograms of chemical per liter of air or water) in air or water and *ng/g* (nanograms of chemical per gram of soil) in soil, since soil varies in density, depending on weather and compaction.

It is quite common practice to express concentrations as a ratio, using the "parts per" method of describing the ratio. Thus, in soil the ratio is simple, 1 *ng/g*, or (10^{-9} g/g), is a *ppb*, or one part per billion[5]. In water or air, the issue is a bit more complex since it is necessary to reconcile the units of mass per unit volume to units of mass per unit mass. We make this reconciliation by dividing by the density of the fluid. For water this is, for purposes of this book, taken as 10^{-3} *grams per liter*. Table 1.4 illustrates this reconciliation.

It may be worthwhile to illustrate the actual meaning of these concentrations: 1 ppb concentration in soil means that there is one gram of chemical contained within one billion grams (1000 tonnes) of soil. The implication is that the chemical is distributed more or less homogeneously within the medium. In that case, how much soil is one billion grams? Using a nominal value of 1.4 for the specific gravity of soil, we find that this comprises about 650 m^3 of soil, which would fill about a 100 large dump trucks.

Similarly, 1 ppb in water implies that a gram of chemical is dissolved in the quantity of water contained in an Olympic-size pool, 50 m long by 10 m wide by 2 m deep. One *ppt* means the gram of chemical is dissolved in 1000 of these pools.

Since the parts per nomenclature for air would be expected to be a volume/volume ratio, in order to reconcile these we must account for the molecular

---

[5] Note the use of common U.S. practice, defining billion as 10^9; other terms follow the same pattern.

TABLE 1.4 Reconciling Concentration Nomenclature in Soil and Water

Parts per... Nomenclature			In Soil	In Water	
Parts per ...	1 part in:	Abbreviation	Mass/Mass	Mass/Volume	Mass/Mass
million	10^6	1 ppm =	1 μg/g	1 mg/L	1 μg/g
billion	10^9	1 ppb =	1 ng/g	1 μg/L	1 ng/g
trillion	10^{12}	1 ppt =	1 pg/g	1 ng/L	1 pg/g
quadrillion	10^{15}	1 ppq =	1 fg/g	1 pg/L	1 fg/g

TABLE 1.5 Molecular Weights and Vapor Molar Densities for Some Common Explosives and Associated Compounds

Compound	Molecular Weight	Mass of Single Molecule (g), m_0	Molar Density (Vapor) (g/L)
DNB	168 [22, pp. 3–43]	2.8×10^{-22}	6.87
DNT	182 [23, p. 1180]	3.0×10^{-22}	7.44
TNB	213 [22, p. 3–66]	3.6×10^{-22}	8.71
TNT	227 [24, p. 125]	3.8×10^{-22}	9.28
RDX	222 [24, p. 125]	3.7×10^{-22}	9.08
PETN	316 [24, p. 125]	5.3×10^{-22}	12.92
Tetryl	287 [24, p. 125]	4.8×10^{-22}	11.74

weight of the explosive molecule. Thus we divide the mass per mole[6] for the molecule of interest by the molar volume. The result may logically be termed the molar density. First, however, since, as we shall see in Chapter 4, the search for explosive molecules at 0°C is normally futile, we will adjust the molar volume to a temperature more often encountered, 25°C. The molar volume at 25°C and 76 cm Hg is 24.45 liters:

$$\begin{aligned}\text{Molar density} &= \frac{\text{mass}}{\text{volume}}\text{ratio} \\ &= \frac{\text{molecular weight}}{\text{molar volume}} \\ &= \frac{\text{molecular weight (g)}}{24.45\ \text{L}}\end{aligned} \tag{1.1}$$

Table 1.5 lists the molecular weights and the calculated molar densities for some of the most common molecules of interest.

---

[6] A mole contains 6×10^{23} molecules. It has mass in grams numerically equal to the molecular weight. The molar volume is the volume occupied by a mole of any gas, measured at standard temperature and pressure (0°C, 101.325 kPa = 76 cm Hg). It has a value of 22.414 L [22, pp. 1–19, 1–5, 1–14, 1–16].

TABLE 1.6 Correlation of Concentration Nomenclatures

Mass/Volume	TNT in Air	TNB in Air	DNT in Air	DNB in Air
1 mg/L	108 ppm	115 ppm	135 ppm	146 ppm
1 μg/L	108 ppb	115 ppb	135 ppb	146 ppb
1 ng/L	108 ppt	115 ppt	135 ppt	146 ppt
1 pg/L	108 ppq	115 ppq	135 ppq	146 ppq

TABLE 1.7 Reconciling Concentration Nomenclatures[a]

Parts per ...	TNT in Air	TNB in Air	DNT in Air	DNB in Air
1 ppm =	9.3 μg/L	8.7 μg/L	7.4 μg/L	6.9 μg/L
1 ppb =	9.3 ng/L	8.7 ng/L	7.4 ng/L	6.9 ng/L
1 ppt =	9.3 pg/L	8.7 pg/L	7.4 pg/L	6.9 pg/L
1 ppq =	9.3 fg/L	8.7 fg/L	7.4 fg/L	6.9 fg/L

[a] Since *parts per* must remain dimensionless, this table actually contains “volume/volume ratios” even though the concentrations are stated in mass/volume units. The correction is made using Eq. (1.2).

With the molar densities we can calculate the volume/volume ratios in air. Equation (1.2) [25, p. 10] yields the data tabulated in Table 1.6:

$$\text{ppt} = \frac{1000c_A}{\text{molar density} } \tag{1.2}$$

where c_A is the concentration in ng/L.

It is often convenient to make the correlations “in the other direction.” This is shown in Table 1.7, where the data are essentially the reciprocals of the correlations shown in Table 1.6, but can be calculated directly from Table 1.5 values.

1.6.1.2 Minimum Possible Concentrations Obviously, the absolute minimum possible concentration of any chemical within any medium occurs when there is only one molecule of the subject chemical in the sample. Knowledge of this concentration will provide a recognizable lower limit to possible sensing. We can find that concentration [25, p. 11] as follows:

If one gram of soil contains a single molecule of the subject chemical of molecular mass m_0 (Table 1.5), then the mass/mass concentration is numerically equal to m_0. For example, using TNT (trinitrotoluene) at molecular weight (MW) of 227,

$$m_0 = \frac{227 \text{ grams per mole} }{6 \times 10^{23}\text{molecules per mole} } = 3.78 \times 10^{-22}\text{g} \tag{1.3}$$

yields the mass/mass concentration for one TNT molecule in one gram of soil as $c_0 = 3.8 \times 10^{-22}$g/g.

We can express this in terms from Table 1.3 in several ways:

$$\begin{aligned} c_0 &= 3.8 \times 10^{-22}\text{g/g} = 3.8 \times 10^{-10} \times 10^{-12}\text{g/g} \\ &= 3.8 \times 10^{-10}\text{pg/g} \\ &= 3.8 \times 10^{-13}\text{ng/g} \\ &= 3.8 \times 10^{-7}\text{fg/g} \end{aligned} \tag{1.4}$$

By reference to Table 1.4 we can also use the parts per nomenclature, recognizing that 1 ng/g is 1 ppb, and so forth:

$$\begin{aligned} c_0 &= 3.8 \times 10^{-22}\text{g/g} = 3.8 \times 10^{-16}\text{ppm} \\ &= 3.8 \times 10^{-13}\text{ppb} \\ &= 3.8 \times 10^{-10}\text{ppt} \\ &= 3.8 \times 10^{-7}\text{ppq} \end{aligned} \tag{1.5}$$

We find similar results in water if we consider one milliliter of water to contain one molecule. Since the 1 mL of water has a mass of 1 g, the mass/mass concentration is again $c_0 = 3.8 \times 10^{-22}$ g/g, numerically the same as the mass/volume concentration, 3.8×10^{-22} g/mL. However, expressing this concentration in the units previously used, g/L, yields

$$c_L = 3.8 \times 10^{-22}\text{g/mL} = 3.8 \times 10^{-19}\text{g/L} = 3.8 \times 10^{-7}\text{pg/L} \tag{1.6}$$

This concentration describes a concentration of one thousand molecules per liter.

Alternatively, considering the case of one molecule in a liter of water, the concentration is then $c_L = 3.8 \times 10^{-22}$g/L. As before, this can also be expressed in several ways:

$$\begin{aligned} c_L &= 3.8 \times 10^{-22}\text{g/L} = 3.8 \times 10^{-9} \times 10^{-13}\text{g/L} \\ &= 3.8 \times 10^{-13}\text{ng/L} \\ &= 3.8 \times 10^{-10}\text{pg/L} \\ &= 3.8 \times 10^{-7}\text{fg/L} \end{aligned} \tag{1.7}$$

Or, from Table 1.4, using the mass/mass concentration, for the 1000 g of water in a liter:

$$\begin{aligned} c_L &= 3.8 \times 10^{-22}\text{g/L} = 3.8 \times 10^{-25}\text{g/g} \\ &= 3.8 \times 10^{-13} \times 10^{-12}\text{g/g} \\ &= 3.8 \times 10^{-13}\text{pg/g} \\ &= 3.8 \times 10^{-13}\text{ppt} \end{aligned} \tag{1.8}$$

Therefore, on the basis of one molecule of the target compound present in a standard sample, a gram for soil, or a liter for water or air, we can calculate the minimum possible concentration for that compound in that size sample of soil water or air. Table 1.8 presents those results. This provides an objective lower bound for the LODs.

1.6.1.3 Flux Rates We use the term flux to describe the movement of material. Flux rate is then the quantity of material moved por unit time. In the literature we find rates quoted in different time units, sometimes seconds, sometimes minutes, or hours, or days. In particular, flux rates are sometimes presented in μg/cm^2-day and sometimes in fg/cm^2-sec. We can simplify this a bit by normalizing these to cm^2. Thus, Table 1.9 provides a correlation of the rates.

1.6.2 Source to Sample

There are a wide variety of possible sources of explosive molecules. No matter what that source is, or where it is located, a similar process may be recognized. First, the molecules must become free from the bulk of explosive at the source. Then they must travel through the local environment to a location where they are accessible to the sampling unit. This journey is full of pitfalls that stop many of the released molecules, so the initial small flux rates may be reduced even more. Chapter 4 discusses the process in considerable detail.

1.6.3 Catch, Count, and Release Cycle

A useful strategy adapted in many sensing systems is to use what we might term “minibatch” processing. By this we mean that the sampling unit takes in material for a short period of time, delivering this “batch” of material to the concentrating unit. The batch may be quite small in order to enable more or less continual motion of the system in search. The batch is delivered to the concentrator where the quarry molecules are collected. Then, through either thermal or chemical cycling, the concentrated molecules are stripped off the concentrator and sent to the sensing unit. While this process is proceeding, another batch may be being collected by the sampling unit. Properly timed, such a strategy can increase overall response rate substantially.

1.6.4 Sensor Sensitivity Versus Sampling Time

Concentration is a most important issue. Each of the sensing technologies discussed in this book, and any other conceivable sensing technology, has some limit of detection, below which it will not provide reliable results. But for most sensors this sensitivity threshold, the lowest concentration of a given molecule that can be reliability detected, is not a static value. The threshold is also a function of the sampling time, in the most general sense. Heuristically, we consider that a certain number of molecules need to be ingested by the sampling unit to

TABLE 1.8 Minimum Possible Concentration, Represented by One Molecule of Explosive

Medium	Units	Concentration per Quantity of Medium						
		TNT	TNB	DNT	DNB	RDX	PETN	Tetryl
1 g soil	ng/g	3.8×10^{-13}	3.6×10^{-13}	3.0×10^{-13}	2.8×10^{-13}	3.7×10^{-13}	5.3×10^{-13}	4.8×10^{-13}
1 g soil	ppt	3.8×10^{-10}	3.6×10^{-10}	3.0×10^{-10}	2.9×10^{-10}	3.7×10^{-10}	5.3×10^{-10}	4.8×10^{-10}
1 L water	ng/L	3.8×10^{-13}	3.6×10^{-13}	3.0×10^{-13}	2.8×10^{-13}	3.7×10^{-13}	5.3×10^{-13}	4.8×10^{-13}
1 L water	ppt	3.8×10^{-13}	3.6×10^{-13}	3.0×10^{-13}	2.8×10^{-13}	3.7×10^{-13}	5.3×10^{-13}	4.8×10^{-13}
1 L air	ng/L	3.8×10^{-13}	3.6×10^{-13}	3.0×10^{-13}	2.8×10^{-13}	3.7×10^{-13}	5.3×10^{-13}	4.8×10^{-13}
1 L air[a]	ppt	4.1×10^{-11}	4.1×10^{-11}	4.0×10^{-11}	4.1×10^{-11}	4.1×10^{-11}	4.1×10^{-11}	4.1×10^{-11}

[a] Volume/volume, from Eq. (1.2).

TABLE 1.9 Correlation of Flux Rate Nomenclature (per cm^2)

fg/sec	pg/sec	ng/sec	μg/sec	fg/day	pg/day	ng/day	μg/day
1	10^{-3}	10^{-6}	10^{-9}	8.64×10^{4}	8.64×10^{1}	8.64×10^{-2}	8.64×10^{-5}
10^{3}	1	10^{-3}	10^{-6}	8.64×10^{7}	8.64×10^{4}	8.64×10^{1}	8.64×10^{-2}
10^{6}	10^{3}	1	10^{-3}	8.64×10^{10}	8.64×10^{7}	8.64×10^{4}	8.64×10^{1}
10^{9}	10^{6}	10^{3}	1	8.64×10^{13}	8.64×10^{10}	8.64×10^{7}	8.64×10^{4}
1.16×10^{-5}	1.16×10^{-8}	1.16×10^{-11}	1.16×10^{-14}	1	10^{-3}	10^{-6}	10^{-9}
1.16×10^{-2}	1.16×10^{-5}	1.16×10^{-8}	1.16×10^{-11}	10^{3}	1	10^{-3}	10^{-6}
1.16×10^{1}	1.16×10^{-2}	1.16×10^{-5}	1.16×10^{-8}	10^{6}	10^{3}	1	10^{-3}
1.16×10^{4}	1.16×10^{-1}	1.16×10^{-2}	1.16×10^{-5}	10^{9}	10^{6}	10^{3}	1

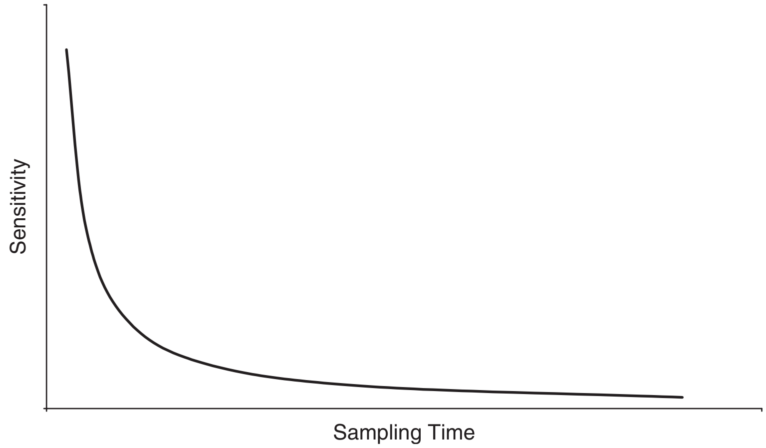

Figure 1.2 Conceptual relationship between sensitivity and sampling time for a fixed probability of detection and fixed sampling rate.

provide the sensing unit with enough product to form an acceptable probability of detection, P_D. A balance thus needs to be struck between the quantity sampled and the sensitivity of the sensing unit. For a given sampling rate and a given P_D, the relationship is visualized as in Figure 1.2.

In any real sensing operation the sensing system is either being moved to search different locations or different objects are being brought to the system for examination. In either case the system will operate in a sequential batch mode. That is, the system will cycle through the series of actions described in Table 1.1. It is necessary to process through the entire sequence of actions in order to extract a determination of each location or object. Sampling time is only one part of the sensing cycle. Detectors or sensing units must be purged of the molecules collected in the previous cycle before a new cycle can continue. Some systems may be configured with multiple, alternating, sensing units in order to reduce or eliminate the “dead time” in the sensing cycle.

Operational application and economics often determine trade-off choices between sensitivity and sampling time. Since sensing units have historically tended to increase in cost and fragility with sensitivity, increasing sampling time may offer a desirable option for some system designs.

1.6.5 The Concentration Gap

As we shall see in Chapter 4 the anticipated concentration of explosive molecules in many search situation, such as for buried landmines, may be very low, perhaps 1 pg/L (or 100 ppq, or 1 in 10^{13} molecules). Most sensing systems are not capable of detecting such low concentrations directly. Hence there usually exists a gap between the available sensitivity of existing systems and our perceived needed sensitivity.

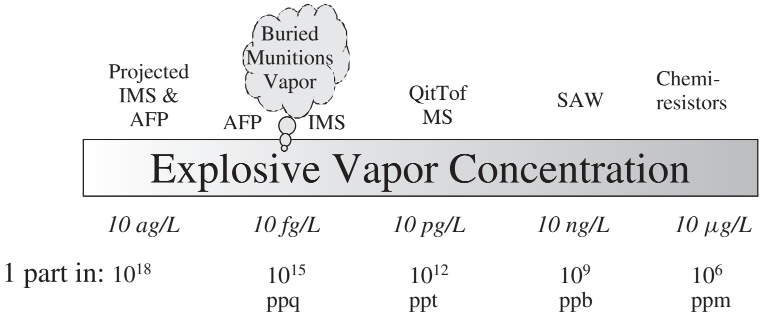

Figure 1.3 Illustration of concentration gap.

There are three potential ways to reduce this gap: (1) The basic sensitivity of the sensing unit could be increased or (2) the degree of concentration accomplished in the concentrating unit could be increased. While it is easy to make a statement like that, actually increasing the performance of either unit will require a great deal of innovative research and development. Alternatively, since explosive molecules tend to stick to solid surfaces such as structures, vegetation, or soil particles, (3) a sampling process that extracts them from those locations, rather than directly from the air, could exploit that natural concentration. See the discussion of this in Chapter 8. Figure 1.3 illustrates the current situation.

Figure 1.3 diagrams the problem faced by system designers. If the sensitivity of the sensing unit is insufficient to detect the available concentration of explosive vapor there is a *concentration gap*. This requires the system to include a concentrator unit to bridge the gap. In the example shown, assuming a part per quadrillion target vapor source, those sensing systems that have lower sensitivities fall to the right of the source concentration and must take action to concentrate the sample in order to successfully detect the target.

1.6.6 Sensitivity Comparison

Many different technologies have been adapted to construct detection systems for finding explosives. The result is a variety of instruments being developed or marketed. The potential user can become bewildered by the variety. Several reviews have been published to categorize the technologies and the available instruments. The following information is extracted from four [26–29] of those reviews. This provides a representative, though by no means exhaustive, comparison of the limit of detection[7] (LOD) of these technologies. Three of the four references describe the technologies and present a reported [26] or advertised [27, 28]

---

[7] As earlier noted, we refer to the smallest quantity of any given compound that a technology can detect as its LOD. The concept of LOD for mass spectrometery is more rigorously defined in Chapter 11, Section 11.4.3. The concept is used here in a parallel way for the other technologies, without specifying measurement procedures.

TABLE 1.10 Published or Advertised Limits of Detection for Sensing Technologies

Technology	Published	Abbreviation	LOD (ppt)	LOD (pg)	Source[a]
Amplifying fluorescent polymer	2005	AFP		0.001	Cumming, 9.3
Ion mobility spectrometer	2005	IMS		0.05	Woodfin 10.2
Lab-on-a-chip/high-performance liquid chromatography	2005	LOC/HPLC	215		Collins, 13.4
Quadrupole ion trap—time-of-flight mass spectrometer	2005	QitTof MS		0.9	Syage, 11.3.4
Chemiluminesence detector a.k.a. thermal energy analyzer	2004	CL or TEA	1000		[28, p. 42; 23, p. 34]
Chemical reagent-based (color change)	2004	Color		1000	[28, p. 42]
Gas chromatography/chemiluminesence	2004	GC/CL		1	[28, p. 42]
Gas chromatography/differential ion mobility spectrometer	2004	GC/DMS		1	[28, p. 42]
Gas chromatography/mass spectrometer	2004	GC/MS		0.001	[28, p. 42]
Gas chromatography/surface acoustic wave	2004	GC/SAW	1000		[28, p. 42]
Ion mobility spectrometer	2004	IMS		1	[28, p. 42]
Ion trap ion mobility spectrometer	2004	ITIMS		1	[28, p. 42]
Nonlinear dependence of ion mobility	2004	NLDIMS	1000		[28, p. 42]
Thermo-redox	2004	TR	1000		[28, p. 42]
Electrochemical[b]	2003	Electrochemical		1000	[29, p. 37]

TABLE 1.10 (*continued*)

Technology	Published	Abbreviation	LOD (ppt)	LOD (pg)	Source[a]
Fluorescent[b,c]	2003	Fluorescent		1	[29, p. 37]
Piezoelectric[b]	2003	Piezoelectric		10000	[29, p. 37]
Spectroscopic[b]	2003	Spectroscopic		1000000	[29, p. 37]
Field ion spectrometer	1999	FIS	10		[27, p. 26]
Gas chromatography/electron capture detector	1999	GC/ECD	10		[27, p. 26]
Gas chromatography/ion mobility spectrometer	1999	GC/IMS		500	[27, p. 26]
Gas chromatography/mass spectrometer	1999	GC/MS	100		[27, p. 26]
Ion mobility spectrometer	1999	IMS		50	[27, p. 26]
Thermo-redox	1999	TR	1000		[27, p. 26]
Gas chromatography/surface acoustic wave	1998	GC/SAW	10000		[27, p. 40]
Infrared spectroscopy	1997	IRS		10	[26, p. 66]
Atmospheric pressure ionization time-of-flight mass spectrometer	1996	API/TOF MS		0.01	[26, p. 54]
Atmospheric sampling-glow discharge-ion trap-tandem mass spectrometer	1996	ASGDI MS/MS		0.5	[26, p. 53]
Electron-capture negative-ion mass spectrometry	1995	ECNIMS		20	[26, p. 60]
Ion mobility spectrometer	1993	IMS		200	[26, p. 73]
Bioluminescence detector	1989	BL	0.25		[26, p. 73]

[a] When a name and section number is quoted, the quoted datum is found in that section of this book. Otherwise, the datum is to be found on the given page in the noted reference work.

[b] Presented as a general class, rather than for any specific system.

[c] Text mentions only AFP.

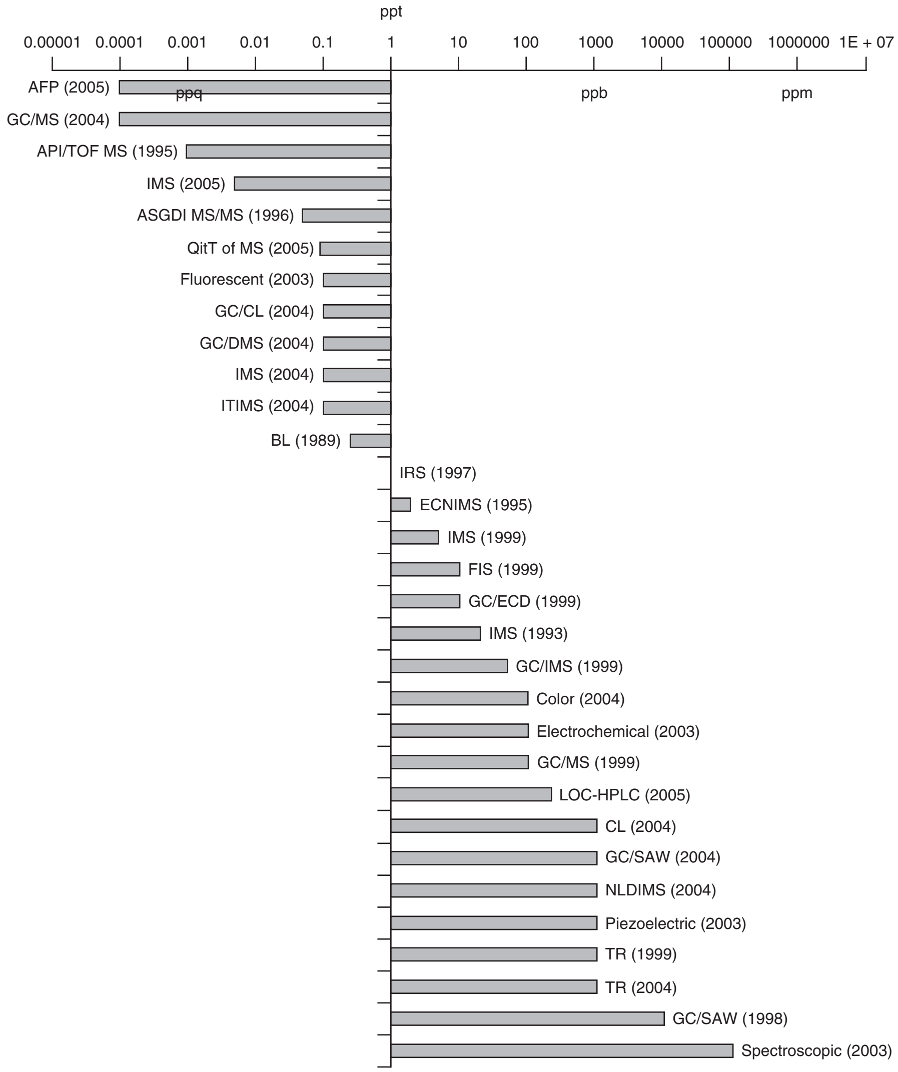

Figure 1.4 Normalized limits of detection reported or advertised.

LOD for each. MacDonald et al. [29], however, aggregate all trace detection technologies into four broad categories.

The rated technologies are presented in Table 1.10. In many reports and advertisements the LOD is presented as a range of values. In each of those cases the most favorable value offered is shown in Table 1.10. However, some are presented in "parts per" nomenclature and some in mass nomenclature. In order to present all in a similar form Figure 1.4 presents them normalized. Normalizing required an assumption that may not be valid in every case. It was assumed that

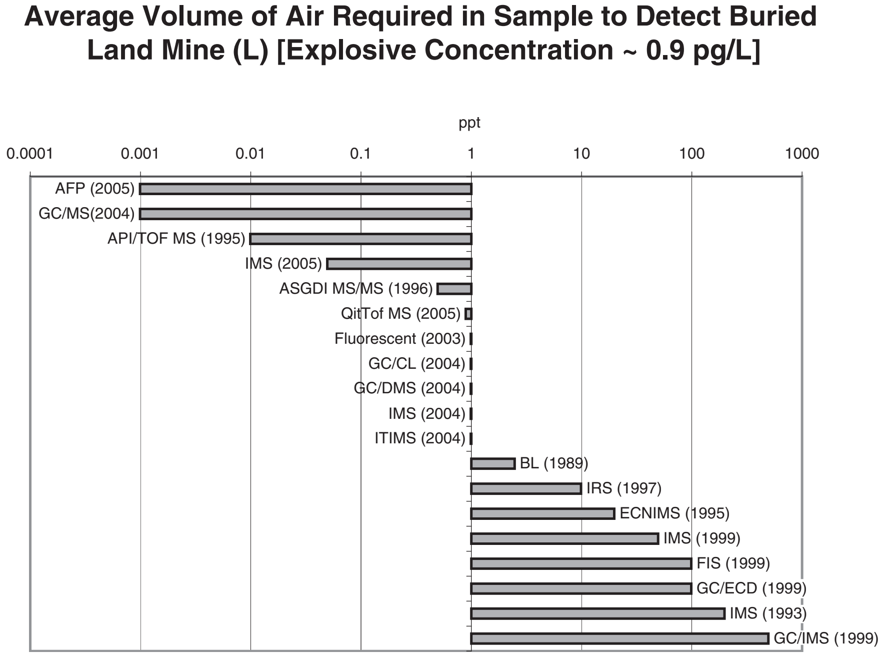

Figure 1.5 Expected volume of air sample required to detect landmine signature.

when a LOD was quoted as a mass, that that mass of explosive was contained in one liter of air. No attempt was made to normalize all to the same explosive molecule, although it is recognized that there may be as much as an order of magnitude between the LODs of two different molecules using the same detector.

Therefore, Figure 1.4 should be used with caution as a relative indicator of LODs. Furthermore, the author apologizes for the omission of those technologies not included; there are constantly emerging technologies that have not been included. A further caution is offered. Since the LODs are based on published or advertised values, there is no way to know whether the one who published or advertised the value was being conservative or optimistic in the disclosure. Likely, there are some of each in the group.

1.6.6.1 Required Sampling Volume Based on this normalization, we can get some idea of the quantity of air that needs to be sampled in order to detect a given concentration of explosive. Of course, this can only be an average value estimate. For an example we can use that concentration predicted for the TNT vapor signature of a buried landmine as given in Chapter 4, Section 4.3.2, Table 4.5, $c_m \approx 10^{-3}$ ng/L. To estimate the necessary volume of air containing TNT at concentration c_m that must be sampled by a system with a given LOD to detect the TNT, we merely divide the LOD of that system by the concentration, c_m, as in Eq. (1.9):

$$\text{Vol (L)} \approx \frac{\text{LOD (ng)}}{c_m(\text{ng}/L)} = \frac{\text{LOD}}{9.4 \times 10^{-4}} \approx 1000 \text{ LOD (L)} \tag{1.9}$$

Sample volume estimates for the technologies reporting the better LODs listed in Table 1.10 are shown in Figure 1.5. Examination of Figures 1.4 and 1.5 indicates the significant progress made in lowering the LODs in the last 5 years or so. Only two technologies reported before 2000 are in the most sensitive group. If progress continues at this rate, within another 5 years trace chemical sensing technologies should be able to detect buried or hidden explosives much more reliably and quickly.

REFERENCES

1. Bruschini, C. *Commercial Systems for the Direct Detection of Explosives (for Ordnance Disposal Tasks), ExploStudy, Final Report,* Ecole Polytechnique Federale de Lausanne, Lausanne, Switzerland, Feb 17, 2001.
2. *Sensor Technology Assessment for Ordnance and Explosive Waste Detection and Location, JPL D-11367, rev B*, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, March 1995.
3. Hibbs, A. D., G. A. Barrall, P. V. Czipott, A. J. Drew, D. Gregory, D. K. Lathrop, Y. K. Lee, E. E. Magnuson, R. Matthews, D. C. Skvoretz, S. A. Vierkötter, and D. O. Walsh. Detection of TNT and RDX Landmines by Stand-off Nuclear Quadrupole Resonance, preprint given author by Andy Hibbs, Quantum Magnetics Inc., San Diego, CA, 1999.
4. Willis, C. M. Olfactory detection of human bladder cancer by dogs: Proof of principle study. *Br. Med. J.* **329** (7468), 712–714 (2004).
5. Fliermans, C. B. and G. Lopez-de-Victoria. Microbial Mine Detection System (MMMDS), A. C. Dubey, J. F. Harvey, and J. T. Broach, Eds. in *Proceedings of the SPIE 12th Annual International Symposium on Aerospace/Defense Sensing, Simulation and Controls, Detection and Remediation Technologies for Mines and Minelike Targets III*, April 13–17, 1998.
6. McLean, I. G., Ed. *Mine Detection Dogs: Training, Operations and Odour Detection*, Geneva International Centre for Humanitarian Demining (GICHD), Geneva, 2003.
7. Townsend, J. Pigs, a demining tool of the future? *J. Mine Action* **7.3**, 43–46 (2003).
8. Phelan, J. M. and J. L. Barnett. Chemical Sensing Thresholds for Mine Detection Dogs, SAND2002-0692C, Sandia Laboratories Report, Albuquerque, NM, 2002.
9. McLean, I. G., H. Bach, R. Fjellanger, and C. Åkerblom. Bringing the minefield to the detector: Updating the REST concept, Proceedings of EUDEM2-SCOT–2003, Vol. 1, 2003, pp. 156–161.
10. Bromenshenk, J. J., C. B. Henderson, R. A. Seccomb, S. D. Rice, R. T. Etter, S. F. A. Bender, P. J. Rodacy, J. A. Shaw, N. L. Seldomridge, L. H. Spangler, and J. J. Wilson. Can Honeybees Assist in Area Reduction and Landmine Detection?, *J. Mine Action* **7.3**, 2003. http://maic.jmu.edu/journal7.3/bromoersheuk/bromenshenk.htm Visited 8/9/06.

11. Bender, S. F. A., P. J. Rodacy, R. L. Schmitt, P. J. Hargis, Jr., M. S. Johnson, J. R. Klarkowski, G. I. Magee, and G. L. Bender. Tracking Honey Bees Using LIDAR (Light Detection and Ranging) Technology, SAND2003-0184, Sandia National Laboratories Report, Albuquerque, NM, 2003.
12. Tomberlin, J. K., M. Tertuliano, G. Rains and W. J. Lewis, Conditioned *Microplitis croceipes* Cresson (Hymenopteria: Braconidae) Detect and Respond to 2,4 DNT: Development of a Biological Sensor, *J. Forensic Sci.,* Sept. 2005, Vol. 50, No. 5, 5 pages. Paper ID JPS2005014, Available online at: www.astm.org
13. Rains, G. C., S. L. Utley and W. J. Lewis, Behavioral Monitoring of Trained Insects for Chemical Detection, *Biotechnol. Prog.* 2006, **22**, 2–8.
14. Rains, G. C., Tomberlin, J. K., M. D'Alessandro and W. J. Lewis, Limits of Volatile Chemical Detection of a Parasitoid Wasp, *Microplitis croceipes*, and an Electronic Nose: A Comparative Study, *Transactions of the American Society of Agricultural Engineers*, Vol. 47(6): 2145–2152, 2004.
15. Hollas, J. M., Ed. *Modern Spectroscopy,* 4th ed., Wiley, Chichester, West Sussex, 2004.
16. Drafts, B. Acoustic Wave Technology Sensors, *Sensors Magazine Online*, October 2000; visited 8/9/04; http://www.sensorsmag.com/sensors/articles/article Detail.jsp?id=327349.
17. Li, J. The Cyranose Chemical Vapor Analayzer, *Sensors Magazine Online*, August 2000; visited 8/9/06; http://www.sensorsmag.com/articles/0800/56/main.shtml.
18. Oxley, J. Detection of Illicit Chemicals and Explosives, Elseveir, in Press.
19. Garner, K. and S. Smith. Volatile Organic Compounds, the good, the bad and the analysis, SPME, University of the West of England, Bristol; updated 9/23/04; visited 9/19/05; http://www.chemsoc.org/exemplarchem/entries/2004/westengland_smith/ExempWeb/methdev.htm.
20. Janusz, P. *Solid Phase Microextraction: Theory and Practice*. Wiley-VCH, New York, April, 1997.
21. Chambers, W. B., P. J. Rodacy, E. E. Jones, B. J. Gomez, and R. L. Woodfin. Chemical Sensing System for Classification of Minelike Objects by Explosive Detection, in A. C. Dubey, J. F. Harvey, J. T. Broach, Eds. *Proceedings of the SPIE 12th Annual International Symposium on Aerospace/Defense Sensing, Simulation and Controls, Detection and Remediation Technologies for Mines and Minelike Targets III,* April 13–17, 1998.
22. *Handbook of Chemistry and Physics, 80th ed.*, Chemical Rubber Publishing Co., Boca Raton, FL, 2000.
23. *Handbook of Chemistry and Physics, 37th ed.*, Chemical Rubber Publishing Co., Cleveland, 1955–1956.
24. Cooper, P. W. *Explosives Engineering,* Wiley-VCH, New York, 1996.
25. Phelan, J. M. and S. W. Webb. *Chemical Sensing for Buried Landmines—Fundamental Processes Influencing Trace Chemical Detection*. SAND2002-0909, Sandia National Laboratories, Albuquerque, NM, 2002.
26. Yinon, J. *Forensic and Environmental Detection of Explosives*. Wiley, New York 1999.

27. Rhykerd, C. L., D. W. Hannum, D. W. Murray, and J. E. Parmeter. *Guide for the Selection of Commercial Explosives Detection Systems for Law Enforcement Applications. NIJ Guide 100-99*, NCJ 178913, National Institute of Justice, Office of Science and Technology, Washington, DC, 1999.
28. Theisen, L., D. W. Hannum, D. W. Murray, and J. E. Parmeter. *Survey of Commercially Available Explosives Detection Technologies and Equipment 2004, Document No. 208861*, National Law Enforcement and Correction Technology Center, a Program of the National Institute of Justice, U.S. Department of Justice, Washington, DC, 2005.
29. MacDonald, J., J. R. Lockwood, J. McFee, T. Altshuler, T. Broach, L. Carin, R. Harmon, C. Rappaport, W. Scott, and R. Weaver. *Alternatives for Landmine Detection*, RAND Science and Technology Policy Institute, Santa Monica, 2003.