Detection Limits of Trinitrotoluene and Ammonium Nitrate in Soil by Raman Spectroscopy

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ABSTRACT: The detection limit of 2,4,6-trinitrotoluene (TNT) and ammonium nitrate (AN) in mixtures of Ottawa sand (OS) was studied using a Raman microscope applying conventional calibration curves, Pearson correlation coefficients, and two-sample t-tests. By constructing calibration curves, the conventionally defined detection limits were estimated to be 1.9 ± 0.4% by mass in OS and 1.9 ± 0.3% by mass in OS for TNT and AN. Both TNT and AN were detectable in concentrations as low as 1% by mass when Pearson correlation coefficients were used to compare averaged spectra to a library containing spectra from a range of soil types. AN was detectable in concentrations as low as 1% by mass when a test sample of spectra was compared to the same library using two-sample t-tests. TNT was not detectable at a concentration of 1% by mass when using two-sample t-tests.

INTRODUCTION

Raman spectroscopy is a spectroscopic analysis method that excites a sample with a laser and collects the scattered and excitation light. Raman spectra are then created by plotting the intensity of the scattered light as a function of the frequency shift from the excitation light. These spectra contain useful information about the structure of molecules within samples, which can be used to determine a sample's chemical composition. Raman spectroscopy is useful when dealing with explosive materials because it is generally noninvasive. Since Raman spectroscopy uses a laser pulse to collect spectra, it can be used effectively in both close contact and standoff applications. The military has an interest in optimizing these types of sensors for field use because they offer a safe and fast solution to detecting traces of explosives.

In the field, traces of explosives are highly likely to be mixed with soil, so it is necessary to understand the detection limits of Raman spectroscopy in these more realistic scenarios. In an earlier study, Diaz et al. showed that a laser-induced breakdown spectrometer can detect ammonium nitrate (AN) in concentrations as low as 1% by mass in mixtures with Florida topsoil when using Pearson correlation (PC) coefficients and spectra libraries to analyze the data. The study also demonstrated a detection limit of 20% by mass when using a calibration curve to analyze the data.

The goal of this study was to determine the detection limits of 2,4,6-trinitrotoluene (TNT) and AN in soil for a Raman spectrometer using a similar approach to that of Diaz et al. This document details the experimental design, data analysis, and conclusions involved with using calibration curves, PC coefficients with spectra libraries, and two-sample t-tests with spectra libraries for the identification of AN and TNT in soil.

RESULTS AND DISCUSSION

Detection Limits Using Calibration Curves. Shown in Figure 1 are calibration curves constructed for AN and TNT. The error bars represent ± one standard deviation of 25 consecutive spectra. The red line represents a linear regression of these data. These spectra contain useful information about the structure of molecules within samples, which can be used to determine a sample's chemical composition. Raman spectroscopy is useful when dealing with explosive materials because it is generally noninvasive.

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When constructing the calibration curve for TNT, the 1357.711 cm$^{-1}$ Raman shift was used because it was the most intense shift to yield a linear relationship with concentration. The standard deviation of the background was measured and found to be 27±4 a.u., and $\rho$ was found to be 40±6 a.u. per 1% TNT using the slope of the regression line in Figure 2. Using the same method used to determine the detection limit of AN, the detection limit of TNT in soil was determined to be 1.9±0.4% by mass. Again, the most significant source of error in this estimate was the heterogeneity of the samples.

The AN regression line (Figure 1, left) seems to underestimate the instrument response to higher concentrations of AN, which is likely a result of less absorbance in the sample when more AN is present. The instrument response may be better modeled using multivariate analysis or by performing two separate linear regressions: one for lower concentrations (<50%) and one for higher concentrations (≥50%). The TNT regression line (Figure 1, right) seems to overestimate the instrument response to higher concentrations of TNT, which is likely a result of more absorbance in the sample when more TNT is present. As with the calibration curve for AN, this could be improved using multivariate analysis or multiple linear regressions.

Signal strength is proportional to the power of the laser, so a lower detection limit is likely achievable by increasing the power output of the laser. The 3.0 mW output level was chosen for this study to avoid damaging the samples, but higher output levels were not tested.

**Material Identification Using Pearson Correlation Coefficients.** A potential disadvantage of using calibration curves is that it relies on a single feature of the spectra, so it may not be effective at distinguishing between two different materials that share a spectral feature. When using PC coefficients to compare a spectrum to spectra in a database, the entire spectrum is considered, meaning that this method may be more reliable for material identification. Diaz et al.$^7$ showed that this method also requires fewer shots to positively identify AN with a laser-induced breakdown spectrometer, which means that it does not require as much analysis time.$^7$

Two libraries were created for data analysis in this study. The first library (LAN) contained 25-shot average spectra of Montana I soil, Montana II soil, San Joaquin soil, OS, AN, and mixtures of AN and OS in concentrations of 1, 5, 10, 20, 25, 50, and 75% by mass. The second library (LTNT) contained 25-shot average spectra of Montana I soil, Montana II soil, San Joaquin soil, OS, TNT, and mixtures of TNT and OS in concentrations of 1, 5, 10, 20, 25, 50, and 75% by mass.

Figure 2 shows the variation of the p-value for OS when compared to the first library (LAN) as the number of averaged spectra increases. For a single shot, the PC was relatively low with a high standard deviation, but it remained consistently above 0.98 when three or more shots were averaged. In

![Figure 1. Calibration curves for AN (left) and TNT (right).](image1)

![Figure 2. Pearson correlation coefficients for Ottawa sand (OS) as the number of averaged spectra increases.](image2)

![Figure 3. Percent of positive identification for AN1 (left) and TNT1 (right) as the number of averaged spectra increases when using PCs.](image3)
general, a higher number of averaged spectra resulted in a higher PC with a smaller standard deviation. At about nine shots, the PC remained fairly constant and above 0.99.

The percent of positive identification (PI) is defined as the probability that a spectrum is correctly matched with a spectrum in the library. Figure 3 shows the variation of the PI as the number of averaged spectra increases for a mixture of 1% AN in OS by mass (AN1) and a mixture of 1% TNT in OS by mass (TNT1). Each dot in the figures represents the mean of five trials, and each trial consisted of 25 spectra. The error bars represent ± one standard deviation of five trials.

When comparing AN1 to the LAN library, spectra were marked as matched if the PC in the library was above 0.99. Shown on the left in Figure 3, as the number of spectra averaged increased, the PI increased and the standard deviation decreased. At about nine averaged spectra and above, PIs of 100% were readily achievable.

TNT1 was compared to the LTNT library, and spectra were marked as matched if the PC in the library was above 0.99. Shown on the right in Figure 3, as the number of spectra averaged increased, the PI also increased and the standard deviation decreased. When at least 14 spectra were averaged, PIs of 100% were readily achievable.

Figure 4 shows the variation of the percent of false identification (FI) as the number of averaged spectra increases for a mixture of 1% AN in OS by mass (AN1) and a mixture of 1% TNT in OS by mass (TNT1). The error bars represent ± one standard deviation of five trials. FI is defined as the proportion of spectra in the library that incorrectly matched with the test spectrum. For example, if an averaged spectrum of AN1 matched with the 5, 10, and 20% AN mixtures in the library, the averaged spectrum would have an FI of 25% (3 out of 12 spectra in the library were incorrectly matched).

In general, when comparing AN1 to the LAN library, as the number of spectra averaged increased, the FI increased and the standard deviation decreased (Figure 4). When nine AN1 spectra were averaged, the FI was 6.4 ± 0.4%. For all points in the figure, AN1 was primarily confused with the 5 and 10% AN mixtures. Generally, when the FI for TNT1 was compared to the LTNT library, as the number of spectra averaged increased, the FI and the standard deviation decreased (Figure 4). The few samples incorrectly identified were either confused with OS or the 5% mixture of TNT. There were no instances of false identification when at least 12 spectra were averaged.

Shown below in Figure 5 is the variation in proportion of false negatives (FN) for AN1 (left) and TNT1 (right) as the number of averaged spectra increases when compared to the LAN and LTNT library, respectively. The FN is defined as the probability a spectrum is identified as free of the analyte when the analyte is present. Each point in Figure 5 represents the mean of five trials, and each trial consisted of 25 spectra. Error bars represent ± one standard deviation of five trials.

Although there were a few instances of false negatives when a small number of spectra were averaged, there were no instances of false negatives for AN1 when at least nine spectra were averaged. For TNT1, there were no instances of false negatives when at least 10 spectra were averaged.

Based on the results seen in Figures 3 and 5, it seems at least nine spectra should be averaged to confidently obtain 100% positive identification of AN in concentrations as low as 1% with no false negatives. However, Figure 4 shows that this method cannot be used to confidently estimate the concentration of AN in the sample. Based on Figures 3 and 5, at least 14 spectra should be averaged to confidently obtain 100% positive identification of TNT with no false negatives. Unlike the 1% AN mixture, Figure 4 shows that this method can also be used to confidently estimate the concentration of TNT in the sample.

The unexpected difference in the trends seen in Figure 4 was caused by fluorescence in the samples containing TNT. As seen in Figure 5, the background signals in the samples containing AN had similar shapes and intensities. As the only
significant difference between the two AN spectra are the slightly higher intensities of a few select peaks in the sample with a higher concentration of AN, the two spectra still yield a linear relationship with a high PC when plotted against one another. This trend continued for higher concentrations of AN, but the PC decreased as the difference between the peak intensities in AN1 and those in samples containing more AN grew larger. This explains why AN1 was commonly confused with the 5 and 10% mixtures but not the mixtures with high concentrations of AN (20% and higher). Due to increased amounts of fluorescence in samples with higher concentrations of TNT, the background signals in samples containing TNT did not keep the same shapes and intensities as the TNT concentration increased. As seen in Figure 6, the background signal became more arched and more intense as the concentration of TNT increased. Since the spectra of samples containing TNT were more distinct from one another than the corresponding spectra of samples containing AN, comparing the spectra of samples with different concentrations of TNT typically resulted in a low PC. This explains why TNT1 had such a smaller rate of false identification than AN1.

**Material Identification Using Two-Sample T-Tests.** This method was tested for the same reason as the PC method: it uses more than one spectral feature for identification. This method is more computationally demanding than the PC method, so only selected spectral features were analyzed for each compound rather than the entire spectrum. For AN, the intensities of the 715.5, 1043.4, 1288.3, 1416.5, and 3179.1 cm$^{-1}$ Raman shifts were analyzed. For TNT, the intensities of the 791.7, 821.6, 1209.2, 1357.7, 1533.2, and 1616.1 cm$^{-1}$ Raman shifts were analyzed. The same two libraries (LAN and LTNT) were used for data analysis in this section, but the 25 spectra for each sample were kept separate rather than averaged together. To identify materials, two-sample t-tests were performed for each of the Raman shifts listed above. If the mean intensity for any of the above Raman shifts in the test sample was statistically significant (p-value < 0.05) from the mean intensity of the same Raman shift in the library, the spectra sample was marked as unidentified. If mean intensities of all Raman shifts of interest were shown to not be statistically significant from one another, the spectra sample was marked as identified.

The variations of the PI for AN1 and TNT1 as the number of sampled spectra increases when compared to the LAN and LTNT library, respectively, are shown in Figure 7. Each point represents the mean of 10 trials, and each trial consisted of 25
spectra. Error bars represent ± one standard deviation of 10 trials.

In general, as the number of sampled spectra increased, the PI increased and the standard deviation decreased for both TNT1 and AN1. When looking at AN1, at about 10 sampled spectra and above, PIs of 95% were readily achievable. At least 16 sampled spectra were needed to achieve a PI of 100%. For TNT1, just four sampled spectra were needed to readily achieve a PI of 100%.

Figure 8 shows the variation of the FI for AN1 and TNT1 as the number of sampled spectra increases when compared to the LAN and LTNT library, respectively. In Figure 8, each point represents the mean of 10 trials, and each trial consisted of 25 spectra. Error bars represent ± one standard deviation of 10 trials. In general, as the number of sampled spectra increased, the FI and the standard deviation decreased for both AN1 and TNT1. For a high number of spectra sampled, the AN1 FI remained fairly constant at around 8%. For the 16 AN1 sampled spectra, the FI was 8.0 ± 0.3%. AN1 was commonly confused with the 5, 25, and 50% mixtures. This was largely due to the high standard deviation in both the test and library samples caused by sample heterogeneity.

The FI remained constant in TNT1 at around 13% for a high number of spectra sampled. When four TNT1 spectra were sampled, the FI was 19 ± 2%. TNT1 was commonly confused with OS and the 5, 10, and 20% mixtures. Again, this was largely due to the high standard deviation in both the test and library samples caused by sample heterogeneity.

Figure 9 shows the variation of the FN for AN1 and TNT1 as the number of sampled spectra increases when compared to the LAN and LTNT library, respectively. When looking at the FN for AN1, there was a relatively high proportion of false negatives for a low number of spectra sampled, but there were no instances of false negatives when at least nine spectra were sampled. The percent of FN for TNT1 appeared to increase as the number of sampled spectra increased, and it remained above 50% when more than three spectra were sampled. When four spectra were sampled, the FN was 53 ± 9%.

Figures 7–9 show that a positive identification of 95% with no false negatives can be achieved for AN in concentrations as low as 1% by mass when at least 10 spectra were sampled. To reach a PI of 100% for AN, at least 16 spectra had to be sampled. However, even with a high number of sampled spectra, this method cannot reliably estimate the concentration of AN in the sample. For TNT, Figures 7–9 show that the two-sample t-test method was not able to confidently identify TNT at a concentration of 1% by mass. Although a PI of 100% was easily achieved, the FI and FN were high, even when a large number of spectra were sampled. It should be noted that the samples containing TNT generally had larger standard deviations than the samples containing AN for concentrations less than 50%, which is apparent in the error bars seen in Figure 1. The higher standard deviations were likely caused by increased heterogeneity in the samples containing TNT, and they explain why t-tests could not be used to confidently identify TNT1.

The two-sample t-test method was not as effective at material identification as the PC method largely due to the large standard deviations in the samples, although it would likely yield better results when used with a more homogeneous sample or if every point on the spectra was tested. On average, a single two-sample t-test took 0.25 seconds of computation time. This means that comparing a spectrum to a library of 12 spectra by performing the t-test at 5 or 6 points took about 15 or 18 s, respectively, but performing the t-test at all 3528 points would take about 3 h. For comparison, using PC coefficients took about 5 s of computation time on average to compare a spectrum to a library of 12 spectra.
CONCLUSIONS

This study estimated the detection limit of TNT and AN in OS for a Raman microscope using three methods: calibration curves, PC coefficients, and two-sample t-tests. The detection limit of AN was estimated to be 1.9 ± 0.3% by mass by constructing a calibration curve from the 1043.371 cm\(^{-1}\) Raman shift and using the definition of the detection limit. The detection limit of TNT was estimated to be 1.9 ± 0.4% by mass using the same method with the 1357.711 cm\(^{-1}\) Raman shift. Since the detection limit is inversely proportional to the instrument sensitivity, increasing the power output of the laser may improve this measurement by decreasing the detection limit. However, increasing the laser power may damage samples that contain energetic materials such as TNT.

Detection of AN and TNT at concentrations of 1% by mass in OS was possible using PC coefficients and spectra libraries. When at least nine spectra were averaged, it was possible to confidently obtain a positive identification rate of 100% for AN1. However, AN1 was confused with 6.4 ± 0.4% of the other spectra in the library when using this method. The sample was primarily confused with the 5 and 10% samples. TNT1 was not confused with other samples when at least 14 spectra were averaged. Although it was not possible to accurately estimate the concentration of the detection limit of AN using this method, it was very effective at identifying the presence of both AN and TNT. There were no instances of false negatives when 9 spectra of AN1 were averaged and 14 spectra of TNT1 were averaged.

Detection of AN at a concentration of 1% by mass was possible using two-sample t-tests, but detection of TNT was not possible at this concentration. To confidently achieve 100% positive identification of AN, 16 spectra needed to be sampled. With 16 sampled spectra, there was a false identification rate of 8.0 ± 0.3% and no instances of false negatives. The 1% AN sample was primarily confused with the 5, 25, and 50% samples. Although a 100% positive identification for the 1% TNT sample was easily achievable with just four sampled spectra, there was a false identification rate of 19 ± 2% and a false negative rate of 53 ± 9%. As the number of sampled spectra increased, the rate of false negatives increased. This method could not confidently identify the presence of TNT due to the high rate of false negatives. This method was effective at identifying the presence of AN in a sample, but it was not effective at determining the concentration of AN. This study performed the t-tests at only five and six points of the spectrum for AN and TNT, respectively, so this method may be improved by analyzing the entire spectra.

The largest source of error in this study was the heterogeneity of the samples, which caused high standard deviations when analyzing the samples at random locations. The high standard deviations of signal intensity caused the large error in measured sensitivity and the high number of averaged spectra required to positively identify materials using PC coefficients. The two-sample t-test method is also affected by high standard deviations, which explains the high rates of misidentification that occurred when using that method. This could be improved by using a larger number of spectra to construct the calibration curves and spectra libraries. The larger sample size would likely decrease the uncertainty in instrument sensitivity as well as decrease the misidentification rate of the PC coefficient method and two-sample t-test method.

Based on the results in this study, using PC coefficients for material identification seems to be best suited for field detection. Out of the three methods studied, using PC coefficients was least affected by sample heterogeneity. Since this method takes the entire spectrum into account, it is also less susceptible to interference than using univariate calibration curves or t-tests. However, this method was not effective at estimating the analyte concentration in samples with low fluorescence. Accurately estimating analyte concentration in samples with high fluorescence would require a large library, which would increase computation time. It took about 5 s of computation time to compare an averaged spectrum against a library of 12 spectra using PC coefficients, which compares favorably to the 15 s computation time using two-sample t-tests. Comparing a spectrum to a calibration curve gave results almost instantaneously. Using two-sample t-tests for material identification may be effective for more homogeneous samples, but it does not seem well suited for field use where the analyte will be mixed with soil. The results of the t-tests were heavily impacted by the large standard deviation caused by sample heterogeneity. Although the t-test method could be used to identify AN1, it required nearly twice as many shots and three times the amount of computation time as the PC coefficient method. To achieve the best results in the field, it seems PC coefficients and calibration curves should be used in tandem. Once a material is identified in a soil using PC coefficients, its concentration could be estimated using a calibration curve built from the same library.

EXPERIMENTAL DESIGN

Raman Microscope. Figure 10 shows the basic setup of a Raman spectrometer. A laser excites the sample, and the scattered light is sent through a filter that stops light of the same wavelength as the incident light. The light that has undergone wavelength changes due to Raman scattering passes through the filter and into a spectrometer. The shift in photon energy is called the Raman shift. A Raman spectrum is then created, which can be analyzed on a computer. A Thermo Scientific DXR Raman Microscope was used to interrogate
samples. The microscope was set to a magnification of 10×, and the laser was operated at a wavelength of 532 nm and a power output of 3.0 mW. The laser passed through a 50 μm pinhole aperture, resulting in a spot size of 2.1 μm on the sample. Each shot consisted of a 6 s photobleaching followed by ten 3 s exposures. The spectra were organized using Microsoft Excel and analyzed using Wolfram Mathematica.

**Samples.** Samples of Ottawa sand (OS), Montana I soil, Montana II soil, San Joaquin soil, TNT, and AN were analyzed. The Montana I soil, Montana II soil, and San Joaquin soil used were National Institute of Standards and Technology (NIST) standard reference materials. Mixtures of TNT and OS were analyzed in concentrations of 1, 5, 10, 20, 25, 50, and 75% by mass. Mixtures of AN and OS were analyzed in the same concentrations. The OS was ground into fine particles using a puck mill grinder, and the TNT and AN were ground into particles of a similar size using an agate mortar and pestle. The substances were mixed until visually evenly distributed in the OS. The NIST soils were not altered. Each sample was pressed into pellets 6 mm in diameter using a hydraulic press. The pellets ranged in mass from 30 to 40 mg. Before pressing, 2 μL of deionized water was added to the pellet die to stop the pellet from crumbling. The samples were then pressed by applying 124 000 kPa for 10 min. Samples containing AN were stored in a glass desiccator to prevent the AN from absorbing moisture in the air. The other samples were stored in a plastic weigh boat with a plastic cover. The samples were placed on an aluminum-coated microscope slide for analysis.

**Calibration Curves.** The detection limit, \( c_L \), is experimentally defined as

\[
c_L = \frac{k\sigma}{\rho}
\]  

(1)

where \( k \) is a statistical constant that takes the value \( 2\sqrt{2} \), \( \sigma \) is the standard deviation of the background signal, and \( \rho \) is the sensitivity of the instrument. The sensitivity can be determined using the slope of a calibration curve and \( \sigma \) can be determined by analyzing a blank soil sample.

To estimate the lowest possible detection limit for TNT and AN, the Raman shift that gave the highest value of \( \rho \) for each compound was used to create a calibration curve.

**Pearson Correlation Coefficients.** Diaz et al. used PC coefficients to estimate the detection limit of AN in soil for a laser-induced breakdown spectrometer. With this technique, an average of multiple spectra is compared to spectra libraries. The PC coefficient, \( R \), is given by

\[
R = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum (x_i - \bar{x})^2 \sum (y_i - \bar{y})^2}}
\]  

(2)

where \( x_i \) and \( y_i \) are intensities and \( \bar{x} \) and \( \bar{y} \) are mean intensities. The value of \( R \) is between −1 and 1, where \( R = 1 \) indicates a completely linear positive correlation and \( R = -1 \) indicates a completely linear negative correlation. When a spectrum is compared to a spectrum in the library, an \( R \) value close to 1 indicates that the two spectra are highly similar.

**Two-Sample T-Tests.** A two-sample t-test is a statistical hypothesis test used to determine whether the mean of two populations is different. The test compares a sample from each population and determines whether there is enough evidence to reject the null hypothesis that the population means are the same. It returns a value between 0 and 1 called the PC coefficient \( p \)-value. If the \( p \)-value is below a predetermined value, called the significance level, then the null hypothesis is rejected, and the alternative hypothesis that the population means are not equal is accepted. If the \( p \)-value is above the significance level, then there is not enough evidence to reject the null hypothesis. Researchers typically use a significance level of 0.05, which means that if the null hypothesis is true, there is a 5% probability to draw the samples being analyzed from both populations by chance. This study used two-sample t-tests to identify spectra by comparing intensities from spectra drawn from a population of test shots to intensities from spectra in a library.

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