Dual-Excitation-Wavelength Resonance-Raman Explosives Detector

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ABSTRACT

Deep-ultraviolet resonance Raman spectroscopy (DUVRRS) is a promising approach to stand-off detection of explosive traces due to: 1) resonant enhancement of Raman cross-section, 2) λ^{-4}-cross-section enhancement, and 3) fluorescence and solar background free signatures. For trace detection, these signal enhancements more than offset the small penetration depth due to DUV absorption. A key challenge for stand-off sensors is to distinguish explosives, with high confidence, from a myriad of unknown background materials that may have interfering spectral peaks. To address this, we are developing a stand-off explosive sensor using DUVRRS with two simultaneous DUV excitation wavelengths. Due to complex interplay of resonant enhancement, self-absorption and laser penetration depth, significant amplitude variation is observed between corresponding Raman bands with different excitation wavelengths. These variations with excitation wavelength provide an orthogonal signature that complements the traditional Raman signature to improve specificity relative to single-excitation-wavelength techniques. As part of this effort, we are developing two novel CW DUV lasers, which have potential to be compact, and a compact dual-band high throughput DUV spectrometer, capable of simultaneous detection of Raman spectra in two spectral windows. We have also developed a highly sensitive algorithm for the detection of explosives under low signal-to-noise situations.

Keywords: Deep Ultra Violet, Resonance Raman Spectroscopy, Dual Excitation Wavelengths, Explosive Detection, Detection Algorithm.

1. INTRODUCTION

Some of the key challenges in standoff detection of explosives [1,2] arise from the myriad of unknown background materials, especially in situations where only minute quantities of explosives are present. DUV Resonance Raman spectroscopy (DUVRRS) [3,4] has very high specificity, compared to other single-modality stand-off detection techniques [5]. Despite this, challenges from interferant materials under low signal conditions place a high demand on DUVRRS stand-off sensor performance metrics such as selectivity and sensitivity.

Resonance Raman spectroscopy [6] refers to highly enhanced inelastic scattering of molecular species when excited by laser radiation that is overlapping with the absorption band of the molecule. Raman excitation wavelengths in the DUV region between 200 nm and 260 nm overlap with electronic resonances of explosive molecules. A DUVRRS technique is of great interest for stand-off detection of energetic materials due to several key advantages. First, the Raman cross-sections of a number of explosive materials are known to show several orders of magnitude enhancement [7] when excited in the DUV compared to the visible and infrared spectral regions due to the resonance effect. The fourth power dependence of Raman cross-section [8] on the excitation frequency further enhances the cross-section. On the downside, DUV radiation has less ability to penetrate and is more easily absorbed in solid samples compared to visible and infrared wavelengths. These negative effects are easily compensated for by the large cross-section increase (due to resonance and λ^{-4} dependence), resulting in several (two or more) orders of magnitude net signal enhancement for solid trace residues. In the DUV spectral region, most solids and liquids exhibit no fluorescence background [9] because molecules excited to their singlet states by the DUV light return to their ground states via non-radiative processes. The DUV region is also free from solar radiation interference.

Under funding from the Office of Naval Research, WVHTC Foundation is developing a new sensor technology that is based on DUVRRS implemented with a dual-excitation-wavelength source and simultaneous detection of Raman photons with a two-band spectrometer. The research project is called Dual-Excitation-Wavelength Resonance Raman Explosive Detector (DEWRRED).

The DEWRRED technique evolved from our earlier work on multiple excitation wavelength (MEW) resonance Raman detection of explosives [10], funded by the Department of Homeland Security. In the earlier work, we thoroughly characterized the DUVRRS responses of fifteen explosives and sixteen background materials at four DUV wavelengths (213 nm, 229 nm, 238 nm, 244 nm, 248 nm, and 266 nm) to better understand the potential performance of MEW-based standoff explosives sensors. According to the 2011 DIA report on Home Made Explosives (HME), 18 out of 43 commercially available inorganic fertilizers can be converted to HMEs with easy or moderate difficulty. Since the functional groups used for explosive detection in HMEs and fertilizers are the same, single-excitation-wavelength (SEW) Raman spectroscopy sensors are easily confused, despite being the best among single modality standoff sensors. Using multiple-excitation-wavelength (MEW) resonance-Raman spectroscopy we experimentally demonstrated the potential for significant improvement in specificity and sensitivity. Improvement to sensitivity and specificity was seen even with a dual-excitation-wavelength (DEW) approach.

Measurements of MEW signatures and experimental verification of specificity were performed [10] by measuring intensity-calibrated Raman spectra using a sequentially tuned Ar^+ laser and sequentially tuned spectrometer. These measurements also demonstrated the feasibility of detecting explosives from a 33-foot standoff distance, with a dwell time of < 1 sec for TNT and < 100 msec for ammonium nitrate, using a sensor system with 17% efficiency and 10 mw of laser power. In the current effort, we are building a DEWRRED sensor with two continuous-wave (cw) DUV lasers, a single dual-band spectrometer and a collection system. We have also developed a sensitive algorithm for the DEWRRED sensor.
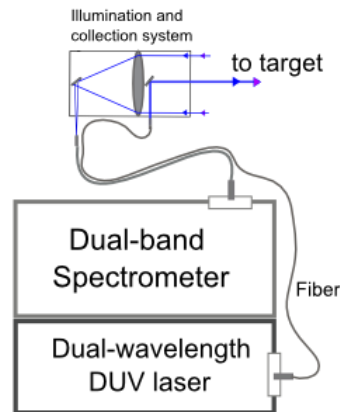
2. DUAL EXCITATION WAVELENGTH CONCEPT

Figure 1: Concept of multiple-excitation-wavelength deep UV resonance Raman detection scheme.

The DEW resonance Raman technique uses a dual-wavelength DUV source with collinear excitation beams of two wavelengths directed onto a sample and a dual-band detection spectrometer that measures the two Raman spectra simultaneously. The collection optics can be a combination of lenses or mirrors with appropriate filters to reject Rayleigh scattered light. A schematic of the DEW concept is shown in Figure 1. An important requirement for the DEWRRED sensor is the simultaneous detection of the dual excitation spectra from a single interrogation area. This ensures that any spatial variation of explosive fill-factor in the sample, or any time-dependent phenomena, such as motion or degradation present in a real detection scenario contribute equally to measurements at both of the excitation wavelengths.

The Raman scattering intensity from an explosive depends on its Raman cross-section, laser penetration depth and the resonance Raman self-absorption. Resonance Raman cross-sections and the absorption of both the excitation and scattered light vary strongly with excitation wavelength. This results in detected Raman band intensities that depend on excitation wavelength in a complex way, forming unique signatures for different compounds (for example see Figure 2). DEW signatures can be constructed as a combination of spectral peak positions (i.e. Raman frequency shifts) and the ratio of the band intensities measured at the two-excitation-wavelengths.

As discussed above, the DEW sensor exploits the orthogonal information from the additional excitation wavelength to improve specificity. As an example to illustrate this, experimental measurements performed on AN, ANFO and Watergel at 229 nm and 244 nm excitation are shown in Figure 2. The figure illustrates the additional band intensity variation information in DEW measurements, which is absent in SEW measurements. The band intensity variations are unique to each material and allow us to distinguish one from the other and from non-explosive nitrates. As mentioned earlier, these complex variations arise from the Raman scattering intensity dependence on Raman cross-section, laser penetration depth and the resonance Raman self-absorption. For solid explosives, the laser penetration depths in the DUV are very small, and thus these variations form a repeatable and unique signature, even for very thin explosive residues.
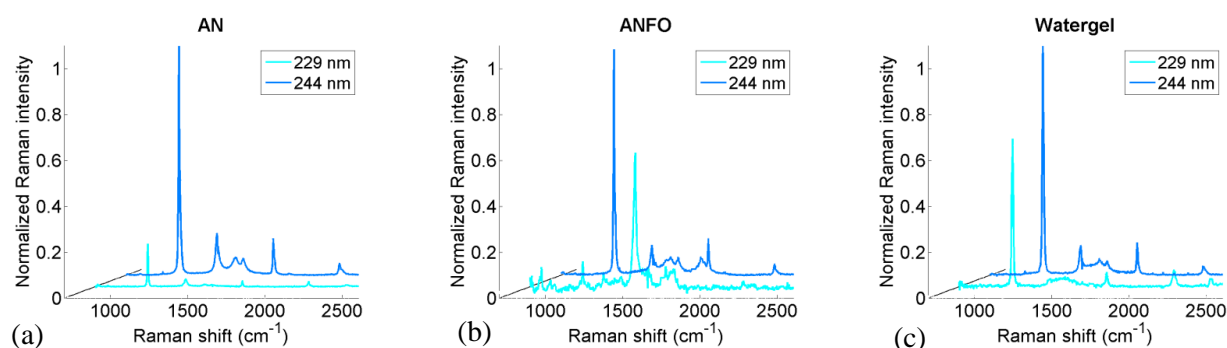

Figure 2: Example of a DEW measurement of (a) Ammonium Nitrate (b) ANFO and (c) Watergel. Using only the 1042-cm^{-1} band intensity at each excitation wavelength, these nitrate explosives can be identified and distinguished from other non-explosive nitrates/fertilizers and from each other.

We measured such signatures for a variety of explosives and demonstrated the value of the DEW approach for explosive detection. Using the combination of band-position and band-intensity as signatures, various explosives could be clearly distinguished from one another and other interferants [10]. A single-excitation-wavelength technique lacks the relative band-intensity information and thus such separation was not possible. For example all nitrate explosives and nitrate based fertilizers would look similar due to similar peak locations.

In the current effort, the DEWRRED sensor under development uses a compact dual band spectrometer and two solid-state DUV sources with potential to be made compact. While the current versions of the lasers and spectrometer are intended initially for a laboratory prototype, the technical approaches were chosen to be consistent with a compact, rugged prototype that will be developed in the later Phases of the project.

3. DUV LASERS

Development of compact DUV lasers are a central part of the DEWRRED effort. Prior to the current effort, we extensively surveyed cw DUV sources for Raman spectroscopy and did not find any compact, high-power, commercial cw DUV sources that are suitable for field use. Currently available commercial cw sources include Argon ion or Krypton ion lasers (very bulky >150 lbs), hollow cathode lasers (produce very low power), and harmonics of infrared pulses (unsuitable due to wavelength choice or are bulky).

In the current project, we have developed a power-scalable, turnkey DUV laser system that can be made compact and has the potential to meet all the requirements of field use. We have already built the first prototypes of the DUV lasers at 257.5 nm and 236.5 nm by coupling diode-pumped solid-state CW blue/green laser sources at 515-nm and 473-nm wavelengths to external resonant-cavity second harmonic generation (SHG) units, to produce coherent DUV light. The highest DUV conversion efficiency seen with the first prototype lasers is ~2% (2mw DUV from 100 mW green). Figure 3 shows the current laboratory breadboard setup of the lasers.
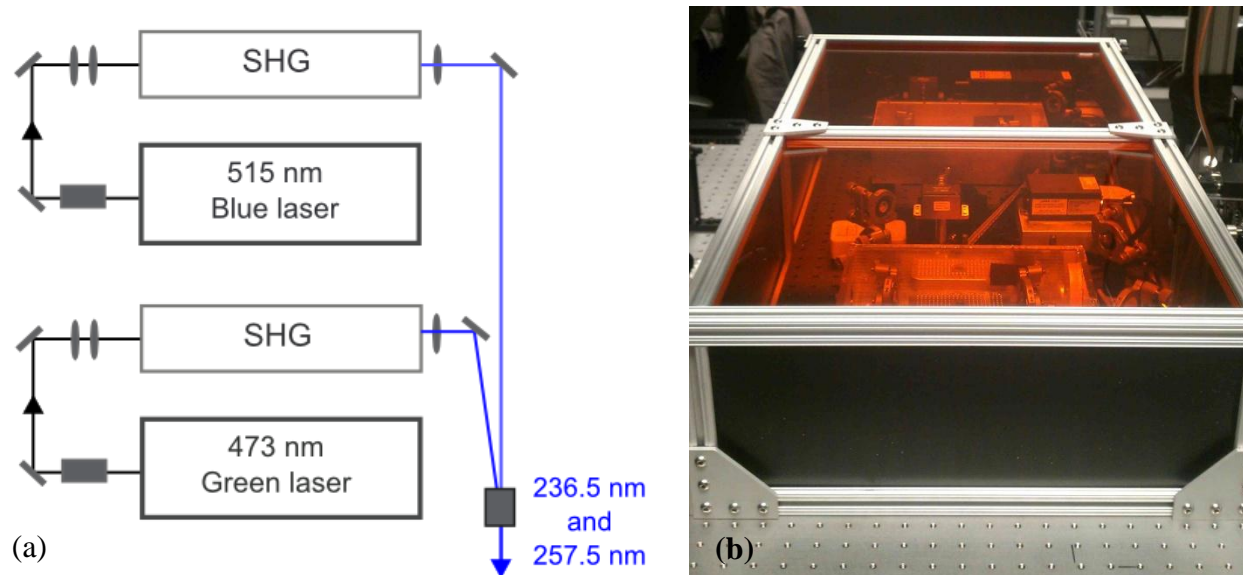
Figure 3: (a) Schematic of a dual-excitation-wavelength deep-UV laser source. (b) First breadboard prototype of the laser source. The approach should scale well to very compact designs in later phases of the project, a key factor to allow the development of a man-portable field sensor.

The beam sizes of the two lasers are shaped appropriately and combined into a collinear beam before directing them to the target illumination optics.

While the first generation prototype of each laser head occupies a footprint of 18"x18" on an optical bread board, the second generation prototype designs, currently under development, are anticipated to be highly compact with a foot print of less than 2"x4" each. The cw DUV power of each laser needed for the final system is anticipated to be in the 10-mW range.

4. COMPACT DUV SPECTROMETER

Figure 4 shows a picture of the spectrometer designed as part of the DEWRRED sensor. The spectrometer design was based on transmission gratings and fused silica optics. The overall throughput of all the optical components, including the input fiber bundle was designed to be >55%. All optics, including the gratings, in the spectrometer were built based on a custom design. The effective theoretical efficiency of the entire spectrometer including quantum efficiency of the CCD was ~25%. The spectrometer has a spectral range from 241 nm to 272 nm. Part of the central region of this range was blocked by custom designed Rayleigh filters in the collection system. The remainder of the range was sufficient to cover the fingerprint regions of the Raman spectra for both the excitation wavelengths. The design resolution of the spectrometer is shown in Figure 4(b). Over the entire spectral range, the resolution varies between 29 cm^{-1} to 34 cm^{-1}. The spectrometer was tested with Raman scattering using a single excitation wavelength at 244 nm. The measured resolution agreed closely with the design resolution. The spectrometer showed low scatter and could be operated in the presence of the room lights. The mechanical design of the spectrometer housing was not optimized for size, weight and power in this phase of the project. The optics (not including the CCD) can potentially be housed in a size of 10 x 12 x 4 cm^3. The unoptimized weight of the spectrometer was 6.6 lbs.
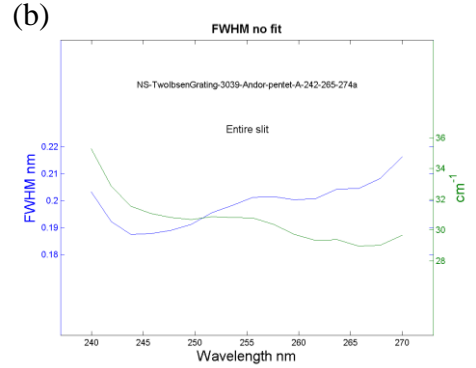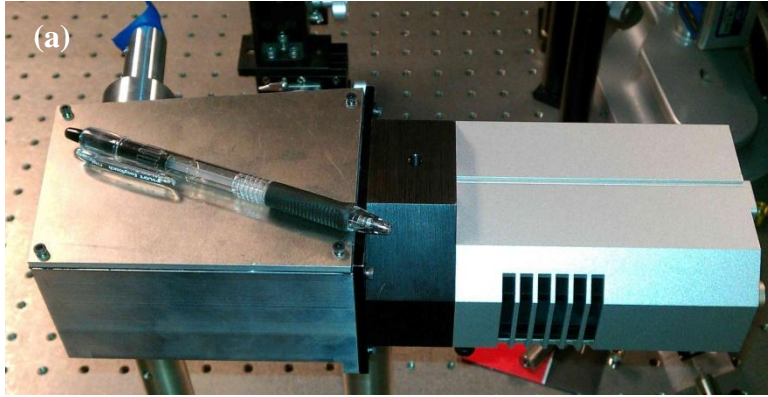
Figure 4: (a) Picture of the high-throughput dual-band DUV spectrometer. (b) Theoretical resolution of the spectrometer design.

5. ILLUMINATION AND COLLECTION SYSTEM

An illumination and collection system for the DEWRRED sensor is currently under construction. The system is based on a reflective primary mirror with optics for filtering Rayleigh scattering near the collection fiber bundle. All the optics are custom designed and built. A picture of the laboratory setup being built is shown in Figure 5. The collection system is designed to image an illuminated target spot from distances of 5 ft to > 50 ft.
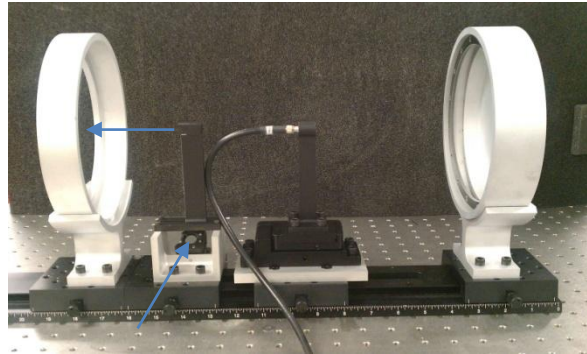

Figure 5: Illumination and collection system for the laboratory DEWRRED prototype.

6. ALGORITHM

In our previous work [10] we had developed an algorithm based on peak positions and peak ratios for determining the presence and type of an explosive from a measured sensor signature. While this algorithm has very high selectivity, it is not optimal for detection in noisy situations. This is because the peak finding approach is less accurate when the noise is large, as in a typical field situation with low SNR. In order to improve the algorithm performance, even in the presence of noise, we have investigated and developed a novel algorithm. The new algorithm uses a combination of least squares approach with correlations. The novelty of this algorithm is its high sensitivity in concentration extraction. The sensitivity of the algorithm is illustrated with an example in Figure 6. Figure 6(a) shows experimentally measured spectra of acetonitrile (ACN) with various exposure times. Figure 6(b) shows spectra with pure noise where ACN signatures are absent. Because of poor SNR the last two spectra in both the sets visually appear to be noise. The algorithm results are shown in Figure 6(c). The algorithm is correctly able to identify the presence of ACN in Figure 6(a) and its absence in Figure 6(b), with good detection even for the second and third spectra where SNR is very close to one.
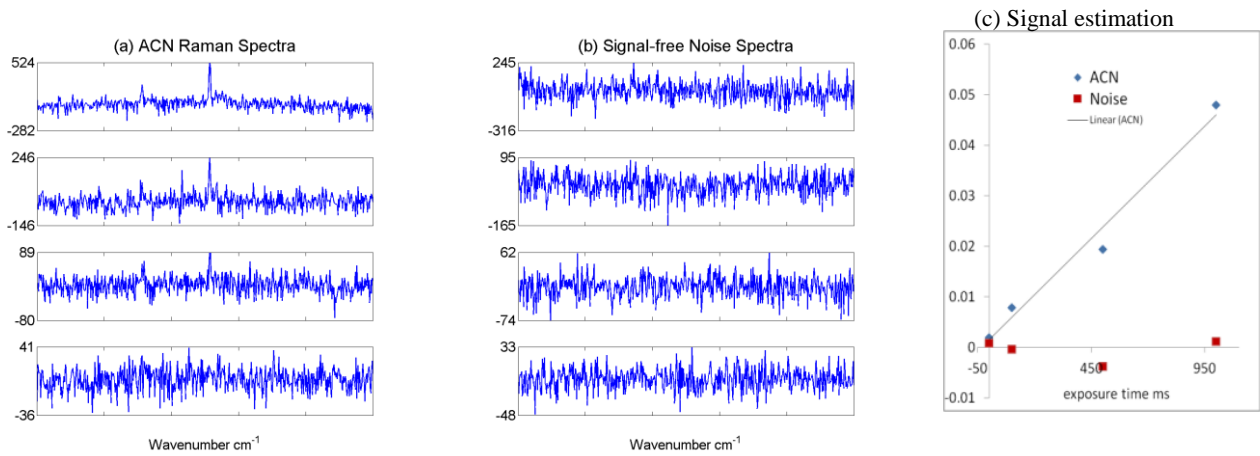
Figure 6: (a) ACN spectra obtained with different exposure times representing different signal to noise ratios. (b) Signal-free background noise spectra (c) Signal estimation using the algorithm.

In order to check the performance of the algorithm at low SNR situations, we computed reciver operating characteristics (ROC) for the detection of a precursor material, Potassium chlorate (PC), when excited with a single excitation source at 244 nm. Results are presented in Figure 7, which suggests that even when the SNR is very small, PC can be detected with a very low false positive rates ($\sim 10^{-4}$).
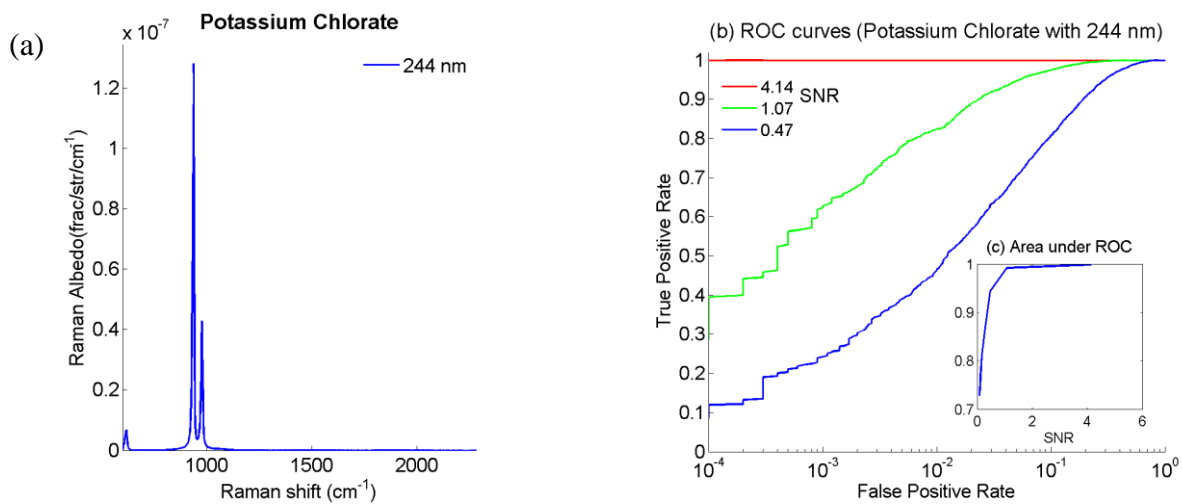

Figure 7: Receiver-Operating Characteristic (ROC) plots generated from measured Potassium Chlorate (PC) Raman signal with 244-nm excitation assuming a spectrometer resolution of 5 cm^{-1} and a signal-to-noise ratio (SNR) of SNR=4.14 (red), SNR=1.07 (green) and SNR=0.47 (blue). For a single wavelength sensor system with a laser power of 1 mw and collection efficiency similar to the DEWRRED sensor we estimate, based on our lab-measured signal levels, that SNR=4.14 corresponds to a standoff distance of ~ 50 ft with a dwell time of only <100 ms. (c) Area under the ROC as a function of SNR.
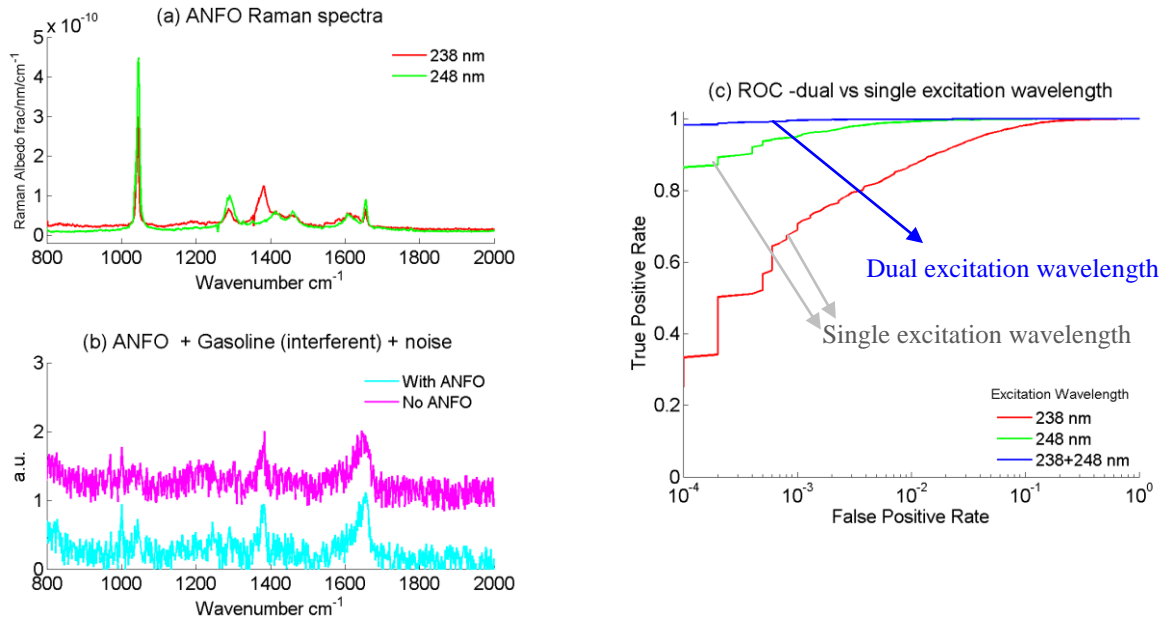
Figure 8: (a) Measured spectra of ANFO at 238 nm and 248 nm in absence of noise. (b) Representative sample of noisy spectra used for computing ROC curves. (c) Receiver-Operating Characteristic plots generated using the new algorithm for single and dual excitation wavelength signatures.

In order to understand the differences in algorithm performance between single excitation and dual excitation wavelength techniques, we computed the ROC curves for the following scenario. ANFO was assumed to be present on a surface that is stained with Gasoline. The fill factor for ANFO used in the simulations was 32%. Using our previous measurements at 238 nm and 248 nm (Figure 8(a)), we created a noisy population of 10000 positive (ANFO present) and negative (ANFO absent) sample spectra for each excitation wavelength. Representative noisy spectra with and without ANFO are shown in Figure 8(b), which illustrate a low SNR (<1 when averaged over the $\frac{1}{e^2}$ full-width of the Raman bands in both spectra) situation. Because of low SNR both the spectra in Figure 8(b) visually appear to be interferent (gasoline). The populations are used with the algorithm to compute ROC curves for two single excitation wavelength signatures (238nm, 248 nm) and for a dual excitation wavelength (238 nm+248 nm) signatures. Significant improvement in the ROC curve can be noticed in the plot shown in Figure 8(c). With the DEW technique, > 98% true positive rates are achieved even at a low false positive rate of 10^{-4}. Of the two SEW ROC curves, the curve at 248 nm is better than 238 nm due to higher Raman signal strength at 248 nm.

7. SUMMARY

We presented the concept of a dual-excitation-wavelength DUV resonance Raman technique for the detection of explosives. The technique is expected to show high sensitivity and specificity. We have built most of the components for the DEWRRED sensor system. Two cw DUV lasers that have the potential to be efficient, compact and rugged were designed and built. A compact DUV spectrometer with high throughput covering two excitation bands (241 nm to 272 nm) was designed and built. A novel algorithm for the DEWRRED sensor was developed and tested with some preliminary data.

8. ACKNOWLEDGEMENT

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