Infrared Spectroscopy

Gamma rays, x-rays, ultraviolet light, visible light, infrared light, microwaves, and radio waves are electromagnetic radiation waves. The only difference among these different types of radiation is wavelength or frequency range. In order, wavelength increases from gamma rays, x-rays, ultraviolet, visible, infrared, and microwaves to radio waves. Table 7.1 shows that the energy level declines as wavelength increases. Infrared (IR) wavelengths range from 0.78 µm to 1000 µm, where 1 µm equals to 10^{-6} m (commonly referred to as 1 micron). Infrared detectors use a chemical's IR radiation absorption characteristics to detect and identify it.

Sir Frederick William Herschel (1738–1822) discovered IR radiation in 1800. He found that temperature increased from the violet to the red part of the visible light spectrum. After noticing this pattern, he measured the temperature just beyond the red portion of the spectrum in a region where color was invisible. To his surprise, he found that this region had the highest temperature. Additional experiments showed that the higher temperature was from a form of light or radiation now known as infrared radiation. The IR wavelength is longer than that of the red end of the visible light spectrum and shorter than that of microwave radiation. Thus, IR photons have lower energy than visible light, but possess more energy than microwaves.

There are two major types of IR instruments: one type detects IR emitted from objects, such as IR cameras; and the other detects IR radiation absorbed by objects, such as IR spectroscopy. The uses of the IR technique in the analytical and detection field are based on IR absorption characteristics at specific wavelengths by the substances of interest.

Function groups in a molecule vibrate at certain frequencies that fall within the IR region. The molecule absorbs energy from IR waves that have the same frequencies, as the vibrating function groups are excited to a higher energy level. Specific function groups absorb IR radiation having specific frequencies. By determining the IR radiation frequencies being absorbed by the function groups composing the molecule, the molecular structure can be determined. The spectrum of a large

153

molecule can be very complex, depending on the number of function groups in the molecule. Therefore, large IR spectra databases have been established for many chemicals. For example, the National Institute of Standards and Technology has a database comprised of 5228 infrared spectra. The identification of a substance and its structure can be determined through matching its IR absorption spectrum with spectra from the databases.

A simplified method is generally used for detecting certain groups of chemicals in a vapor sample. For field applications of CWA and TIC detection, the objective of course is to determine whether the sample contains the targeted chemical(s) rather than identifying the structure of these chemicals. The characteristic frequencies of targeted chemicals are known based on their function groups and confirmed in laboratory studies. Therefore, it may suffice to check the IR absorption using a few characteristic wavelengths to achieve the detection objective. This can be done by exposing the sample to IR radiation at several selected wavelengths that are characteristically absorbed by the targeted chemicals. This greatly simplifies the instrumentation design of IR detectors. We will focus on detection aspects rather than structure identification using various IR technologies.

Detectors based on IR technique have the advantage of reasonably high sensitivity and fast detection. More sophisticated instruments can offer better selectivity. IR is a nondestructive technique and requires minimal sample preparation. Remote detection of chemical clouds can also be made using the infrared emission technique. Environmental conditions, especially humidity, may significantly affect its performance, however.

8.1 PRINCIPLE OF OPERATION

Figure 8.1 shows a block diagram illustrating the principle of operation of IR detectors in general. A sample is introduced into the detector and exposed to IR irradiation. The irradiation can derive from a filtered IR source at a certain wavelength or an IR source that does not use filters to cover the entire IR wavelength range for different applications. Ideally, when the targeted chemical is present in the sample, IR absorption at characteristic wavelengths occurs. The intensity of IR absorption for those wavelengths changes according to the concentration of the targeted chemical. Signals are sent to the central processor for chemical identification and/or concentration determination.

8.1.1 Infrared Sources

IR wavelengths range from 0.78 μm and 1000 μm. Consequently, the frequency of an IR radiation is in the range of 3×10^{11} Hz to 3.8×10^{14} Hz. Table 7.1 shows the IR radiation region relative to other types of radiation in the electromagnetic spectrum. IR radiation can also be expressed in terms of wave numbers, or the number of full waves per centimeter. Wave numbers are expressed in number of waves per centimeter units (cm⁻¹). Unlike wavelengths, a wave number is directly related to its energy level. Higher wave numbers possess higher energy levels.
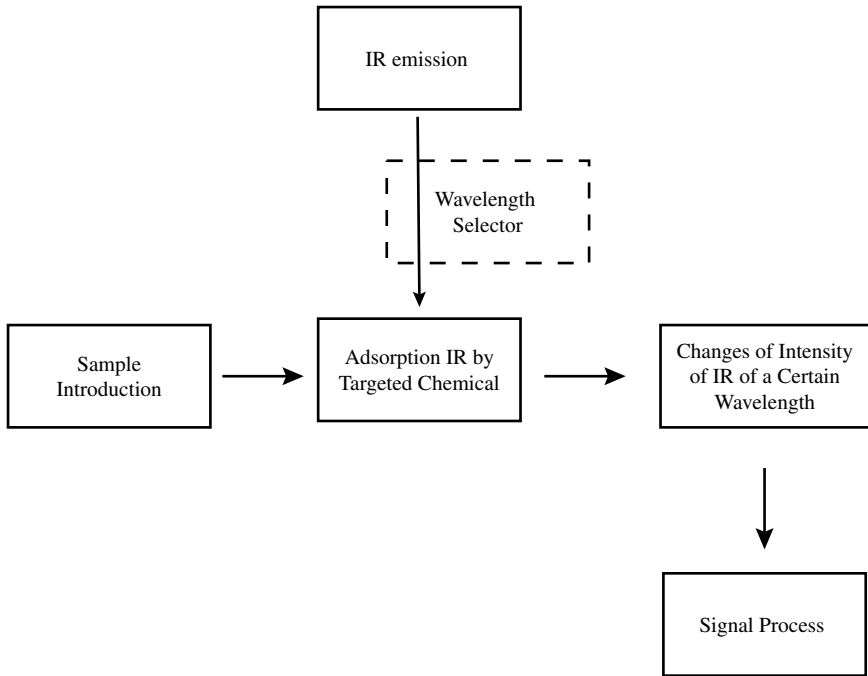
Figure 8.1   Block diagram of IR detector.

IR radiation is further subclassified into three types according to wavelength. The near visible IR (NVIR) wavelengths range from 0.78 μm to 2.5 μm, equivalent to wave numbers ranging from 12,800 to 4000 cm^{-1}. The wavelengths of middle IR (MWIR) range from 2.5 μm to 50 μm, equivalent to wave numbers 4000 to 200 cm^{-1}. Far IR (FIR) covers wavelengths ranging from 50 μm to 1000 μm, equivalent to wave numbers 200 to 10 cm^{-1}. IR with wavelengths between 2.5 μm and 15 μm (670 to 4000 cm^{-1}) are the most frequently used in detection applications.

In the real world, any object will always have a temperature above absolute zero (−273.15°C or 0°K). Because the vibration of atoms or function groups in a molecule emits electromagnetic waves having frequencies in the range of IR radiation, all objects produce infrared radiation. Night-vision cameras are examples of remotely detecting objects based on IR emissions. While passive, remote-sensing IR monitoring devices make use of objects' IR radiation for detection, active types of IR devices require an IR source of their own to irradiate the sample after which the absorbed irradiation is measured. The primary source of IR is made available through the use of heat or thermal radiation. An inert solid that is heated to a temperature of 1500 to 2000°K will continually emit the necessary IR for a detector. However, the intensity of the generated IR at different wave numbers varies. Maximum intensity occurs between 5000 cm^{-1} and 5900 cm^{-1}, with gradual decline toward smaller wave numbers and sharp decline toward higher wave numbers.

8.1.2 Molecular Absorption

Organic molecules are composed of various atoms and function groups that are connected to each other through different types of bonds. Each of these bonds vibrates in a specific manner at a certain frequency. Figure 8.2 illustrates some of these vibration modes, including stretching, in-plane bending, and out-of-plane bending. Stretching vibration is the rhythmic movement along an axis of a bond (Figure 8.2a). The bond length increases and decreases at a certain frequency characteristic of the specific bond. In-plane bending vibration is the rhythmic change in the bond angle or movement relative to the rest of the molecule within the plane of the molecule (Figure 8.2b). Similar to in-plane bending, out-of-plane bending vibration is referred to as the rhythmic change in the bond angle relative to the rest of the molecule, but the bending is out of plane with the rest of the molecule (Figure 8.2c). In various chemicals, the same characteristic function group vibrates in the same fashion and absorbs IR radiation of same frequency. For other substances, the same characteristic function group vibrates similarly and absorbs IR with the same or similar wavelength. For example, when the C-C bond vibrates in the stretching fashion, it absorbs IR of 2800 to 3000 cm^{-1}. This similarity is most apparent from the wave numbers greater than 1200 cm^{-1}. This range is called the group frequency region.

Different structures, however, may affect the vibration frequency of the characteristic function group, resulting in different absorption characteristics at the low wave-number range of less than 1200 cm^{-1}, known as the fingerprint region. This feature makes it possible to identify the function groups in a molecule based on the frequencies absorbed by the molecule when scanned through the entire IR spectrum.

When an object absorbs energy from IR radiation, the electromagnetic wave from the IR source is transformed into mechanical vibration of the molecules as an IR photon with same vibration frequency collides with the molecule. The intensity of the IR at that frequency declines after it passes through the sample. Measuring these changes during the scanning through the IR wavelength range produces the fingerprint of the substance.

Molecules can be grouped into symmetric and asymmetric molecules. It was found that the symmetrical molecules with symmetric vibration (e.g., N_2, O_2, CH_4, C_6H_6, and CCl_4) do not absorb IR radiation (however, symmetrical molecules with asymmetric vibration such as CO_2 will still absorb IR). This is the most fortunate and important feature that permits the use of IR techniques for atmospheric vapor–monitoring applications. Because the two major components of air, N_2 (78%) and O_2 (21%), are dipoles and symmetrical molecules, they do not absorb IR. Thus, their presence and abundance will not interfere with IR detection of other chemicals in the air.
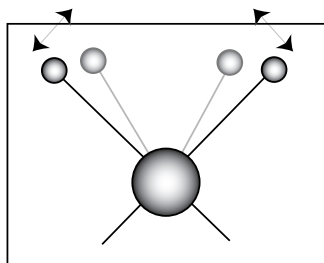
8.1.3 Beer's Law

When an IR beam at a certain wavelength passes through a sample, the molecules that vibrate at the same frequency as the bombarding IR radiation absorb the radiation. This absorption decreases the intensity of the IR beam (Figure 8.3). The absorbance (A) value is a measurement of this loss in intensity, as follows:
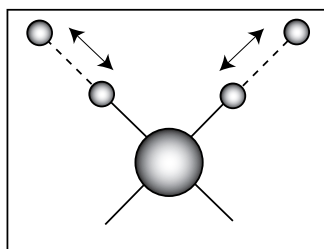
a
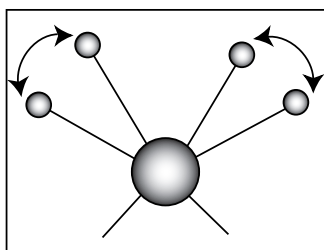
b

c

Figure 8.2   Examples of molecular vibration model.

$$A = \log_{10} \frac{I_0}{I} \qquad (8.1)$$

where I_0 is the initial intensity of the incoming radiation at the wavelength emitted from the source to the sample, and I represents the radiation after passed through the sample. Beer's law states that the absorbance of radiation at a certain wavelength is linearly related to the total amount of molecules that absorb the radiation in the sample. The total number of molecules is directly related to the path length (L) and

Sample Cell
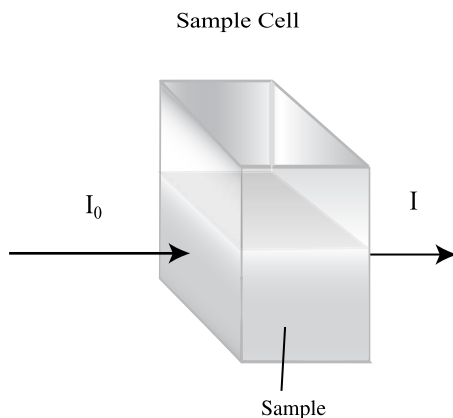
Figure 8.3 Beer's Law.

the concentration of the sample (C) that the IR beam travels through as expressed in Equation 8.2:

$$A = eCL \tag{8.2}$$

where e (in the unit of area/mass, such as square centimeter per milligram) is the molar absorptivity known as the extinction coefficient.

Most substances obey Beer's Law at low to moderate concentrations that still permit transmission of the IR beam. Higher percentages of IR transmitted through the sample produce lower absorbance values. Once the absorbance versus concentration relationship has been established by a calibration curve through the plotting of absorbance values measured for standard samples at different concentrations, the unknown sample concentration can be determined when its IR absorbance is measured. Sample concentration can be calculated as

$$C = \frac{A}{eL} \tag{8.3}$$

A field air sample will likely contain more than one chemical that will absorb IR radiation. Simple application of Beer's Law can be problematic since different chemicals absorb IR of same frequency differently. The total absorbance (A_T) of a certain frequency (v_1) is the sum of the absorbance of each chemical (C_1, C_2 ... C_n) for that frequency:

$$A_{T,v_1} = A_{C_1,v_1} + A_{C_2,v_1} + \cdots + A_{C_n v_1} \tag{8.4}$$

For multiple wavelengths, a set of similar equations can be obtained. These equations can be resolved using matrix algebra, and the concentration of each chemical can be determined.

It should be understood that for IR spectrometers, Beer's Law might not be followed perfectly, especially at the low end of detectable limits. Therefore, field detection using IR is generally considered qualitative with semiquantitative features. For quantitative analysis of a sample, calibration curves using high-quality reference materials are required to determine sample concentration.

8.1.4   IR Transducers

After the IR passes through the sample, the resulting IR radiation is monitored using a transducer. An IR transducer changes the received IR signals to electrical signals that can be processed. Thermal, pyroelectric, and photoconducting transducers are common.

Thermal transducers are based on the following principles: (1) some materials build up electrical potential when there is a temperature difference (thermocouples); and (2) others change resistance when temperature changes (bolometer and thermistor). When a thermal transducer receives the IR radiation, its temperature changes, and therefore its potential or resistance changes as a consequence. These changes generate electrical signals that are then processed.

Simply put, a pyroelectric transducer is a piece of pyroelectric material placed between two electrodes. Pyroelectric material produces electrical polarization, such as in a crystal, via a change of temperature. The charge distribution on the pyroelectric material changes when it senses temperature variation. Therefore, the received IR at different intensities will produce electric signals that can be processed.

Photoconducting transducers use a thin film of semiconductor material. The conductivity of the thin film alters when it receives IR radiation. This change of conductivity is then detected and processed.

IR transducers are usually enclosed in a vacuum chamber to protect them from environmental variations, such as temperature fluctuations.

8.1.5   Photoacoustic Effect

The photoacoustic effect, which transforms electromagnetic radiation into acoustic waves, is also used as an IR detection technique in both qualitative and quantitative analyses of various materials. Alexander Graham Bell (1847–1922) discovered the effect in 1880. He observed that when a beam of sunlight was interrupted rapidly, sound was produced from the diaphragm he used in his experiment.

The photoacoustic effect is the generation of acoustic waves as a consequence of light absorption. As previously discussed, a molecule is excited to a higher vibration state when it absorbs energy from IR radiation. The higher energy of the excited molecule releases the absorbed energy in radiative decay and nonradiative decay. Radiative decay is the process of emitting radiation spontaneously, and nonradiative decay is the transfer of energy into mechanical vibrations of neighboring atoms. As a consequence, both types of decay raise the temperature of the sample. This increase in temperature increases pressure, and creates pressure waves in the gas. Pulsing, chopping, or modulating IR radiation at a certain frequency — for example, at a frequency of an audible sound wave — will produce a pressure wave
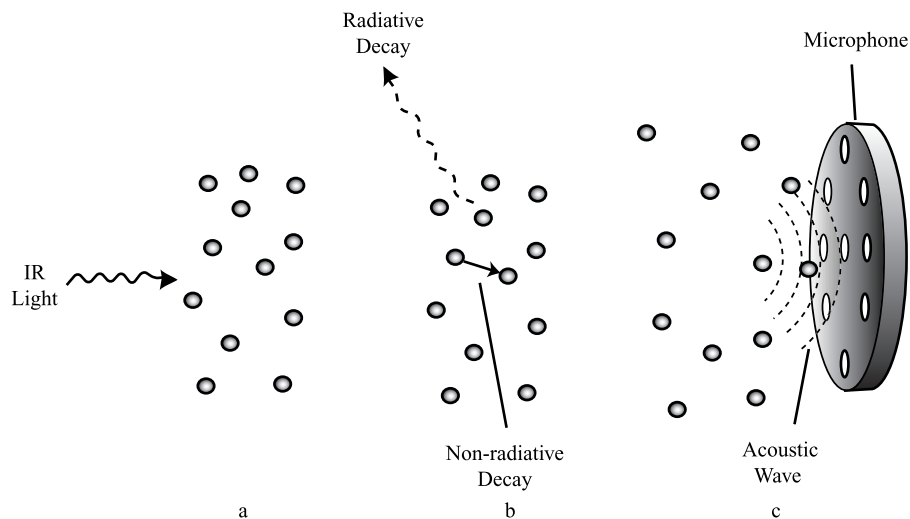
Figure 8.4 Photoacoustic effect principle.

at the same frequency of the modulation and generate an acoustic wave. If the gas is enclosed in a cell with a microphone or other measuring device such as an attached piezoelectric device, the pressure waves generated can be detected.

In a detector based on the photoacoustic effect (photoacoustic spectroscopy), an IR beam at a known frequency is used as the irradiation source. The IR radiation used should have a frequency at which it can be absorbed by the targeted chemical. This IR radiation is modulated at a desired frequency. Exposing the sample in a closed cell to this modulated IR frequency will generate the characteristic acoustic wave if the sample contains the targeted chemical. Signal amplitude is directly related to sample concentration. A schematic diagram illustrating the photoacoustic effect principle is shown in Figure 8.4.

8.2 INSTRUMENTATION OF FILTER IR AND PHOTOACOUSTIC DETECTORS

Many different kinds infrared instruments of various sizes are available for quantitative and qualitative vapor analyses. Some are manufactured specifically for detection of only one chemical, such as the carbon monoxide (CO), using a specific wavelength. Others can be very complicated, such as Fourier transform–based infrared (FT-IR) detectors that scan the entire IR wavelength for both chemical identification and concentration determination.

The absorption spectrum of CWAs or TICs is very likely known, or can be obtained in the laboratory and incorporated into libraries. Therefore, it may not be necessary to scan through the entire IR absorption spectrum of the sample. Exposure of the sample to a few important wavelengths that correspond to significant absorption wavelengths of the targeted chemicals may be a simpler and effective way for

manufacturing point-sampling detectors. Since wavelengths are filtered so that only desired IR wavelengths reach the sample, detectors based on this method are called filter IR detectors. The vapor sample in a cell is bombarded with one or several known wavelengths from an IR source. Detection of changes in IR absorbance by the sample with a transducer can be related to determine sample concentration. If the signal is generated based on photoacoustic effect, the instrument is a photoacoustic detector.

8.2.1 IR Source and Wavelength Control

Among the most common ways of generating IR radiation is a solid block of rare-earth element oxide or silicon carbide electrically heated to a temperature of approximately 2000 K. A wavelength selector, either a monochromator or a wavelength filter, is used to achieve desired wavelengths from the IR source since the source produces radiation with a broad range of wavelengths. A monochromator is a device that separates radiation into its distinct wavebands using a diffraction prism. A wavelength filter is a device that allows only the radiation of a certain wavelength to pass through while suppressing radiation in other wavelengths. The sample could be irradiated with more than one of the characteristic wavelengths to achieve more reliable identification of the targeted molecules.

8.2.2 Sample Cell

The sample is drawn into or continuously through a sample cell of fixed dimensions. IR radiation enters the sample cell through a window made of material that permits the IR beam to penetrate. This cell and window are set in such a way that the window is perpendicular to the radiation path to permit maximum IR radiation. The IR beam can pass through the cell and reach the absorption photometer in a single pass, or in multiple passes through the use of properly aligned mirrors to reflect the IR beam multiple times back and forth through the sample cell to increase the effective path length. Highest sensitivity is achieved when path length is maximized.

8.2.3 IR Intensity Detectors

The absorption of IR can be detected by using one of the IR transducers or photoacoustic methods. Figure 8.5 illustrates how transducers measure the intensity change of IR absorption after it passes through the sample. The absorbance of the sample can be calculated based on IR radiation beam intensity (Equation 8.1). Since absorbance of the IR follows Beer's law and the path length of the cell is a constant, substance concentration can be calculated using Equation 8.3.
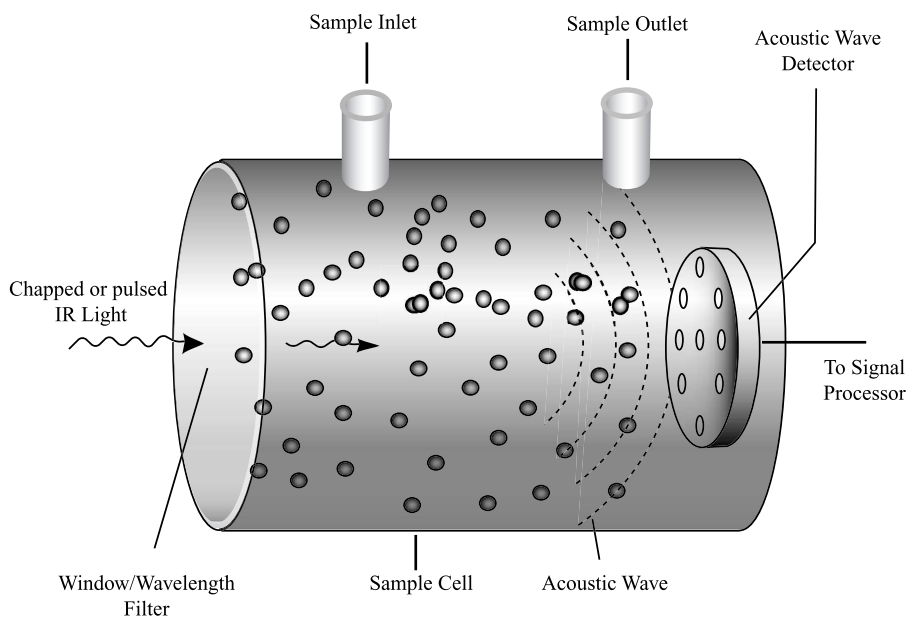
8.2.4 Photoacoustic Detectors

As discussed earlier, the photoacoustic effect can be used in IR instruments as a way to detect the presence of targeted substances. A diagram illustrating the operational principle of photoacoustic spectroscopy is shown in Figure 8.6. After an
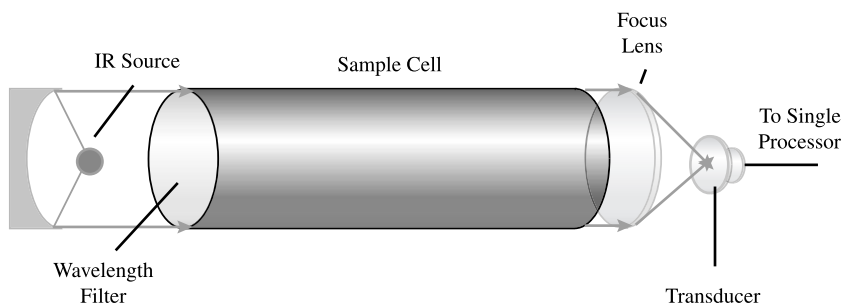
Figure 8.5   Schematic diagram of signal wavelength IR detector.

IR beam passes through the wavelength selector, the beam is modulated with a radiation chopper to a desired frequency. This can also be achieved by pulsing the IR radiation. This modulated radiation then enters the sample cell through the window. If the substance that absorbs the IR at the selected wavelength is present in the vapor, a photoacoustic wave will be generated. Through either a highly sensitive microphone or a piezoelectric sensor or other detector such as pressure sensor, the acoustic signal is translated into an electrical signal that can be further processed. The magnitude of the pressure generated by the expanding gas is proportional to the concentration of the substance that absorbs the IR radiation. Consequently, concentration is determined based on the magnitude of the measured signal.

Figure 8.6   Schematic diagram of photoacoustic spectroscopy.

8.2.5   Detector Operation

The filter IR detector, similar to most other spectrophotometers, consists of an IR radiation source, specific wavelength filter, sample cell, transducer, and signal processor. Vapor is drawn into the sample cell by an internal pump through the sample inlet and irradiated by an IR beam through the filter. Analysis may begin after the sample vapor fills the sample cell. Usually a parabolic mirror is used to focus the radiation beam. If the sample contains the targeted substance, the transducer detects it in the intensity of the exiting beam. For instruments equipped with a monochromator that varies wavelengths automatically or manually, changing filters is not necessary. The monochromator permits automatic selection of multiple wavelengths of interest to penetrate the sample such that various function groups can be detected simultaneously.

Similarly, photoacoustic IR detectors consist of an IR source, wavelength filter, radiation chopper, sample cell, microphone or piezoelectric detector, and signal processor. The chopper is used to modulate the IR radiation before it enters the sample cell, which in turn occurs after the sample cell is filled and closed. Here the sample is not continually introduced through the cell; instead the sampling procedure is pulsed for each analysis. IR radiation, modulated at a certain frequency, is used to excite the vapor sample. The generated photoacoustic effect signal is captured by the signal sensor and sent to the processor.

Both types of detectors do not analyze sample continuously. Each sample is pumped into the detector for analysis, and the sample is purged after each analysis and the cell is flushed with clean air. Analysis resumes after a new sample is introduced into the cell. Similar to photoionization techniques, discussed in Chapter 11, this technique is nondestructive. The chemicals in the sample are not decomposed or altered chemically by the analysis.

8.2.6   Technique Specification of Filter and Photoacoustic IR Detectors

8.2.6.1   Detectable Substances and Selectivity

Since CWAs and many TICs absorb IR of certain wavelengths, they can be, at least theoretically, detected using IR detectors. Selectivity is controlled by the careful selection of wavelengths for each of the targeted chemicals. To enhance selectivity, a sample may be exposed to IR radiation of several characteristic wavelengths. Various chemicals may contain the same function groups that absorb IR of similar wavelengths. Detection determination based on a single wavelength may result in higher false positive and/or false negative alarm rates due to reduced discriminatory ability. When the detected sample produces an alarm suggesting the presence of a targeted chemical, checking the sample using one or more additional characteristic wavelengths to confirm the finding is recommended. This is possible because the IR method does not destroy sample integrity. After exposure to IR radiation of a certain frequency, the sample in the cell is chemically unchanged and can be analyzed again. This technique improves sample identification reliability. To do this, after the sample in the cell is analyzed with a single frequency, it is then exposed to a second

IR radiation at another frequency to supplement or confirm the detection observed in the first analysis. A third wavelength can be used, if necessary, to further enhance detection reliability.

Unlike other techniques in which samples can be continually introduced into the detector, these two techniques use pulsed sampling methodology. The sample is introduced into the sample cell, which is then closed during the analysis. Sample volume can be rather large. Therefore, no GC separation technique is coupled with these types of detectors currently.

8.2.6.2   Sensitivity and LOD

Both IR techniques discussed above are believed to have relatively high sensitivity with low LODs. Under ideal conditions, IR detectors may be able to sense CWA concentrations at the lower parts-per-million level.

8.2.6.3   Environmental Effect

Several factors can affect IR detector performance. Relative humidity is among the most notable. Moisture molecules composed of two hydrogen atoms and an oxygen atom is an asymmetric molecule that strongly absorbs IR radiation. Changes in sample moisture level may generate false IR absorption responses, as well as interfering with the calibration. To reduce this effect, a filter for measuring background moisture content can be used, which then facilitates calculating a correction.

The photoacoustic technique is very sensitive to vibration and environmental effects. Thus, its use in handheld detection devices for field operations is limited at present.

8.2.6.4   Response Time

The analysis cycle includes sampling time, IR analysis time, and recovery time. Among them, the sample introduction and cell flushing are main factors affecting an analysis cycle. The actual IR analysis response time can be within seconds. Total cycle for a complete analysis can be several seconds to minutes and depends on the size of the cell and the rate of sampling.

8.3 FOURIER TRANSFORM INFRARED DETECTORS

The Fourier transform infrared (FT-IR) spectrometer scans a large range of IR frequencies by using an interferometer, while simultaneously acquiring the spectra. Analysis with an FT-IR spectrometer actually includes two main steps. The instrument collects the interferogram of the sample using the interferometer and then applies the Fourier transform to the interferogram to obtain the final IR spectra. FT-IR spectrometers once were very expensive. However, thanks to development of related technologies, prices have dropped significantly and small detectors can be made based on this technique.

Detectors based on dispersive IR techniques also scan a large region of IR and obtain the spectra. The dispersive IR technique employs a monochromator or other methods to generate IR radiation of various wavelengths. It has to sequentially produce different wavelengths in the IR region of interest. This process can be slow with low resolution due to limitations on controlling wavelength. The FT-IR spectrometer significantly improves analysis time, resolution, and other performance-related issues. FT-IR has also largely replaced dispersive IR. Because FT-IR scans broadband IR in a very short time, it enables the IR technique to be used along with a GC or high-performance liquid chromatographic separation. FT-IR spectrometers have also been used for detecting CWAs and TICs.

8.3.1   Interferometer

The heart of an FT-IR spectrometer is the interferometer. Most FT-IR spectrometers use the Michelson interferometer, invented by Albert A. Michelson (1852–1931) in 1891, and for which he received the 1907 Nobel Prize in physics.

Basically, the Michelson interferometer, illustrated in Figure 8.7, is composed of a beam splitter, fixed mirror, and moving mirror. Incoming IR radiation is split into two beams that are reflected by the mirrors and then recombined before reaching the IR transducer. Changing the moving mirror position enables the interference of the two beams to form an interferogram that is used to obtain the spectra.

As Figure 8.7a shows, the IR beam (1) emitted from the IR source strikes the splitter, which then divides the beam into two vertical beams (2 and 3). Due to the special property of the splitter, about 50% of the incoming beam is reflected by the splitter toward the fixed mirror and the other 50% is allowed to penetrate the splitter to hit the moving mirror. These beams are reflected back by the fixed and moving mirrors toward the splitter (Figure 8.7b). The splitter then reflects half of the beam
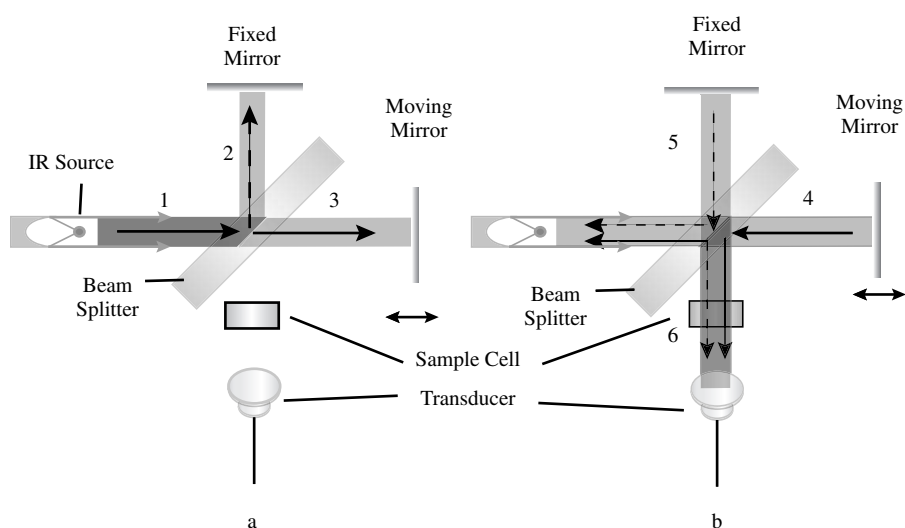
Figure 8.7   Schematic diagram of Michelson interferometer.

from the moving mirror (4) to the transducer, and also allows the other half of the beam from the fixed mirror (5) to penetrate it. These two beams then recombine (6) and pass through the sample cell. The rest of the radiation that is reflected from the moving mirror penetrates the beam splitter in the direction of the radiation source. Similarly, the rest of the radiation from the fixed mirror is reflected by the splitter in the direction of the radiation source. Therefore, only about half of the initial IR radiation goes through the sample cell and reaches the transducer.

The recombination of the beams after the splitter and the sample cell results in the interferogram, which is a plot of the output power versus the difference (δ) in path lengths for the two recombined beams. The δ value depends on the relative position of the moving mirror. Since the radiation strikes the moving mirror and is then reflected back, δ is equal to two times the difference between the path lengths of the moving mirror (M) and the fixed mirror (F) (Figure 8.8a). For radiation of a single frequency, the output power will be maximum when the two beams that recombine are in phase at $\delta = 0$ (Figure 8.8b). This occurs when the moving mirror is at position (a). When the moving mirror moves, the power of the recombined beam changes due to the destructive interference of the two beams. Figure 8.8c illustrates the recombination of the beams when the moving mirror moves a distance of $\lambda/8$ ($\delta = \lambda/4$) to position (b). When the moving mirror moves $\lambda/4$ ($\delta = \lambda/2$) to position (c), the two beams will be totally out of phase, and the lowest output power is observed (Figure 8.8d). As the IR radiation is composed of different wavelengths, the output power will vary when the moving mirror is at different positions and an interferogram is observed. If the sample in the sample cell absorbs the incoming IR of certain wavelengths, a characteristic interferogram is generated. By applying the Fourier transform to the interferogram, a distinctive spectrum is then obtained.

8.3.2 Fourier Transform

Discussion of how the Fourier transform is applied to the interferogram is beyond the scope of this book. Suffice it to say that data are obtained for each precise position of the moving mirror in small intervals during the scan to acquire an interferogram. This interval determines the resolution of the FT-IR. In an FT-IR spectrometer, a pyroelectric transducer is commonly used due to its fast response to signal changes. The observed interferogram is digitized and stored in the computer. Since the interferogram contains information about every frequency in its IR source, individual frequency intensity is therefore found by applying the fast Fourier transform to construct the spectra.

8.3.3 Background Handling

A background spectrum that is converted from a background interferogram by Fourier transform is usually first obtained for correcting effects from common factors such as water, CO_2, and noise from the IR source, interferometer, and detector, among other sources. The sample spectrum is then obtained. The difference between the sample and background spectra gives the final spectrum that is corrected for effects from common factors. This process enables more precise identification of unknown substances.
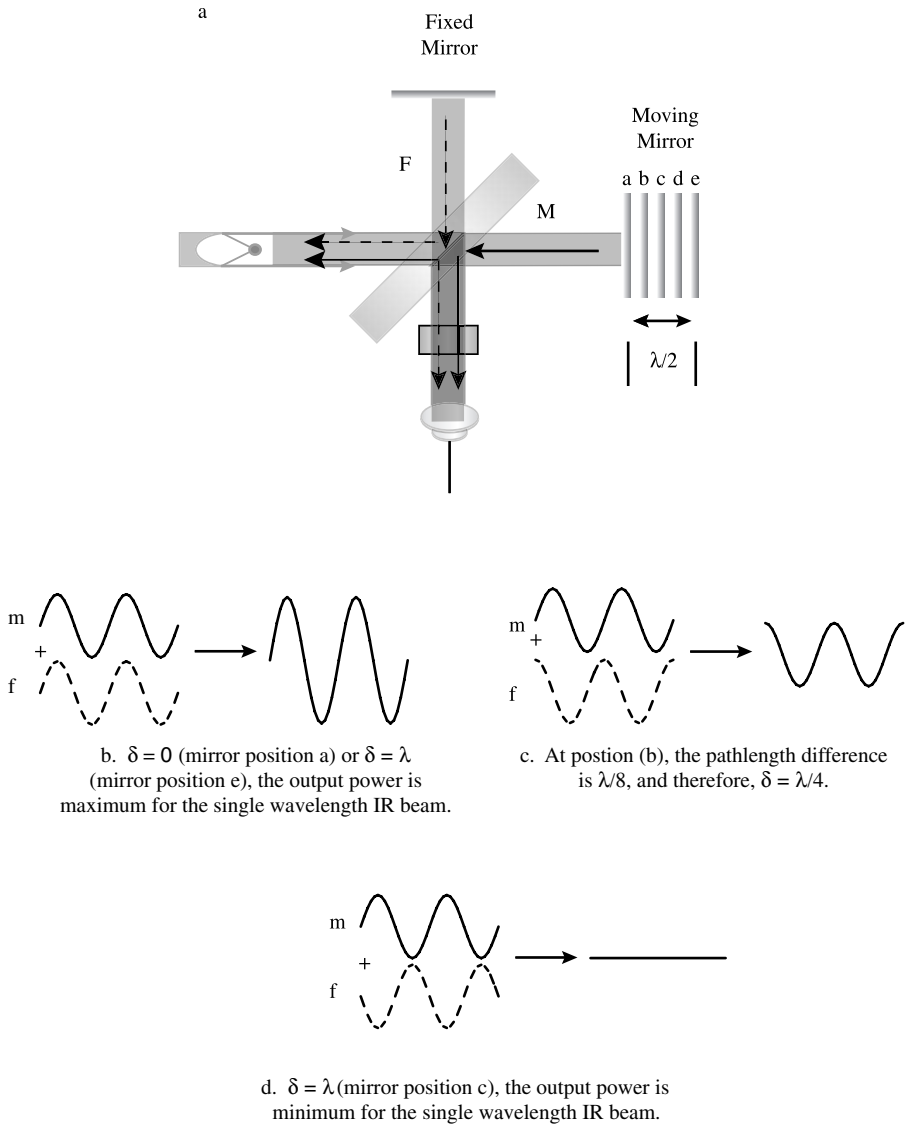
a

Fixed
Mirror

Moving
Mirror

F

a b c d e

M

λ/2

b. δ = 0 (mirror position a) or δ = λ
(mirror position e), the output power is
maximum for the single wavelength IR beam.

c. At postion (b), the pathlength difference
is λ/8, and therefore, δ = λ/4.

d. δ = λ (mirror position c), the output power is
minimum for the single wavelength IR beam.

Figure 8.8   Formation of interferogram.

8.3.4   CWA and TIC Detection

FT-IR can be used for detection of CWAs and TICs in vapor, liquid, or solid
samples. The most common method used in identifying chemicals in samples is to
compare the resulting spectrum to the various libraries stored in the instrument. For
instruments used in detection of CWAs and some TICs, the library may be limited
to the chemicals of interest for faster search results. This is different from attempts
to identify unknown chemicals, as the spectrum may have to be compared with a

large database for positive identification. Concentration can be determined as discussed in Section 8.1.3.

8.4 REMOTE IR MONITORS

The spectrometers discussed thus far use an internal IR source to generate desirable IR radiation for detection. Since IR radiation is part of the environment, it is possible to monitor changes in background IR radiation. Remote IR monitors work in a similar fashion to human eyes, except that the monitors sense IR radiation instead of visible radiation. The presence of CWA vapor in the background will change the incoming IR spectra. By comparing incoming spectra with stored library patterns, the detector can determine whether a CWA cloud exists within a certain range. As it scans the area, the monitor could also report the position of the cloud and direction of its movement.

8.5 APPLICATIONS

Laboratory instruments can provide accurate identification of various substances through library searches of spectra collected with known substances. Detection devices using IR techniques in field applications include remote and point sample detectors. The M21 Detector and the Rapid Air Pollution Infrared Detector (RAPID® or HAWK®), used by the U.S. military in field operations, are examples of remote devices that detect IR radiation changes in the background. The MIRAN SapphIRe Portable Ambient Air Analyzer (Figure 8.9) manufactured by Foxboro Company is an example of how IR technology is used in a portable instrument. The MIRAN SapphIRe has been tested at the U.S. Army Soldier and Biological Chemical Command (SBCCOM) under the Domestic Preparedness Program in an attempt to qualify it for possible CWA detection.

Figure 8.9   MIRAN Detector. Photo courtesy of K. Y. Ong.

The MIRAN SapphIRe portable ambient air analyzer is an IR spectropho-tometer. The intensity of the IR energy absorbed by the air sample in the cell is displayed on the detector panel in absorbance units (AU). The optimum detection wavelength for the compound of interest must be stored in the instrument's memory to enable detection of that compound. The factory usually provides the appropriate wavelength to be used for detection of a specific substance. The instrument also has a multigas mode that allows the detector to indicate absorption responses at three wavelengths simultaneously. The MIRAN SapphIRe can oper-ate at different path lengths. The longest path length is 12.5 m, which provides the highest possible sensitivity of the instrument toward detection of CWA vapors. It is equipped with an external particulate filter to prevent dirt from entering its internal plumbing, and a chemical filter that is interchangeable with the particulate filter to zero the instrument as well as to provide clean air for the instrument in a contaminated environment.

The Multi-gas Monitors® 1312 and 1314, manufactured by Innova Airtech Instru-ments A/S (Denmark), are examples of instruments using the photoacoustic technique. Another type of detector uses FT-IR technology to analyze liquid or solid samples. The Travel*IR*® (Figure 8.10) manufactured by SensIR Corp. has also been tested at SBCCOM under the Domestic Preparedness Program for its application in identifying unknown samples including those that may contain CWAs. The Travel*IR* is an FT-IR spectrometer that can be used to identify unknown solids, powders, pastes, gels, and liquids. The technique involves placing a sample on top of a diamond crystal (which has a high refractive index) embedded in a stainless steel disk, called the DuraDisk®. An infrared beam from the spectrometer passes through the crystal and penetrates slightly into the sample to permit analysis of strong infrared absorbing solutions, such
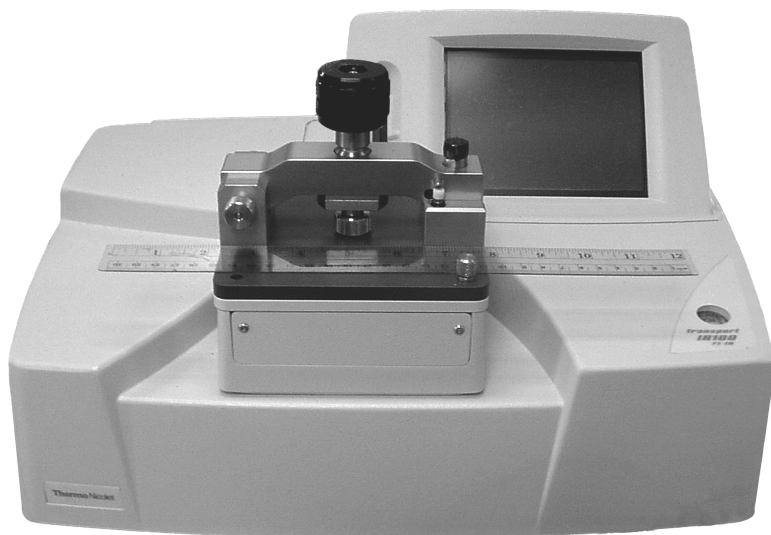

Figure 8.10 Travel*IR* Detector. Photo courtesy of K. Y. Ong.

as emulsions or aqueous solutions. The technique can also be useful for solid samples. The process is nondestructive of the sample and the instrument.

Unknown samples are identified by looking for pattern matches in reference database libraries. The Travel*IR* can identify pure substances readily and reliably with reproducibility. However, identification of a substance in a mixture is considerably more difficult. The complex spectrum from the mixture often leads to erroneous results. For example, a mixture of the nerve agent GB and diesel fuel showed a higher spectral quality value for GF (another nerve agent) than for GB itself. Perhaps this was due to the structural and spectral similarity of these two agents and incomplete compensation in the C-H (carbon-hydrogen) stretching region. The problem becomes much more complex when the CWA is dissolved in or interspersed with different substances. Therefore, the Travel*IR* should be used in conjunction with other approved CWA detectors. If the solvent containing the agent is volatile and its evaporation leaves behind a concentrated sample of CWA, the Travel*IR* can readily identify the agent. These tests led to a chloroform extraction technique tried on VX mixtures. These findings were encouraging. Perhaps, by implementation of a simple extraction process, the Travel*IR* will be much more useful for identifying potential CWAs in a mixture.

The Transport Kit® (Figure 8.11) from Thermo Electron Corp. is similar to the Travel*IR*. Testing of the Transport Kit is underway as of this writing.

Results of testing the Travel*IR* could provide insights leading to successful application of this FT-IR technology in identifying air samples. The Travel*IR* has the software capability to subtract the suspected background spectrum to isolate the substance spectrum for subsequent identification search. Such a feature may provide a means of minimizing potential interference.

Figure 8.11   Transport*IR*100 Detector. Photo courtesy of K. Y. Ong.

Unfortunately, the tested detectors based on IR techniques do not have sufficient sensitivity to detect CWAs in vapor to meet IDLH levels. Given the ability of these instruments to reliably identify targeted chemicals, they could become useful tools in assessing incidents where concentrations higher than IDLH levels are likely to exist.

8.6 FACT SHEETS FOR SELECTED IR-BASED DETECTORS

Detector Name

HAWK Long-Range Chemical Detector

Manufacturer/Distributor and Contact Information

Bruker Daltonics Inc.
40 Manning Park
Billerica, MA 01821
Tel: 978-663-3600

Technique Description

The HAWK is a portable instrument that uses infrared for stand-off remote sensing detection of a chemical cloud. It is a passive IR detector that identifies the characteristic signatures of chemicals in the near-infrared spectrum. Identification is made through spectrum matching from libraries.

Chemical Detection Capability and Performance

The detector is designed to serve as a remote sensor for the presence of CWAs and important TICs. The sensor is mounted on a tripod or on vehicles that permit 360° field of regard coverage at an angle of −10° to 50° using a spatial scanner in 3 sec. It has a spectral range of 700 to 1300cm^{-1} and a scanning rate of 20 spectra/sec at 4 cm^{-1} resolution.

Other Features

Includes visual indication of alarm through connection with a PC via the RS 422 interface using Windows-based interface displays. Audio and remote alarms are also available. Interface for network connections. The PC software graphically visualizes the detected cloud's extension and direction. Built for rugged environment operations.

Detector Name

HazMatID™/Travel*IR*-HCl™ Chemical Identifier

Manufacturer/Distributor and Contact Information

SensIR Technologies
14 Commerce Drive
Danbury, CT 06810
Tel: 203-207-9700

Technique Description

These portable instruments use infrared detection for solid or liquid chemical identification via identifying characteristic chemical signatures. Identification is done through spectrum matching from many libraries. A spectra subtraction routine permits identification of components in a matrix.

Chemical Detection Capability and Performance

The detector is designed to serve as an on-the-spot sensor for identification of unknown solid or liquid substances for the existence of CWAs, drugs, bioagents, and TICs, all within a few minutes. The HazMat ID is the waterproof version of the Travel*IR* that can identify simple mixtures through automated subtraction software. The unit can operate in hostile environments and can be immersed in decontamination solution without harm to the internal mechanism.

Other Features

Visual component identification occurs through connection with a PC or built-in Windows-based interface displays. Interface for network connection. PC software graphically visualizes the spectra for comparison.

Detector Name

Innova Photoacoustic Infrared Spectroscopy

Manufacturer/Distributor and Contact Information

Innova Airtech Instruments A/S (Denmark)
Distributor:
California Analytical Instruments Inc.
1238 West Grove Avenue
Orange, CA 92865-4134
Tel: 714-974-5560

Technique Description

These instruments comprise IR detectors using photoacoustic infrared spectroscopy for monitoring the ambient air for targeted chemical(s). Photoacoustic audible signals created from bombardment of the sample with modulated light are detected. Chemical agents are distinguished from interference chemicals by relative signals when sequentially bombarded by modulated light at different wavelengths. Interference rejection improves when more wavelengths are used to identify an unknown.

Chemical Detection Capability and Performance

The detector is designed to serve as an on-the-spot monitor for the presence of CWAs, TICs, or other chemicals within seconds. The instrument is sensitive to external vibration and humidity effects, and requires calibration in each operating environment immediately before use.

Other Features

Visual indication of component spectrum. The instrument has not been tested under the Domestic Preparedness Program.

Detector Name

JSLSCAD Joint Service Lightweight Stand-off Chemical Agent Detector

Manufacturer/Distributor and Contact Information

General Dynamics
128 Lakeside Ave.
Burlington, VT 05401
Tel: 703-414-1800 (Crystal City office)

Technique Description

This instrument is a fixed-site detector using infrared for stand-off detection of a chemical cloud. It is a passive IR detector that identifies the characteristic signatures of chemicals in the near-infrared spectrum. Identification is through spectrum matching from libraries.

Chemical Detection Capability and Performance

The detector is designed to serve as a remote sensor for the presence of CWAs and important TICs. The sensor is mounted on various platforms for ground, aerial, and shipboard operations that permit a 360° field of regard coverage at an angle of −10° to 50° using a spatial scanner. It searches the 7 to 14 micron region of the surrounding atmosphere for chemical agent vapor clouds.

Other Features

Visual alarm indicator through RS232/422 interface using Windows-based displays. Audio and remote alarms are also available. Interface for network connections. PC software graphically visualizes the detected cloud's extension and direction up to 5 km. Built for rugged environment operations.

Detector Name

MIRAN SapphIRe Portable Ambient Air Monitors Model (1, 5, 30, 30E, 100, and 100E)

Manufacturer/Distributor and Contact Information

The Foxboro Company
33 Commercial Street
Foxboro, MA 02035-2099
Tel: 888-369-2676

Technique Description

These instruments are single-person portable, single-beam IR detectors used for monitoring the ambient air for the presence of targeted chemical(s). The number of chemicals (stored in the internal library) that can be monitored is indicated by the model number. The high-numbered models offer additional features. The E series permits the user to avoid interference by nontargeted chemicals by selecting a peak wavelength that effectively filters them out.

Chemical Detection Capability and Performance

This device is designed to serve as a near real-time monitor for CWAs, TICs, or other chemicals. The instrument displays the detected chemical concentration in parts per million, parts per billion, percentage, milligrams per square meter, or absorbance units. The instrument draws in 15 L of sample per minute to fill the gas cell volume of 2.23 L. The 100E has seven fixed bandpass filters and one continuously variable filter (7.7 to 14.1 microns) together with two selectable path lengths (0.5 and 12.5 m).

Other Features

Visual indication of component concentrations. Operable in temperature range of 5°C to 40°C at noncondensing relative humidity. Serial port for linking with PC.

Domestic Preparedness Test Report

Domestic Preparedness Program: Testing of MIRAN SapphIRe Portable Ambient Air Analyzer [100E] Against Chemical Warfare Agents Summary Report, July 2000 (http://hld.sbccom.army.mil/ip/reports.htm#detectors).

Detector Name

Remote Sensing Chemical Agent Alarm, M21 (RSCAA4)

Manufacturer/Distributor and Contact Information

Tradeways Ltd.
184 Duke of Gloucester Street
Annapolis, MD 21401
Tel: 410-295-0821

Technique Description

This instrument is a stand-off type of CWA detector that uses passive IR for remote detection. It provides early warning of CWAs in vapor form, including GA, GB, GD, HD, and L from distances up to 5 km.

Chemical Detection Capability and Performance

It can detect nerve and blister agent surface contamination at approximately 90 mg/m^2 of nerve and 500 mg/m^2 of HD. Interference is eliminated by using the FT-IR detection/discrimination algorithm at 1250 to 780 cm^{-1} region.

Other Features

Audio and visual alarm indicators. Can be upgraded to detect new compounds. Operable in a field environment between –25°C to 48°C, and met military specifications.

Detector Name

Transport IR-100 Spectrophotometer Chemical Identifier

Manufacturer/Distributor and Contact Information

Thermo Nicolet Corporation
5225 Verona Road
Madison, WI 53711-4495
Tel: 800-642-6538

Technique Description

This portable instrument uses infrared detection for solid or liquid chemical identification, based on characteristic chemical signatures. Identification is through spectrum matching from many libraries. A spectra subtraction routine permits identification of components in a matrix.

Chemical Detection Capability and Performance

This detector is designed to serve as an on-the-spot sensor for identifying CWAs, drugs, bioagents, and TICs in solids or liquids within few minutes. The IR100 has a built-in computer, or can be connected to a PC. It can identify simple mixtures through the EZ OMNIC software.

Other Features

Visual indication of component identification through connection with a PC or built-in displays. Interface for network connection. The PC software graphically displays spectra for comparison. This instrument has not been tested under the Domestic Preparedness Program as of this writing.