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The Possible Relationship of Remote Sensing Technologies To BWC Verification

Executive Summary. This paper discusses state-of-the-art in remote spectroscopic detection and identification of trace effluents in the environment. The success of remote sensing techniques depends strongly on the implementation scenario and on evaluating what species are present and at what concentrations and with what optical signatures. A number of spectroscopic techniques have been successfully applied to the detection of small, isolated gas phase chemical molecules at trace levels in effluents. The detection and identification of biological materials emitted from a facility is a much more difficult undertaking than chemical molecules given the size and complexity of these materials and the nature of the processes and facilities associated with the handling of hazardous organisms. Ultraviolet fluorescence laser identification and ranging (lidar) is one technology that has been successfully demonstrated for the detection of proteins associated with biological substances in the environment. This technique is based on detecting the fluorescence signatures of amino acids in the proteins on the membrane surface of the organism. While this technique is capable of detecting the presence of these amino acids in the material, it cannot determine the identity of the overall biological material carrying the protein. In addition, fluorescence techniques must compete with the fluorescence of materials occurring naturally in the environment and with attempts at intentional masking of the target signature by the monitored party.

Introduction

The focus of this report is on the remote optical spectroscopy of gaseous and aerosol airborne effluent plumes in the environment. There are many different remote sensing technologies and numerous variations in how they are implemented to achieve high sensitivity for various target signatures. This report is intended to provide a survey of some of the relevant technologies for detecting chemical and/or biological substances and does not pretend to be a comprehensive survey of the entire field of remote optical sensing. Many fine monographs and treatises have been published and are available for further inquiry into details that are beyond the scope of this report.[1-4]

Most of the effort to date has been applied to chemical species in the plumes, either for environmental monitoring or for chemical weapons verification purposes. Some success has been achieved for specific chemical weapons related scenarios. There are extensive information gaps when attempting to apply those technologies to biological materials. A comprehensive effluents signatures study for biological warfare agent production or use has not been conducted. This has a major impact in evaluating these remote sensing techniques for application to BW. It is necessary to know what is present (both in terms of biological substances and related chemicals) and at what expected levels to determine the effectiveness and applicability of these techniques. In addition, it will be necessary to identify a suite of signatures, if present, to provide unambiguous indication of the activities and processes occurring inside the facility. Until this is done, and the optical cross-sections of the signature compounds have been measured experimentally, it is premature to judge the efficacy of optical remote monitoring technologies to BWC verification.

I. Basic Concepts of Remote Sensing

There are both general and chemically-specific remote sensing techniques. Examples of non-chemically specific techniques are radar (including synthetic aperture radar or SAR), photography, and thermal imaging. In contrast, remote optical spectroscopic sensing techniques are those that provide information about the chemical identity of the compounds. Spectral information is provided either by scanning the frequency of the excitation source, analyzing the frequency components of the return signal, or both, to provide a recognizable pattern that is characteristic of and uniquely identifiable as belonging to a particular target species. In addition, broadband frequency multiplexing techniques can be used at either the source or the detector to improve the sensitivity of the technique through parallel processing of multiple frequency components.

The electromagnetic spectrum is continuous from the radio and microwave bands through the infrared, visible, and ultraviolet regions, to x-ray and gamma ray wavelengths. More pertinent to the discussion of remote sensing are the various wavelength regions in which the atmosphere is transparent to electromagnetic radiation. These atmospheric windows are the wavelength regions in which remote sensing over useful distances is possible (see Figure 1). Outside these windows, the atmospheric constituents O_2, N_2, N_2O, O_3, CO_2, H_2O, and CH_4 are major absorbers of electromagnetic radiation making remote sensing more difficult. Various computer databases have been compiled for calculating atmospheric transmission. Most notably are the HITRAN and LOWTRAN databases from the Air Force Geophysical Laboratory (AFGL). The degree of scattering by aerosols (dust, fog, clouds, precipitation, and particulates) also affects the transmission of the atmosphere. The diameters of these aerosols range from less than a micron up to 100 microns. Scattering from aerosols increases the turbidity of the atmosphere and decreases the visibility, both to the human eye and to sensor systems. Scattering from molecules and particles in the atmosphere is a function of wavelength of the light, becoming more pronounced at shorter wavelengths.

The interactions between photons and isolated, gaseous molecules fall into three major categories. Photons may scatter elastically (with no energy exchanged, also known as Rayleigh scattering), they may scatter inelastically (e.g. Raman scattering), or they may be resonantly absorbed and possibly re-emitted (absorption, fluorescence, and phosphorescence). Scattering is a nonresonant process and occurs via a virtual excited state with an essentially zero lifetime. Aerosols can also elastically scatter photons (termed Mie scattering) if their diameters are significantly greater than the wavelength of the incident radiation. All remote sensing techniques make use of one or more of these basic interaction mechanisms.

The nature of the interaction that electromagnetic radiation takes with matter varies with wavelength. At long wavelengths (such as radio waves), in which the photon energies are too low to be absorbed by isolated molecules, the interaction is entirely due to elastic scattering. As the wavelengths become shorter and the corresponding photon energy becomes greater, additional molecular interactions are possible. In the microwave region, the photon energies are sufficient to resonantly excite the molecule between two rotational energy levels. As the photon energy increases to the infrared region, interactions can take place with molecular vibrations, and in the visible and ultraviolet regions, molecules can be excited between electronic states. Since each electronic state can have vibrational levels and each vibrational state can have rotational levels, molecular spectra become increasingly complex at shorter wavelengths. The complexity of a molecule, which influences the number of accessible energy levels, and a set of optical selection rules also affect the number of observable transitions. Thus, large molecules can have very dense or congested spectra as a result of the large number of transitions, especially in the visible and ultraviolet regions. In addition, the linewidths of the transitions and the frequency resolution of the sensor system will affect the appearance of the spectrum for a particular chemical. At low resolution, a spectrum may show unresolved bands, whereas at higher resolution, individual, isolated lines may be discerned. The chance of finding a significant number of resolvable features is more likely in the microwave and infrared regions and the locations and intensities of these transitions can form a molecular fingerprint capable of uniquely identifying a compound.

Remote sensing of effluent plumes is done relatively near the earth's surface where the pressure and density of the atmosphere (1 atm = 2.55 x 10^{19} molecules/cm^3) are highest (see Appendix). This high density near the surface means that the rate of collisions between molecules is greater than in the upper atmosphere. These collisions perturb the energy levels of the molecule and increase linewidth of a transition. This is important in spectrally resolving transitions due to other molecular species and in optimizing the overlap between the bandwidth of the source and linewidth of the molecule. Collisions also affect the excited state lifetimes since energy transfer by collision is one of several nonradiative means of de-exciting a state, in competition with the more useful (for remote sensing purposes) radiative emission.

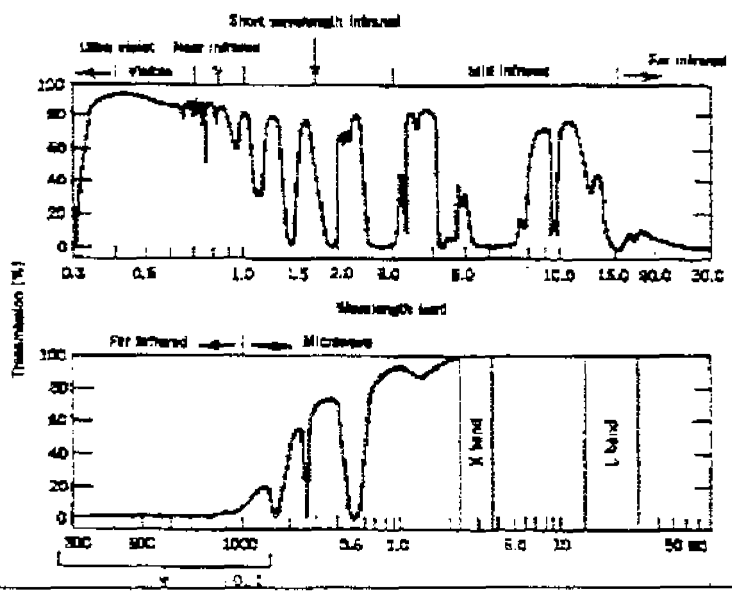

Figure 1. Generalized atmospheric transmission at low resolution.

~~II~~. Remote Spectroscopy Hardware

A generalized sensor system is composed of the following components: an illumination source, transmission optics, collection optics, a wavelength analyzer, the detector(s), and a data acquisition and reduction electronics/software package. The frequency dependence of the interaction provides the spectroscopic information necessary for chemical species identification. The spectral resolution for some active techniques is provided by the illuminator rather than the detector. A passive sensor system will not have a source, unless it is for calibration purposes, and transmission optics.

Illumination sources: Both active and passive techniques are employed in remote sensing. Passive techniques rely on natural illumination of the target by its environment, while active techniques require an user-supplied source of illumination, typically a microwave or laser source. Natural illumination can be sunlight or the ambient thermal background. Lasers are often the source of choice for active optical techniques due to their narrow bandwidth, high intensity, and the high degree of directionality associated with their output.

Lasers can be either single frequency, narrow band or broadband. Eye safety, which is determined by both laser frequency and intensity, is a consideration for remote sensing lasers. Both gas discharge (e.g. carbon dioxide), excimer (KrF, XeCl) and flashlamp pumped solid state lasers (Nd:YAG) have been used. All-solid-state lasers are being developed for increased ruggedness and higher wall-plug efficiency (the conversion of electrical power to laser output power). While fixed frequency output is sufficient for some remote sensing techniques, wavelength tunability is required for species identification in others.

The **wavelength analysis** section can be passband, gas cell, dispersive or interferometric. Passband techniques use absorption or interference filters to isolate a particular wavelength region of interest. These filters are often mounted on a rotating filter wheel in front of the detector. Gas cell techniques use a reference cell with the target gas inside for discrimination. Wavelength dispersive techniques use a grating or prism to spatial by separate wavelengths. Such spectrometers are composed of either a single detector and wavelength scanning mechanism or a multi-element array of detectors in a fixed configuration on the focal plane and no scanning mechanism. Examples of the latter type are the multispectral analyzers flown on various satellite platforms. Interferometric methods combine a single (or array) detector and a temporal (or spatial) multiplex technique. A Michelson interferometer is a common multiplexing device and mathematical techniques such as the Fourier Transform (FT) are used to derive the frequency information from the interferometer output.

Detectors are classified as photoelectric, photoconductive, and photoemissive. These different devices have different responsivities for different wavelength regions. Detectors are typically cooled to below ambient temperature to reduce internal thermally generated electronic noise.

The **system architecture** of active systems can be either monostatic (detector and source together on the same side of the target) or bistatic (detector and source on opposite sides of the target). Monostatic configurations are more amenable to fielding from an airborne platform. In addition, the system can be non-imaging (fixed point) or imaging (2-dimensional). A photograph is an example of a passive two-dimensional imaging technique. A non-imaging technique can be turned into an imaging technique by physically rastering the source and/or detector field of view across the area of interest to create an image. Spectral information is recorded for each image element in sequence. Multispectral scanning systems (MSS), thematic mappers (TM), and hyperspectral scanning systems (HSS) are examples of such scanning imagers.

Deployment platforms: Optical techniques, by necessity, require line-of-sight operation. Ground-based sensors can be employed as perimeter or point monitors at a facility. Airborne sensors may be mounted on unmanned autonomous vehicles (UAVs) or remotely piloted drones (RPVs), aircraft (0-20 km altitude), the Space Shuttle (100-300 km), or satellites (100-36000 km). See the Appendix for a comparison of operational altitudes for these platforms.

III. Passive Remote Sensing Techniques

Passive remote sensing techniques range from photographic imaging (panchromatic to color film with three wavelength bands) to multispectral, hyperspectral, and Fourier Transform (FT) methods.

Radiometry is the general term defined as the precise measurement of intensity of electromagnetic energy emmissions.

Thermal imaging is a related imaging technique to derive the effective (apparent) temperature from the thermal emissions (8-12 micron wavelength region) of a target. The wavelength dependent emissivity relates the measured thermal energy radiated by a target at a temperature to that emitted by a black body radiator at the same temperature. Current radiometric techniques are capable of measuring apparent temperature differences of 0.01 to 0.1 deg K (relative). In order to distinguish a target compound from its background, the emissivity difference and/or the temperature differential against the background must combine to yield an effective temperature greater than this level of resolution. Under some conditions, it may be able to spectrally resolve molecular absorptions with sufficient resolution in regions not saturated by other absorbers/emitters to make chemical identification possible. The Navy's AN/KAS-1 is an example of an imaging filter radiometer.

Fourier Transform Infrared (FTIR). The Army XM21 Remote Sensing Chemical Alarm is a passive FTIR spectrometer operating in the 8-13 micron band optimized to detect the use of chemical weapons on a battlefield. It is capable of detecting a warm effluent against a cold sky, but it cannot detect a plume against terrain with the same effective temperature of the target molecules. Midec Corporation (Costa Mesa, CA) manufactures a ruggedized FTIR spectrometer for field use (in either passive or active moodes).

Passive microwave detection is used to measure the characteristic absorption and emission of rotational energy from molecules in the atmosphere. This techniques can penetrate clouds and rain and can operate under day or night conditions. It also provides highly chemical-specific identification. It is capable of measuring temperature differences down to 0.01 K. In an upward looking configuration against a cold sky, the passive microwave technique has demonstrated ppb level detection at up to 40 km. In the down-looking configuration, contrasting the target plume against the terrestrial background is much more difficult.

Multispectral and hyperspectral analyzers: Satellite imaging systems, like the familiar LANDSAT imagers, are considered multispectral scanner systems with multiple wavelength channels centered on a few well-defined frequencies with narrow passbands. These frequencies and passband widths are chosen specifically to provide the most useful information toward the mission of the satellite. Due to constraints of flying onboard a satellite, including size, weight, power consumption, and data rate, only a limited number of wavelengths (6 to 10) can be covered by these imagers. Hyperspectral analyzers have been developed for satellite applications of many more spectral channels (over 100). A passive, hyperspectral spectrometer operating in the near infrared has been designed and built by researchers at Lawrence Livermore National Laboratory.[5] The spectrometer measures absorption of ground-reflected sunlight by the target plume. An echelle grating and cross dispersive element are used to generate a wavelength spectrum across the face of a two-dimensional infrared detector. The spectrometer covers the entire 2-5 micron atmospheric transmission window at the pressure limited resolution of 0.1 cm^{-1}. The spectrometer has high throughput and no moving parts, and, unlike FTIR, is not as subject to noise generated by a moving background when fielded from an airborne platform.

IV. Active Remote Sensing Techniques

In addition to the techniques listed below, sensors developed for passive use can usually be employed in conjunction with an active illumination source as well for increased sensitivity or day/night operation. Thus, by adding a broadband infrared glow bar source and a retroreflector, a passive FTIR system can be turned into a active system.

BAGI (Backscatter Absorption Gas Imager) is an imaging technique based on the absorption of the source laser wavelength by the target gas in front of a reflective background, such as a building.[6]

DOAS (Differential Optical Absorption Spectrometer) is a long-path absorption technique using a broadband (300-700 nm) arc lamp source. The broadband source does provide spectral identification and chemical analysis. The setup requires two point access on either side of target for source and the receiver or retroreflector. Thus, it is more appropriate as a ground based perimeter monitor. In addition, this technique requires the accurate measurement of small differences between two large signals (typically to at least 1 part in 10^4). Thus, it has a limited role for trace chemical species detection.

Radar is the nonspecies-specific, elastic scattering of radio and microwaves from atmospheric aerosols. Rayleigh scattering occurs if the source wavelength is greater than the particle diameter, otherwise Mie scattering occurs. The backscatter cross section is dependent on the complex index of refraction and on the physical cross section of the material. Range information is derived from the round trip time of single radar pulses.

Lidar in general is a chemically nonspecific technique similar to radar which measures the elastic backscatter of laser pulses from the target. High power laser sources such as CO_2 (line-tunable between 9-11 microns) or Nd:YAG (1064 nm) lasers have been used.

DISC (Differential Scattering LIDAR) is an attempt to make lidar more indicative of the chemical species that is back scattering the laser beam by scanning the excitation frequency to measure the variation in backscatter cross section with wavelength, particularly near a molecular absorption for the target compound. This technique is limited by fluctuations that occur during the time required to complete a scan of the frequency.

DIAL (Differential Absorption LIDAR) is an elastic laser scatter technique employing two (or more) closely spaced laser frequencies. One frequency is tuned to the peak of an absorption feature of the target compound and the other is tuned off resonance. The difference in the backscattered intensities due to the difference in absorption for the two frequencies is measured, usually with a heterodyne technique in which the two frequencies are combined to create a beat frequency. The frequencies are closely spaced so that both signal pulses are affected equally by the broader absorptions and fluctuations (on timescales greater than 100 microseconds) in the atmosphere. The two wavelengths can be generated from multiple lasers or with a single tunable laser by generating sidebands with an acousto-optic modulator.

Broadband lidar. The DIAL technique can be extended to a continuum of frequencies by using a broadband laser pulse. The broadband pulses can be generated using ultrafast (femtosecond) laser techniques. A system based on this technique has yet to be demonstrated.

Raman lidar. Among the advantages of Raman spectroscopy are its generality, since nearly all molecules have Raman active transitions. In addition, the return signal simultaneously carries all the frequency components of the Raman-active vibrational modes characteristic of the target compound. It uses a fixed laser frequency that, in ordinary Raman, can be chosen at any convenient frequency. The major disadvantage of Raman spectroscopy is that the Raman scattering cross sections are inherently very low. Shorter excitation frequencies can be selected to take advantage of the improvement in the signal with the fourth power of the laser frequency. Several orders of magnitude improvement is possible through resonance enhancement by selecting an excitation wavelength near an electronic absorption of the target molecule (typically in the visible and ultraviolet region). Even with this strong resonant enhancement, the low signal levels severely limit the range of this technique in remote sensing applications.

Laser Induced Fluorescence lidar. Fluorescence at a molecular level is characterized by the absorption of a photon followed by a short delay and the subsequent re-emission of a photon at the same or lower frequency. For an ensemble of molecules, the fluorescence emission decays exponentially and is characterized by a molecule dependent fluorescence lifetime. In addition, this lifetime is strongly influenced by the immediate environment of the molecule. At standard atmospheric pressure, collisions can be a major nonradiative (occurring without emission of a photon) pathway competing with fluorescent emission. Unfortunately, not all molecular species fluoresce and of those that do fluoresce, not all those fluoresce strongly. Large organic molecules often have strong electronic absorptions due to conjugation and aromatic rings in the molecular structure and more are likely to show fluorescence. Laser induced fluorescence has been used successfully in lidar remote sensing scenarios.[7] Despite the lack of characteristic fine structure, a spectrometric fingerprint can be obtained though the combination of the scanned excitation frequency and the dispersed fluorescence at each excitation frequency. The resulting two-dimensional plot can be used to distinguish one compound from among others in a mixture.

V. Specificity, Sensitivity and Range Considerations

Detectability is related to the signal-to-noise ratio of the measurement, and depending on the statistical correlation of the noise with the signal, the period of time over which the observation is made. It is important to distinguish between the range or standoff distance from the sensor to the target and the interaction pathlength or zone. The target is likely to be a spatially well-defined plume located at some distance from the detector. For example, a system may be desired to monitor the output from a smokestack from the facility fence line. The standoff distance could be on the order of a kilometer, but the actual region of interaction of the source with the effluent plume may be only 0.5 meter at the stack opening where the effluent concentration is greatest.

The detected signal strength depends on:

- the range between the target and sensor system
- the source intensity and directionality
- atmospheric transmission at the source wavelength
- spectral overlap with the target molecules or chromophore
- geometric overlap with plume, including the interaction pathlength
- the concentration of the target species
- absorption, scattering, or emission cross sections
- emission or scattering directionality
- atmospheric transmission of the return signal
- the field-of-view and area of collection optics
- the transmission efficiency of bandpass, dispersive, or interferometer optics for providing wavelength discrimination
- the quantum efficiency of the detector(s) at the requisite wavelengths

Sources of noise include:

- source amplitude and frequency fluctuations
- solar background or terrestrial scatter
- atmospheric fluctuations, turbulence, and scattering
- contaminants, masks, or spectral interferant molecules
- detector/amplifier electronic or thermal noise

All of these factors go into evaluating a particular technique for a specific scenario.

VI. Possible Application to BWC Verification

The techniques described above could possibly be applied to the to detection of the chemicals associated with the production of biological weapons if:

- there are actual chemicals associated with the production biological weapons production

- such chemicals are released into the environment

- the chemicals appear in sufficient quantities in effluents

- the chemicals alone represent a unique signature indicating that biological weapons production is occurring inside the facility.

In contrast to volatile chemical species, the biological materials are not small, isolated molecules, but are physically much larger and complex entities. Optical techniques are typically not capable of interacting with such large structures. Instead, a portion of the structure can be responsible for absorption (and emission) and act as an optical tag (chromophore) for the much larger molecule/structure. In biological systems, toxins, cells and spores all have proteins imbedded in the cell membrane surface. Proteins are composed of amino acids. Of the twenty most common amino acids, three have aromatic rings as part of their molecular structure. As a result, the amino acids tryptophan, phenylalanine, and tyrosine are fluorescent. These molecules can act as observable tags for biological materials which can be detected with remote sensing techniques.

The most promising work to date on the remote optical detection of biological agents has been performed using a ultraviolet fluorescence lidar system.[7] Most biological matter containing proteins will have one or more of the fluorescent amino acids present to some degree. <u>This technique will not be</u>

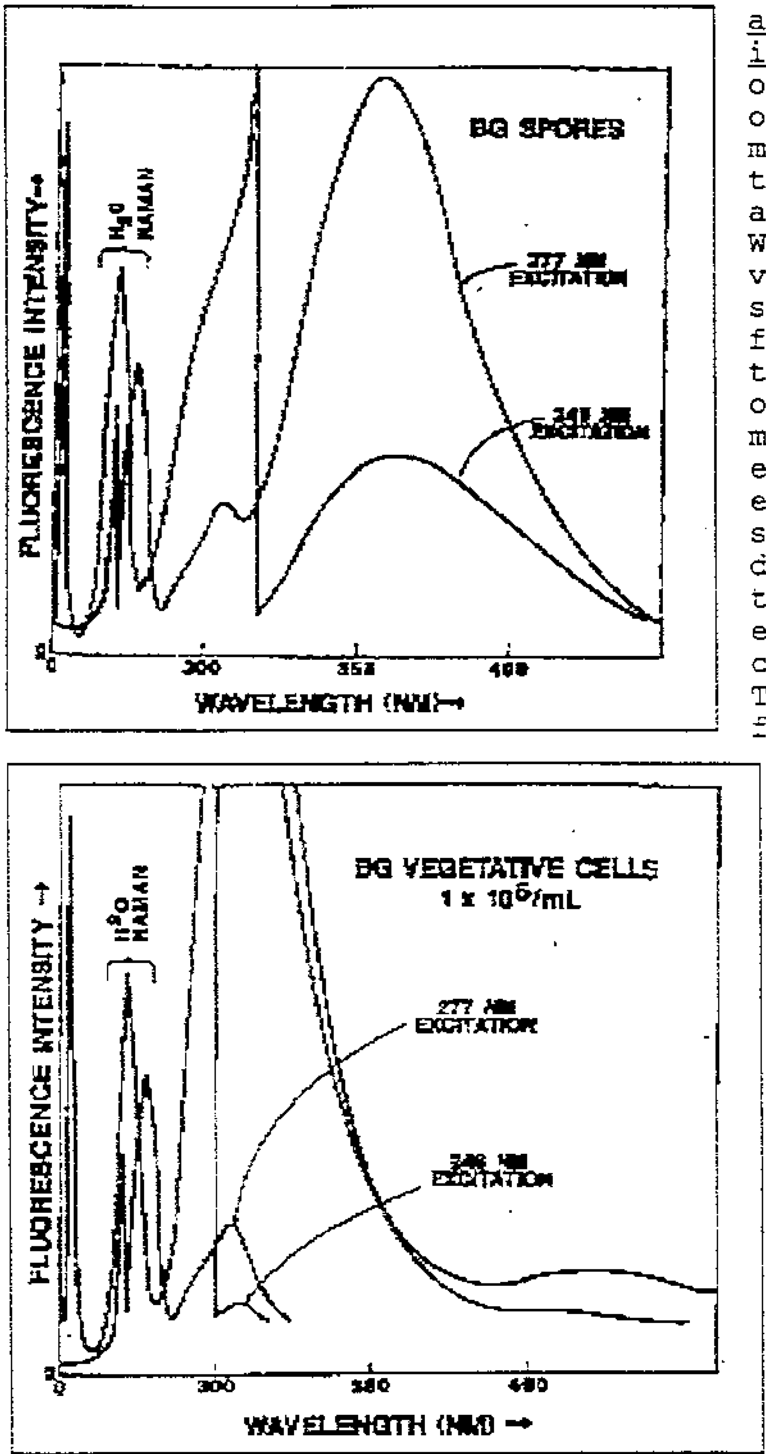

Figure 2. Tyrosine Spectra. Ref 7.

able to establish the identity of the material, only that it is some type of organic or biological material that has the target amino acid present as part of its structure. While there may be minor variations in the overall structure of the fluorescence spectra due to the local environment of the chromophores, in most cases, there is not enough information extractable for the spectra to unambiguously determine the identity of the remainder of the entity to which the chromophores are attached. The result is that fluorescence lidar, at its present state of development, can detect the presence of protein, and only if it is present in sufficient quantities. It cannot uniquely identify specific biological substances. In addition to its inability to uniquely identify biological materials, fluorescence can be easily masked by volatile organic compounds that may be naturally or intentionally present in the effluent stream at much higher concentrations than what can reasonably be expected for the biological substances themselves. Detection of biological substances in facility effluents is extremely unlikely given the high containment requirements associated with the handling of hazardous biological materials.

Remote optical sensing is an area of active research for environmental monitoring and for nuclear and chemical weapons proliferation. Among passive remote sensing technologies, the high spatial resolution multispectral and hyperspectral scanners deployed on satellites are the techniques of choice. For example, the mapping of the seasonal and year-to-year variations in the Antarctic ozone hole is conducted from space using satellite multispectral and hyperspectral imagers. Among active remote sensing techniques providing chemical species identification, DIAL and fluorescence lidar are the most commonly used. These spectroscopic techniques, both passive and active, can realistically be used for the detection and identification of relatively small, gas-phase molecules only. While these technologies can be employed for the detection of chemical effluents associated with biological weapons production, they are of limited utility for identifying the agents, cells or toxins themselves. There may be some limited scenarios in which these techniques have some utility. These scenarios are battlefield assessments or accidental release tracking (such as from the Chernobyl nuclear power plant fire and explosion) where the identity of the compound is known, the concentrations are relatively high, and information on spatial distribution of the release is of primary concern.

VII. References

1. See, for example, "Introduction to the Physics and Techniques of Remote Sensing", by Charles Elachi, Wiley Interscience, New York, 1987;
2. "Physical Principles of Remote Sensing", by W. G. Rees, Cambridge Press, Cambridge, 1990;
3. "Physical Fundamentals of Remote Sensing", by E. Schanda, Springer-Verlag, Berlin, 1986;
4. "Space Remote Sensing Systems: An Introduction", by H.S. Chen, Academic Press, Orlando, 1985.
5. C.G. Stevens and N. Thomas, "Echelle-Prism Spectrograph for Remote Sensing of Chemical Effluents at 2.5 - 4.5 Microns", SPIE Conference on Infrared Technology XVII, San Diego, July 25, 1991.
6. J.M.C. Plane and C-F Nien, "Differential Optical Absorption Spectrometer for Measuring Atmospheric Trace Gases", Rev. Sci. Instrum. 63, 1867 (1992).
7. Robert Karl and Gary Salzman, "Remote Agent Detector", Los Alamos National Laboratory, Sept. 1990.

VIII. Appendix A Aerial Remote Sensing

The density of the atmosphere decays approximately exponentially with increasing altitude out to 150 km (Figure A-1). At an altitude of 30 km, a satellite or balloon is above 99% of the Earth's atmosphere. A nadir-(straight down) looking satellite sensor views an air mass equivalent to only a 7 to 8 km horizontal pathlength on the surface. It is possible that the atmospheric attenuation may be less for a nadir-looking sensor on a satellite than for a sensor mounted on the ground or under an aircraft restricted to large standoff distances. Low earth orbits (80 to 105 minute periods) range from 200 to 1000 km above the surface. The Space Shuttle operates at low earth orbit. Geostationary earth orbit (24 hour period) occurs at an altitude of 35,800 km above the Earth's surface. While orbital height does not effect the atmospheric attenuation of a nadir-looking sensor once it is above 30 km, it does have an effect on the size of the optical footprint of the sensor on the surface (at constant source divergence or detector field of view).

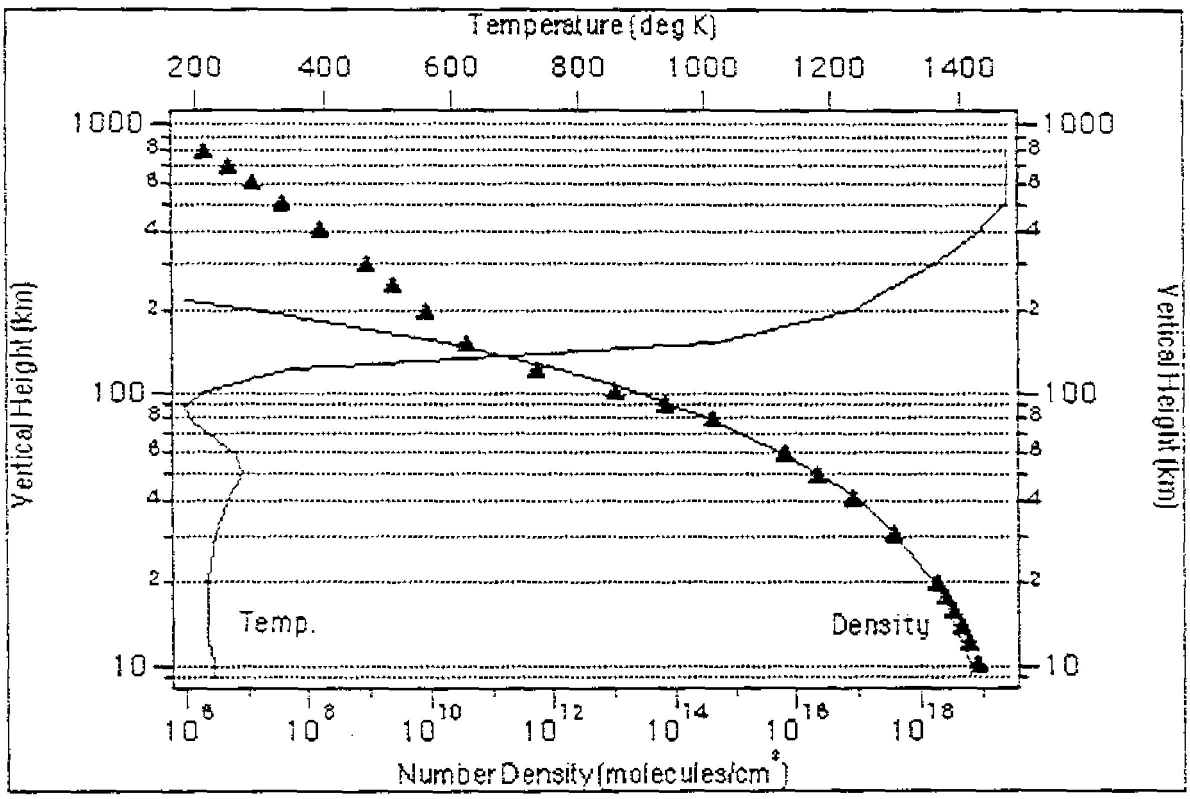

Figure A-1. International Standard Reference Atmosphere.

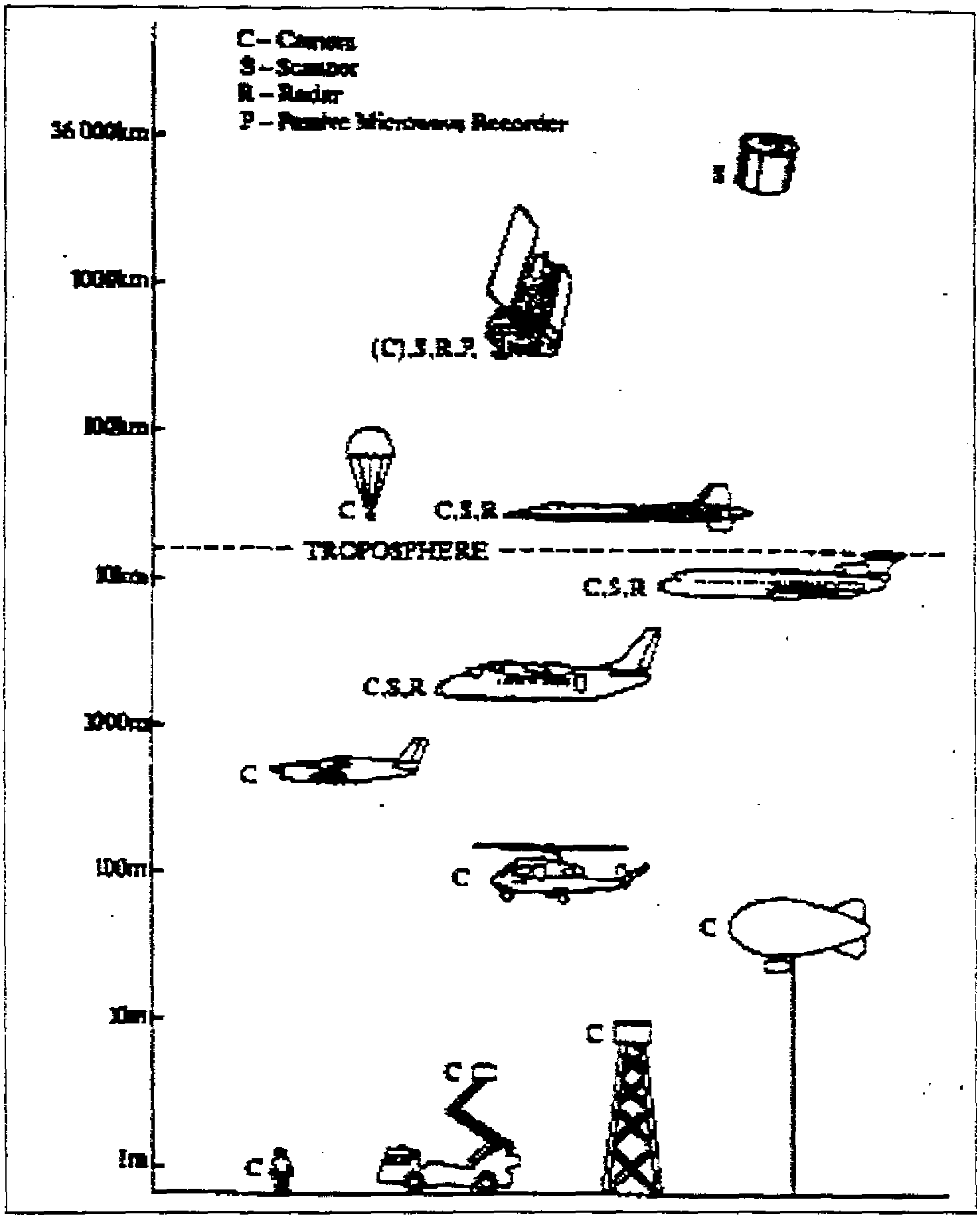

Figure A-2. Ground, air, and space borne remote sensing platforms from Ref. 4.