

АНАЛІТИЧНЕ ТА ЕКОЛОГІЧНЕ ПРИЛАДОБУДУВАННЯ

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OPTICAL CORRELATION SPECTROSCOPY FOR REMOTE CONTAMINANT DETECTION

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Recent advances in spectral correlation signal processing can enhance the detection sensitivity of spectrally complex signals, such as those generated by a Raman lidar. By means of optical correlation, the resulting optical signal is a direct measure of the similarity of the received unknown and known reference spectra, being responsive not to the intensity of individual spectral lines, but to the combination of many spectral lines thus creating an increased sensitivity. It overcomes the small cross-sections of target chemicals and makes Raman lidar practical for many important applications. In particular, the short-range, stand-off detection of explosive residue or narcotics on the exterior of packages, luggage and vehicles now appears to be possible. This paper presents the theory of operation, the results of initial proof of principle experiments and the projected performance of an optical correlation spectroscopy Raman lidar when used to remotely detect typical chemical agents in the presence of common industrial materials and natural backgrounds which could interfere with the detection process. These experiments also mark the first known instance where a received optical signal is analyzed and processed prior to photodetection.

Keywords: *spectroscopy, optical signal, Raman lidar.*

Introduction

Many applications would benefit from the ability to detect, monitor, track and/or measure the concentration of contaminants on surfaces and in the atmosphere. In the 1995 terrorist attack of the Tokyo subway, first responders spread sarin contamination over a much larger area than did the terrorists. Unaware of the nature of the attack, Tokyo's trains continued to operate and spread contamination for more than 90 minutes after the attack began [1]. The effects of the massive release of methyl isocyanate gas from the Union Carbide pesticide plant in 1984 near Bhopal, India, whether the result of sabotage or negligence, could have been minimized if recognized earlier [2].

The problems involved with the detection, monitoring, measurement and/or prediction of the spread of hazardous and lethal materials are complex and globally significant. Many techniques exist satisfying only a portion of the requirements.

Multiple research teams in multiple nations have vigorously investigated three distinct optical techniques for remote chemical detection and analysis. These techniques are: incoherent backscatter lidar - Differential Absorption Lidar (DIAL), Fourier Transform Infrared (FTIR) spectroscopy, and Raman lidar. Each has encountered technical difficulties that have prevented any large-scale use. Incoherent aerosol backscatter lidar has been successfully tested to track the dispersal pattern of chemical or biological agents [3]. However, this technology lacks the capability to analytically identify or quantify the threat without additional information or metrics. The engineering complexity of the rapidly retuned, frequency agile laser required for

DIAL has prevented its adoption for almost any non-research application. FTIR performance has been limited by interference generated by non-stationary background sources. Although adaptive signal processing techniques are promising, they remain undemonstrated for an operational FTIR chemical detection system. Raman lidar has been hampered by low sensitivity, which is a result of the small Raman cross-sections of the chemicals of interest, and by the complexity of the Raman spectra of these chemicals and interfering background materials.

Conventional Raman Lidar

The offset of the wavelength of the radiated colors from the transmitted signal (i.e., the Raman spectrum) is a characteristic of the chemical of interest. However, while the offset is fixed, the wavelength of the transmitted laser light is not. The transmitted light must be highly monochromatic, but the absolute wavelength of Raman lidar transmitter is of less significance than in other remote sensing systems, such as Differential Absorption Lidar (DIAL) systems. The transmitter in a Raman Lidar may be considerably simpler than in a DIAL system. Since all airborne chemicals are exposed to the transmitted light simultaneously, all re-radiate their characteristic Raman spectra simultaneously. Thus, multiple chemical species can be detected in parallel [4].

In a typical Raman lidar receiver, the received optical signal is separated into its component colors by a dispersive filter. Received light is separated into its component colors by a blocking filter or by a dispersion filter (e.g., a grating or a prism). The separated light is imaged onto a single detector element or onto a linear detector array. The spectral resolution of the system is determined by the filter or grating, the f-number of the imaging lens and the size of the individual detector element(s). The spectral range of a system that employs a linear array is the resolution of a single detector multiplied by the number of elements in the array. If a single detector element is used, then extending the total spectral range of the system requires scanning of the dispersion filter. The very close spacing of some Raman lines often dictates high spectral resolution. The wide spectral separation of other lines simultaneously requires a large spectral range. Satisfying both requirements necessitates a large number of detectors or long dispersion filter scanning times. Over 4000 detector elements (and in some cases 10,000) are not uncommon.

All Raman lidar architectures use a laser as the monochromatic source. Each of them has important deficiencies which prevent the use of this technique. Narrow band spectral filtering by a fixed line filter is fine if the target chemical has a strong, characteristic line in its Raman spectrum and that line is isolated from any lines produced by any possible interfering chemical. It is simple and low cost. The use of a single detector permits the selection of very sensitive photodetectors having a fast response time. The use of a fast detector with a pulsed laser permits time-resolved (and, therefore, range-resolved) chemical detection. This is the technique commonly used to measure the vertical profile of atmospheric components from a fixed site (e.g., water vapor, ozone). Unfortunately, most chemicals of interest in many other applications

are complex and devoid of any strong lines. Raman spectra generated by interfering chemical create an equally complex noise background. Narrow band spectral filtering is not effective in these applications.

The use of a scanned, dispersive filter permits the detection of the entire Raman spectra and not just a single line. It employs a single detector, which enhances detection sensitivity and preserves the range-resolved measurement capability of the narrowband spectral filter approach. However, the laser must fire at least once for each wavelength collected in the received spectra. This complicates the laser design as the transmitter must operate at a much higher pulse repetition rate in order to avoid slowing down the detection process. Furthermore, all pulses in a measurement must be transmitted before the measurement conditions (i.e., atmospheric conditions, line of sight, etc.) can change. The receiver must be retuned for each spectral line as well. The reduction in speed virtually precludes any surveillance functions.

The use of a fixed dispersive filter and a linear array of detectors solves the collection speed problem associated with the scanned filter. However, large format, multi-element detector arrays (i.e., >500 elements) lack the sensitivity and response time of single element or small format arrays. Long integration times are required to achieve acceptable signal to noise ratios. CCD detector arrays are commonly used in Raman receivers since they permit a large number of detectors with a minimal number of electrical connections. Unfortunately, CCD array elements are not highly sensitive detectors. Furthermore, the sensitivity of the system is defined by the ability to detect the weakest (critical) line in the Raman spectra. An additional disadvantage is that the range resolution of a Raman lidar is limited by the readout time of the detector array and not by the pulse length of the laser. A readout time of 10 microseconds corresponds to a range resolution of about 1.5 kilometers.

Optical Correlation Spectroscopy Raman Lidar

Optical Correlation Spectroscopy (OCS) Raman lidar transmits a monochromatic signal just as in a conventional Raman lidar. OCS [5] compares the unknown, received spectra with a known, reference signal by calculating the correlation of the two spectra. The correlation function is well known as a reliable measure of the similarity between two sets or functions. It is slightly less well known that certain properties of optics permit the calculation of the correlation function using simple imaging lenses. From Fourier analysis, it is known that the correlation of two functions, f and g , is the inverse Fourier transform of the product of the Fourier transforms of f and g . It is a property of optics that a simple imaging lens is a Fourier transform device (the Fourier transform pairs for a lens are angle and spatial frequency instead of the more familiar pairs of time and frequency). Another property from Fourier analysis is that the Fourier transform is its own inverse function. As a result, a lens may be used to perform either a Fourier transform or an inverse Fourier transform. Furthermore, the correlation of two functions may also be expressed as the inner product of two functions (or dot product of two vectors). While this property is not important in the operation of the instrument, it will be of significant importance in the derivation of optimal filters later.

Spectroscopic chemical detection and analysis systems use this basic mathematical approach, but implement it by measuring the amplitude of each spectroscopic line individually using a photosensitive detector and then calculating the correlation with known reference spectra using digital electronics. However, in OCS, the calculation is performed directly on the received light before it is measured by a photodetector. This is an analog calculation performed in the optical domain. The photosensitive element in the receiver no longer measures the spectra of the incoming light. Instead, it measures the result of the calculation that compares the incoming light to the stored reference [6, 7]. Applying this technique to Raman lidar corrects many of the limitations of previous systems.

The OCS receiver first disperses the Raman spectrum with a grating or prism as in a conventional Raman receiver (Figure 1). The Raman spectrum of an unknown sample is then imaged (i.e., Fourier transformed) onto a semi-transparent filter that contains the Fourier transform of a known material. The light that passes through the filter performs the equivalent of an analog multiplication. If this light then passes through a second imaging lens, this lens will perform an inverse transform. The result is an analog calculation of the correlation of the received spectra with a known reference. The resultant appears as a single focal spot whose intensity is proportionate to the amplitude correlation function (i.e., the similarity of the unknown spectrum to the known reference). A single detector may be used to detect the brightness of this spot. No additional processing is required. By training of filter, this similarity measure can be calibrated to indicate the concentration of any desired chemical species.

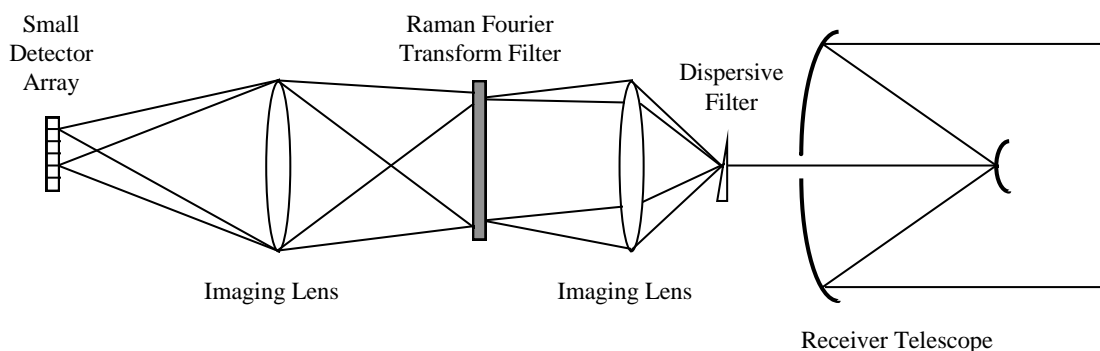


Figure 1. Schematic of receiver of the Optical Correlation Spectroscopy lidar

The filter plane may contain multiple filters, each having the Fourier transform of the Raman spectrum of a different chemical of interest. One detector is then required for each chemical of interest. Since only a small number of detectors is required, system design allows for more sensitive and faster detectors to be used. Furthermore, since all lines from the Raman spectra from a single chemical species are focused onto a single detector, the amplitude of the light to be detected can be much larger than it would have been even for the strongest line in the Raman spectra, if detected individually. This circumvents the detection limit that is created by the weakest, critical spectral which must be detected by a conventional Raman lidar receiver. These two effects can increase the detection sensitivity by 1000 times or more.

These higher sensitivity detectors may also have faster response times. The range resolution of a Raman lidar is no longer limited by the readout time of the receiver. Higher spatial resolution may then be achieved.

Filter Design

The simplest filter is the Fourier transform of the spectrum of the chemical of interest. This filter is optimum only for single chemical species in the presence of broadband, white noise. More advanced filters are required to efficiently differentiate between similar chemical species or to detect a desired chemical in the presence of non-white noise. Filter training is then required in order to discriminate for spectra of interest and against all probable interferants. The spectral correlator filter, therefore, forms a linear discriminant in the optical domain and detects the result. A linear discriminant has the form

$$L = \sum_{i=1}^N w_i s(v_i),$$

where L = the linear discriminant
 w_i = elements of a weighting function
 i = summation index
 $s(v)$ = samples of the Raman spectrum

L is a number such that target species have high L and interferant species have low L . Again we either detect N samples and compute L electronically or compute L optically (before detection) and simply detect the answer. As N is typically between 100 and 1000, the spectral correlator has obvious advantages. If a single linear discriminant with a weight vector given by $\mathbf{w}_\alpha = (w_1, w_2, \dots, w_N)$ is used on a spectral vector $\mathbf{s} = [s(v_1), s(v_2), \dots, s(v_N)]$ to form $L_\alpha = \mathbf{w}_\alpha \bullet \mathbf{s}$, we may or may not achieve good discrimination. For example, broadband background sources can generate significant values of L . However, signals of this type are equally well correlated with orthogonal signals as well. If needed, we can calculate a second weight vector, \mathbf{w}_β , such that $\mathbf{w}_\alpha \bullet \mathbf{w}_\beta = 0$ and forms a second discriminant, $L_\beta = \mathbf{w}_\beta \bullet \mathbf{s}$. The $L_\alpha - L_\beta$ space offers improved discrimination. More discriminants may be added (up to N) as needed.

It should be noted that in many Raman systems (e.g., atmospheric Raman lidars), determination of the presence of a particular chemical species is made by detecting received light at a single wavelength that is highly characteristic of the particular chemical species of interest. This is actually a degenerate case of a linear discriminant and corresponds to $N = 1$ and $w_1 = 1$. Preliminary investigation of the Raman spectra of explosives and chemical warfare agents of interest indicates that N should be typically between 100 and 1000. The Raman spectra of several, common explosives are shown in Figure 2. However, all previous systems have been based upon $N = 1$. A spectral correlator has an obvious advantage if all of this information is to be used in the discrimination process.

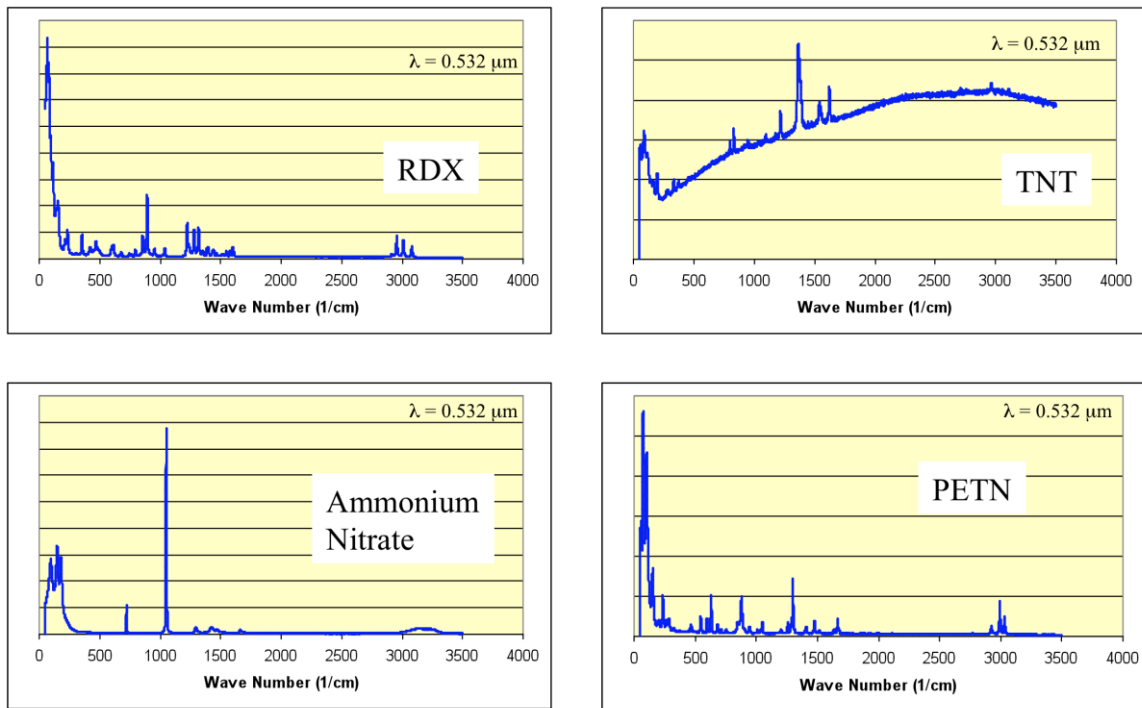


Figure 2. Raman spectra of common explosives filter optimization

Ideally, the mask or filter used to identify any particular chemical species is orthogonal to the filters used to recognize any other chemical. This is non-trivial as the spectra of many important chemicals are similar (i.e., they are non-orthogonal functions). Orthogonal filter sets may be developed by many procedures. In principle, the filter weights can be nonnegative, real, or complex. Recent work [8] has shown that nonnegative weights work extremely well, and are the easiest to implement optically.

Experimental Results

Laboratory measurements were conducted to validate the concept of the optical correlation spectroscopy. The concept of the experiment is shown in Figure 3. Materials placed in the sample container were illuminated by an Argon laser source. The Raman scattered light was then collected by an optical system placed at right angles to the laser illumination path. This maximized the signal to noise ratio (SNR) by minimizing the Rayleigh scattered signal. Raman scattering is omnidirectional, so the intensity of the Raman signal was unaffected by the choice of geometry. The Raman signal was then passed through a dispersive element and was then imaged onto a spatial filter. The spatially filtered signal was then re-imaged onto a detector array.

The specimen consisted of individual chemical compounds, mixtures of similar compounds, and mixtures of similar compounds in the presence of interferants. Since the objective of the test was to demonstrate the ability to identify individual chemical species, and to demonstrate the ability to quantify the concentration of these species in mixtures and in the presence of broadband noise generated by interferants, similar chemical species were chosen.

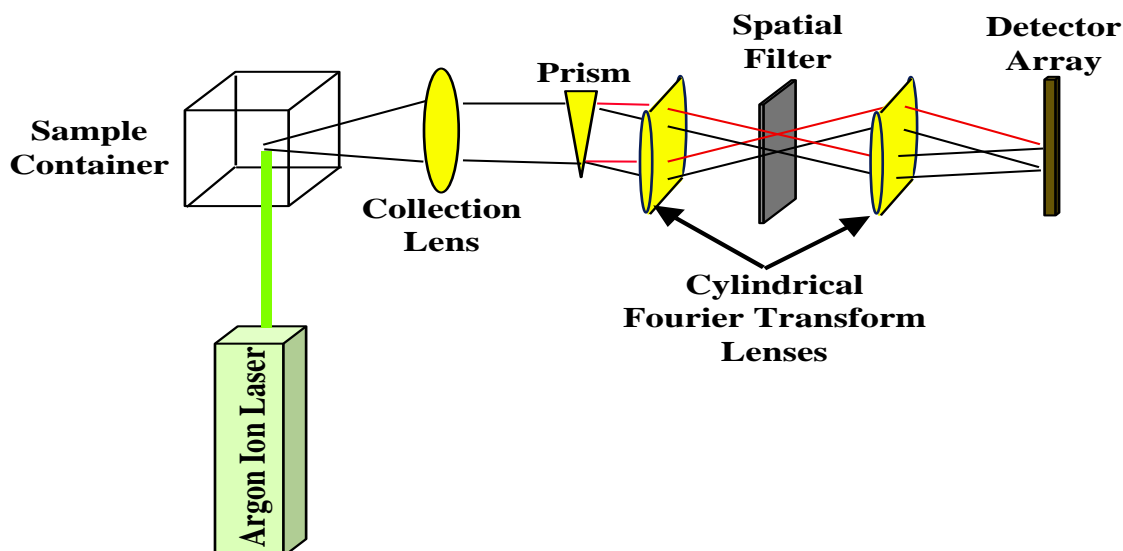


Figure 3. Optical spectral correlation proof of principle experiment

The filter was constructed to maximize the ratio of the intensity of Raman scattered light which passes through the filter to the intensity of background and other noise sources. If the background consisted of only uniform broadband noise (i.e., white noise), then the filter would consist of the Fourier Transform (i.e., the image) of the Raman spectrum of the chemical species of interest. Interferants require that the optimal filter deviate from the simple and familiar case of the “matched filter.”

In the absence of any interferant or background sources, the electrical signal produced by the detector will be proportional to the concentration of the chemical of interest in the specimen. The presence of background sources or interferants introduces a complication. In this case, two, separate filters may be required in order to separate broadband white noise from the signal. If this is the case, then the concentration of the chemical of interest will be proportional to the difference between the signal produced by the two detectors which are used to detect the intensity of light which passes through the two filters.

Ethanol and methanol system were selected as the candidate materials for the experiment. These two solvents were chosen because they can be mixed in any arbitrary concentration ratio, have limited toxicity, and have overlapping, sufficiently complex peaks in the spectral region chosen for study. Raman spectra of ethanol and methanol in the 2800 to 3000 cm^{-1} range are shown in Figure 4.

Test Setup

A Spex Model 1402 double monochromator was modified in order to function as an optical spectral correlator. The modification consisted of replacing the exit slit of the monochromator with a laboratory-built adapter, which was designed to hold the correlator masks in the focal plane of the instrument. The masks were prepared on 1" glass microscope slides, and could be inserted into the adapter through a slot in the top. The masks were prepared by taping the regions of the microscope slides which

were to remain transparent, spraying one surface of the taped slide with flat black paint, and then removing the tape.

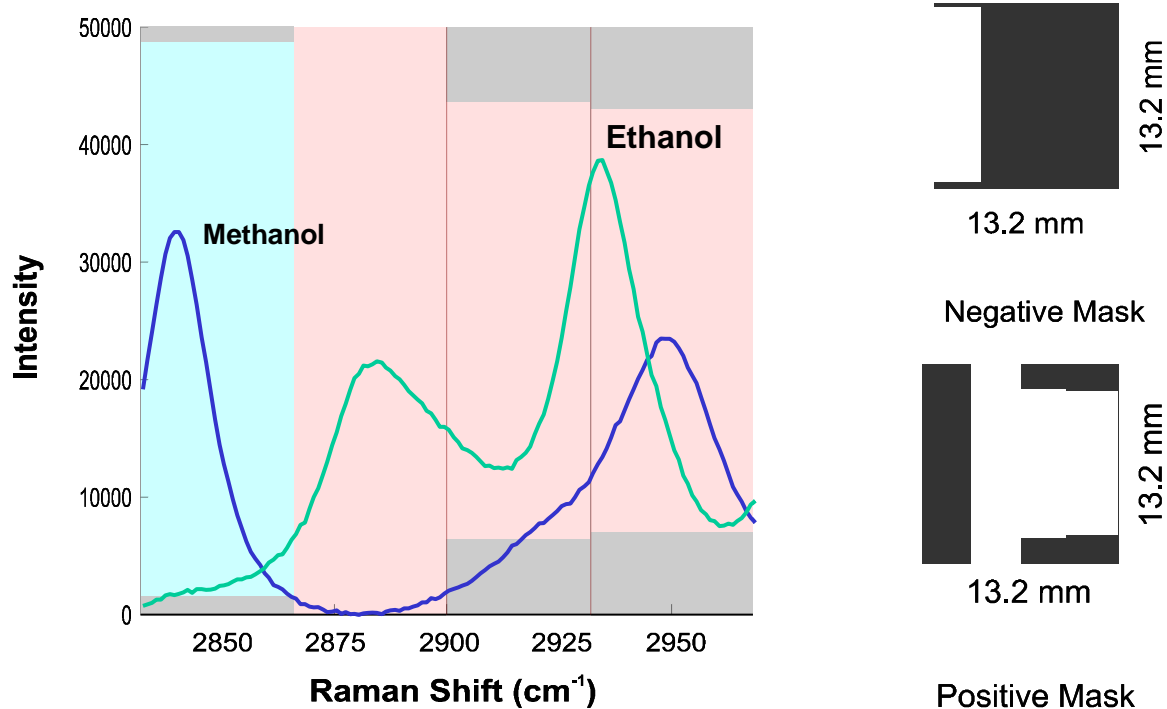


Figure 4. Raman spectra of ethanol and methanol showing four spectral segments and transmittances of positive (pink) and negative (blue) masks

The total area of the masks was determined by the dispersion of the monochromator, the area of the PMT photocathode, the entrance slit height, and the magnification (or demagnification) produced by the two lenses in front of the PMT. These same factors (with the exception of the slit height) also defined the width of the spectral region which could be “seen” by the detector. The combination of these factors resulted in a mask size of 13.2 x 13.2 mm, which corresponds to a spectral range of 136 cm^{-1} .

All spectral correlator data were taken with the monochromator centered at 2900 cm^{-1} (relative to the laser line), which resulted in a spectral range from 2832 - 2968 cm^{-1} for the analysis. In order to simplify mask preparation, this range was divided into four equally spaced segments, each having a spectral width of 34 cm^{-1} . Figure 4 also shows the four segments used in the mask calculation. The transmittances of the positive mask (pink) and the negative mask (blue) are overlaid on the spectra. Reproductions of the two masks are shown on the right in Figure 4.

Test Results

Results for a series of ethanol/methanol mixtures were obtained by inserting the positive mask and reading the total counts from the computer screen (Positive mask throughput). The positive mask was then removed, the negative mask inserted, and the total counts again read from the computer screen (Negative mask throughput). The normalized difference between these two numbers gave the measured ethanol

concentration in percent. These data are presented graphically in Figure 5 with a best fit linear regression.

Based upon a series of trials in which, for the same concentration, a mask was repeatedly removed and reinserted, we determined that the major contribution to the scatter in the data is poor reproducibility in the positioning of the mask.

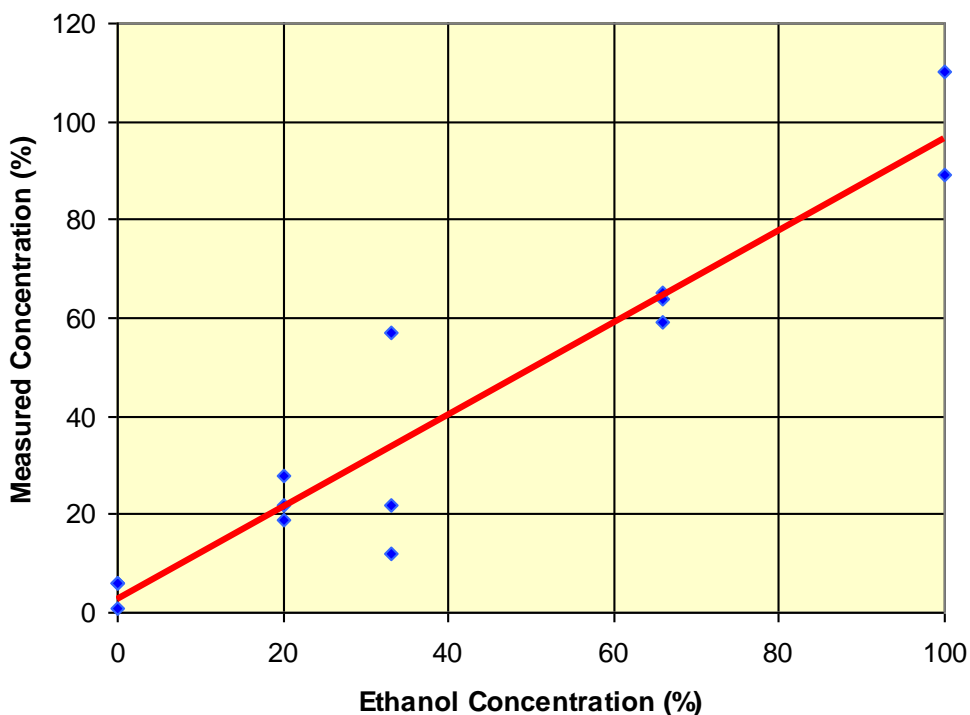


Figure 5. Proof of Principle Experiment Results

Applications

As previously mentioned, any law enforcement and military applications could benefit from remote chemical detection and analysis. Many of these applications do not require on-site identification or quantitative analysis. Rather, a simple determination that a chemical of interest is present is sufficient for many applications.

As previously noted, an ideal filter would generate no response for a material which is not the object of interest. This would imply that the dot product between the spectra of an interfering material and the filter is very small (i.e., their spectral vectors are nearly orthogonal), while the dot product between the spectra of the targeted material and the filter is very large (i.e., their spectral vectors are nearly parallel). This gives rise to a very interesting property. If individual filters are designed to be orthogonal to a common set of interfering materials (e.g., sunlight, water vapor, known pollutants, etc.) but highly sensitive to a specific chemical of interest, then the sum of any two or all of these filters will still be orthogonal to the same common set of interferants. Such a sum filter will also still have a larger response for any of the specific chemicals of interest. A sum filter of this type will be able to detect the presence of any of the interesting chemicals from the training set, but it will not be able to identify which one was present without additional filters to further screen the sample.

Figure 6 shows the design of a filter designed to detect multiple explosives, including RDX, TNT, PETN, EGDN, KNO_3 , and NH_4NO_3 over the spectral range from 300 cm^{-1} to 1700 cm^{-1} . Furthermore, this filter is designed to be orthogonal to background noise and common interferants, including water, common petrochemicals (kerosene, Diesel fuel, gasoline) and solvents (e.g., ethanol & methanol).

The Persian Gulf War also demonstrated the need to track the dispersal of toxic materials on the battlefield. Chemical warfare agents, dispersed when an Iraqi munitions dump was destroyed, have been linked to numerous medical conditions experienced by military personnel downwind of the dump. Detection and tracking of this toxic cloud could have permitted defensive actions that would have reduced or eliminated injury to the coalition forces. Although this dispersal was not the result of the intercept or detonation of a ballistic missile, the same conditions could have been generated by the intercept of a chemical warhead. A comprehensive post intercept debris cloud assessment must, therefore, include chemical composition and concentration. Toxic debris dispersal tracking is required for efficient defensive management.

More severe conditions may be generated by a successful chemical weapons attack. Such an attack could have a debilitating effect upon the performance of theater ballistic missile defense assets. The ability to characterize, quantify, track and thereby plan defensive strategies is an important part of ballistic missile defense.

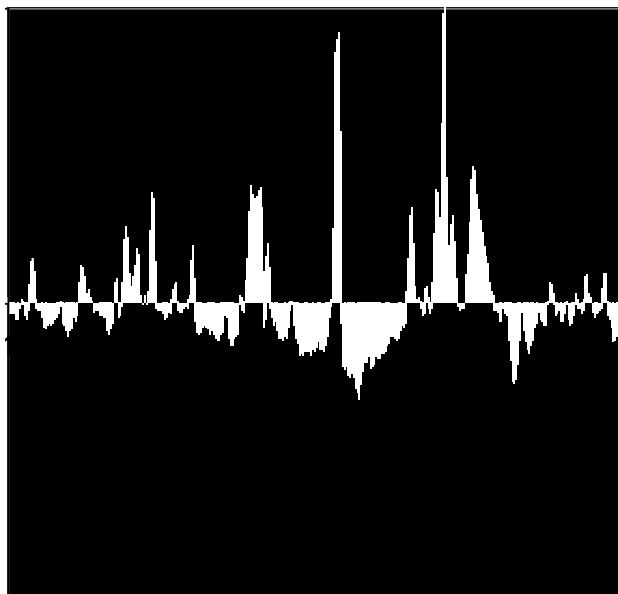


Figure 6. Prototype OCS Detection Filter for Multiple Explosives

Other, potential applications include:

- short range detection of drugs and explosive contamination as surfaces for law enforcement;
- large area and point of origin (e.g., smoke stack) pollution measurement and mapping;
- detection of camouflage by the absence of chlorophyll or related compounds;
- identification of friend or foe from externally applied or indigenous taggants;
- post-intercept debris cloud chemical analysis;
- contamination detection for emergency management or environmental clean-up;
- short range (5 to 10 meters) detection of narcotic or explosive residue on the exterior of packages, luggage, containers or vehicles;
- chemical and/or biological warfare agent detection, measurement and tracking for military or counter-terrorists operations; and

- surveillance and reconnaissance.

Conclusions

The concept of operation of the Optical Correlation Spectroscopy Raman Lidar has been presented and the validity of this concept has been experimentally demonstrated. The technology appears to have utility for a wide range of military, law enforcement and civil defense applications.

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