The limit of detection for explosives in spectroscopic differential reflectometry

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ABSTRACT

In the wake of recent terrorist attacks, such as the 2008 Mumbai hotel explosion or the December 25th 2009 "underwear bomber", our group has developed a technique (US patent #7368292) to apply differential reflection spectroscopy to detect traces of explosives. Briefly, light (200-500 nm) is shone on a surface such as a piece of luggage at an airport. Upon reflection, the light is collected with a spectrometer combined with a CCD camera. A computer processes the data and produces in turn a differential reflection spectrum involving two adjacent areas of the surface. This differential technique is highly sensitive and provides spectroscopic data of explosives. As an example, 2,4,6, trinitrotoluene (TNT) displays strong and distinct features in differential reflectograms near 420 nm. Similar, but distinctly different features are observed for other explosives.

One of the most important criteria for explosive detection techniques is the limit of detection. This limit is defined as the amount of explosive material necessary to produce a signal to noise ratio of three. We present here, a method to evaluate the limit of detection of our technique. Finally, we present our sample preparation method and experimental set-up specifically developed to measure the limit of detection for our technology. This results in a limit ranging from 100 nano-grams to 50 micro-grams depending on the method and the set-up parameters used, such as the detector-sample distance.

1. INTRODUCTION

Our research group has developed during the past years a detection system, based on differential reflectometry (DR) which is capable of detecting explosive materials on surfaces such as luggage, shoes, garments, containers, parcels, etc. from a certain distance. We performed differential reflection spectrograms on a large number of explosive and non-explosive substances. The common shortfall of essentially all of the competing techniques is that the explosive substance has to be ingested into the detection device or at least has to be brought into close proximity (1-10 cm) of the sensor in order to obtain a signal (with the exception of Raman spectroscopy, which is, however not eye-save because of laser involvement). Differential reflectometry -an optical technique- does not suffer from this shortcoming since the investigative light beam can emanate from a certain distance onto the substance under investigation, thus rendering it to be a standoff method. For our application a working distance of 1 m is sufficient, which has been shown by us to be accessible, convenient, and feasible.

We present here how differential reflectometry works, how it can be applied to trace detection of explosives and we will discuss further the sample preparation of this application and the limit of detection.

2. DIFFERENTIAL REFLECTOMETRY

Differential reflectometry measures the normalized difference between the reflectivities of two adjacent parts of the same surface. A broad band light source shines blue and near ultra-violet (UV) light on a surface (for example on a piece of luggage or a parcel situated on a moving conveyer belt). Upon reflection, the light is collected with a spectrometer and a CCD (charge couple device) camera. A computer processes the resulting data and produces in turn a differential reflection spectrum. In our present design, two reflectivities \( R_1 \) and \( R_2 \) are measured microseconds apart (see Figures 1 and 2). Once the reflected light is acquired the differential reflectogram is computed \( \Delta R = \frac{R_2 - R_1}{R_1} \) for a large range of wavelengths (200 to 500nm) in 1 nm intervals.
and $R = (R_1 + R_2)/2$ is the average reflectivity. Measuring $R_1$ and $R_2$ at nearly the same time and forming the ratio $\Delta R/R$ eliminates possible influences from fluctuations of the line voltage. It also eradicates spectral effects including intensity variations of the light source, the spectral sensitivity of the detector, the spectral reflectivities of the mirrors or the substrate, and it minimizes the influence of ambient light. In our system we use an array detector (CCD camera) which allows the acquisition of spectral as well as spatial information at the same time. As shown schematically in Figure 1, 512 pixels or spectra are acquired simultaneously across the scanned surface (perpendicular to the conveyor belt) providing high sensitivity, fast scanning and the location of potential threats detected.

Figure 1. Schematic Representation of our Differential Reflectometry detection system.

Differential reflectometry (also known as differential reflection spectroscopy) is a surface investigatory technique that reveals details about the electron structure around the Fermi energy. In other words, the method detects the energies that electrons absorb from photons as they are raised into higher, allowed quantum (energy) states. Since each material has a specific electron structure, the measurement of the characteristic energies for “electron transitions” serves as a fingerprint for identifying these substances. In essence, the differential reflectometer modulates the electron structure of materials, (such as explosives), and measures the derivative of the spectral reflectivity with respect to the perturbation. A line shape analysis can be used to yield the imaginary part of the complex dielectric constant $\varepsilon_2 = 2nk$ (often called the absorption) as a function of the excitation energy (where $n$ is the index of refraction and $k$ is the damping constant). The complex dielectric constant as a function of wavelength is unique to each material, yielding DR among the best methods to classify materials and particularly explosives.

Figure 3 depicts characteristic differential reflectograms (a plot of $\Delta R/R$ versus the excitation energy, or the wavelength) for TNT (2,4,6-Trinitrotoluene), m-DNB (dinitrobenzene), 2,4 DNT (dinitrotoluene), C4 (95% RDX (1,3,5-Trinitro-1,3,5-triazacyclohexane), plus 5% plasticizer) and PETN (Penta-erythritol tetranitrate). For TNT, it is observed that with increasing excitation energies, (decreasing wavelength) $\Delta R/R$ begins to gradually rise at about 435 nm and reaches a plateau near 400 nm, hereafter referred to as the “420 nm structure”. In contrast, other explosives display similar but recognizably different structures, e.g. at 410 nm for DNB, at 315 nm for DNT, at 360 nm for C4 and 340 nm for PETN.
Figure 2. Trace explosive detection baggage sensor. While a piece of luggage is moved through the system, a light beam scans the outside of the bag while a detector collects the reflected signal. Custom analysis software compares the signal to a library of known explosives in order to classify the signal. An output buzzer indicates to the security officer if traces of explosive are detected.

Figure 3. Differential reflectograms of various explosive materials.
We have previously shown that these spectral features are unique to explosives and not present in common material which are expected to be found on an average person, or the bag of a traveler. We present here differential reflection spectra of white powders which look similar to DNB, DNT, TNT and C4, namely, salt, Splenda® and flour. None of these materials yield DR spectra with all of the same features as TNT or other tested explosives, (see Figure 4). Additionally, the differential reflectogram of a carbon-pad (the substrate used in this experiment) is plotted as a reference. The reproducibility of the results are demonstrated by displaying several reflectograms which were taken on different locations of a given substance. It should be added in passing that the DR spectra of the explosive materials presented here are fundamental to the pure material and do not result from added taggants or accidental impurities.

![Figure 4. Differential reflectograms of TNT and other common substances similar in aspect to TNT. The spectra of TNT are very different from the other materials.](image)

### 3. LIMIT OF DETECTION

The limit of detection (LOD) for explosive materials is one of the paramount parameters for explosives detection systems. We present in this section experiments and calculations to evaluate the LOD for TNT, utilizing differential reflectometry.

The LOD is defined as being the mass which provides a detection signal equal to three times the standard deviation of the noise level of the system being used to detect a substance. Using the differential reflection spectrum of TNT we define the detection signal being the height of the 420nm structure (described above). In order to vary the sample mass (see below for mass determination) and therefore the detection signal, a TNT sample was prepared in a triangular shape such that when scanned with our system, a series of spectra was acquired simultaneously while the spatial position across the sample was recorded. It is observed that the amount of TNT decrease in a linear fashion as a function of the spatial position (see Figure 5 inset). Figure 5 also displays the recorded spectra of TNT for the different sample masses. It can be observed that the signal of the 420nm structure height decreases with decreasing sample mass.
Plotting the 420nm structure height divided by the observed noise as a function of the mass we obtain a linear relationship as seen in Figure 6. A coefficient of correlation of 0.98 is found. Please note that the observed noise is a constant, taken as the standard deviation around the average signal seen by the detector. For a signal to noise ratio of three, that is the limit of detection, we obtain a sample mass of 100 nanograms.

Similar experiments were done on C4, PETN and DNT. We found limits of detection of 50, 130, and 80 nanograms respectively.

![Figure 5](image_url)

Figure 5. Differential reflectogram of TNT as a function of sample mass. Inset: optical micrograph of a triangular shaped TNT sample overlaid schematically with the acquisition pixel grid. The white area is TNT, the black area is the carbon pad substrate.

The sample mass was determined by measuring the volume of material present in a given pixel area, such as the ones displayed in the inset of Figure 5. The volume was multiplied by the density of TNT (1.65 g/cm³). In this study, the pixel width (X) was 0.3 millimeter and the length was 2 millimeters. In the perpendicular direction (Y), the length of TNT coverage within a pixel is measured with a micrometer. Finally, the thickness (Z) is taken as 4 micrometers (see explanation below). For example, a full pixel of TNT (X = 0.3mm, Y = 2mm, Z = 4μm) weights 3.96 μg. By changing the amount of material in the Y direction we obtain samples which weight down to 0.2 μg.

The optical relevant thickness is determined by considering that the photons which are shone on the probed surface of the tested material are being absorbed by the surface molecules. In order to measure the interaction thickness between the incident photons and the absorbing material we prepared several samples of various thicknesses. The samples used in Figure 7 were prepared by crushing large TNT crystals (from a commercial vendor) and then laying them flat in a film fashion using a scalpel. Finally, a profilometer was used to obtain very accurate value of the sample thicknesses. Then we measured the height of the 420nm structure (in the case of TNT) from the collected differential reflectograms. Figure 7 displays these results. It can be seen that above 4μm the feature height of TNT does not increase. Since we have not been able to prepare samples thinner than 4μm, we can confidently state that the interaction thickness is equal or less than 4 μm.
Figure 6. Signal to noise ratio of TNT feature height as a function of sample mass. Inset, triangular shaped TNT sample overlaid schematically with the acquisition pixel grid.

Figure 7. Feature height of TNT spectra as a function of sample thickness. The error bars are based on variability from multiple measurements.
Further work is being conducted to improve our knowledge of the optical dampening constant of explosives such that a more accurate value can be given for the limit of detection using differential reflectometry. Additionally, other method of sample preparation such as inkjet printing\(^{10}\) or casting will be explored. These methods have the potential to allow the fabrication of very thin samples, that is, way below the 4µm thickness we have currently achieved.

The limit of detection of an instrument such as ours depends on a range of parameters such as the sample to detector distance, the sample orientation, light source power output, instrument noise, detector sensitivity, etc. The most important parameter, namely, the distance between the sample and the detector is considered. In the present study, we used a distance between detector and samples of 17cm while the available range reaches from 7 to 35cm. As the sample is moved closer to the detector, more reflected light is acquired while the intensity of collected light decrease with distance. We have previously shown\(^{11}\) that at the closest distance, a 50% in the detector signal increase is observed while at the farthest distance a decrease of 150% is observed. This leads to a range of limit of detection for TNT of 66 nanograms to 250 nanograms based on sample to detector distance.

4. CONCLUSION

We have presented a novel technique called differential reflectometry for the detection of trace amounts of explosives. This technique is fast, can potentially scan large quantities of parcels or luggage for surface explosives threads with a fairly sensitive level. The sample preparation method and experimental set-up is discussed. This results in a limit of detection ranging from tens to hundreds of nanograms. It is particularly emphasized that differential reflectometry include automatic sampling of the probed surface which is in contrast with currently used sensing techniques which do not include auto-sampling.

5. ACKNOWLEDGEMENT

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6. REFERENCES