



Quantum cascade laser (QCL) spectroscopy, explosives detection, classical least squares (CLS), cotton fabrics, discriminant analysis (DA), highly energetic materials (HEMs)

Journal:	<i>Applied Spectroscopy</i>
Manuscript ID	ASP-16-0366.R1
Manuscript Type:	Submitted Manuscript
Date Submitted by the Author:	n/a
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Manuscript Keywords:	Quantum cascade laser (QCL) spectroscopy, explosives detection, classical least squares (CLS), cotton fabrics, discriminant analysis (DA), highly energetic materials (HEMs)
Abstract:	Quantum cascade laser spectroscopy was used to detect the presence of residues of highly energetic materials (HEMs) on cotton fibers. The discrimination of the vibrational signals of HEMs from a highly mid-infrared (MIR) absorbing medium was achieved by a simple and fast spectral evaluation using the classical least squares (CLS) algorithm without preparation of standards. CLS focuses on minimizing the differences between spectral features of real spectra acquired by direct MIR spectroscopy and the spectral features of calculated spectra modeled from linear combinations of the spectra of the neat components: HEMs and the cotton fibers, and the bias. HEMs samples in several combinations with cotton fibers were used to validate the methodology. Three (3) independent sets of experiments considering binary, ternary, and quaternary combinations of components, including cotton, TNT, RDX, and PETN, were performed. The models parameters obtained from linear combinations of the calculated spectra were used to perform discrimination analyses and to determine the sensitivity and selectivity of the studied HEM with respect to the substrates and to each other. However, the discrimination analysis was not necessary to achieve successful detection of HEMs samples on cotton substrates. The only requirement to achieve HEM detection (determine the presence or absence of HEM on a substrate) is that the library contains the spectra of all the HEMs and substrates or that the later be added in the field, on the fly. In addition, the extracted spectral signals of several amounts of RDX on cotton (> 0.02 mg) were

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	used to calculate the limit of detection (LOD) based on the spectral signal-to-noise ratio (S/N). The calculated S/N values were obtained from the spectra for cotton dosed with several amounts of RDX deposited in decreasing mass order until the calculated S/N reached a value of 3. The LOD determined for RDX on cotton was $22 \pm 6 \mu\text{g}$.

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Classical Least Squares Discriminant Analysis of High Explosives Detected on Cotton Fabrics by Quantum Cascade Laser Spectroscopy

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Abstract

Quantum cascade laser spectroscopy was used to detect the presence of residues of highly energetic materials (HEMs) on cotton fibers. The discrimination of the vibrational signals of HEMs from a highly mid-infrared (MIR) absorbing medium was achieved by a simple and fast spectral evaluation using the classical least squares (CLS) algorithm without preparation of standards. CLS focuses on minimizing the differences between spectral

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3 20 features of real spectra acquired by direct MIR spectroscopy and the spectral features of
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6 21 calculated spectra modeled from linear combinations of the spectra of the neat components:
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8 22 HEMs and the cotton fibers, and the bias. HEMs samples in several combinations with
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10 23 cotton fibers were used to validate the methodology. Three (3) independent sets of
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12 24 experiments considering binary, ternary, and quaternary combinations of components,
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14 25 including cotton, TNT, RDX, and PETN, were performed. The models parameters obtained
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16 26 from linear combinations of the calculated spectra were used to perform discrimination
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18 27 analyses and to determine the sensitivity and selectivity of the studied HEM with respect to
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22 29 achieve successful detection of HEMs samples on cotton substrates. The only requirement
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24 30 to achieve HEM detection (determine the presence or absence of HEM on a substrate) is
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26 31 that the library contains the spectra of all the HEMs and substrates or that the later be
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28 32 added in the field, on the fly. In addition, the extracted spectral signals of several amounts of
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30 33 RDX on cotton (> 0.02 mg) were used to calculate the limit of detection (LOD) based on the
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32 34 spectral signal-to-noise ratio (S/N). The calculated S/N values were obtained from the
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34 35 spectra for cotton dosed with several amounts of RDX deposited in decreasing mass order
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36 36 until the calculated S/N reached a value of 3. The LOD determined for RDX on cotton was
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38 37 $22 \pm 6 \mu\text{g}$.

38
39 **Keywords**

40 Quantum cascade laser (QCL) spectroscopy, explosives detection, classical least squares
41 (CLS), cotton fabrics, discriminant analysis (DA), highly energetic materials (HEMs)

Introduction

Remote sensing of chemical residues on substrates using active mode remote infrared spectroscopy (RIRS)¹⁻⁵ depends on various parameters, among which the most important are the excitation energy, the source type, the range (operator to target distance), and the angle between the source, target, and detector⁶⁻¹⁰. Other important factors to consider include the reflectivity of the substrates, the surface concentration of the target chemicals, and the optical power of the source. When going into more phenomenological details, attention must be given to surface roughness, effective cross-sectional scattering, optical properties of samples and substrates, such as refraction index and extinction coefficient, and finally the RIRS operational mode used for the measurements: specular or diffuse reflection, transmission, and transflection. In the present study, highly energetic materials (HEMs) were deposited onto cotton fiber substrates, which are considered non-ideal substrates because of their low reflectivity and, in principle, have the potential to hinder the characteristic HEM MIR bands required for sensing, detection, and subsequent classification and discrimination studies by RIRS. Hence, a large number of transflected or reflected/scattered photons are required to obtain an optimal signal in the back reflection setup, such as those generated by an MIR laser source such as a quantum cascade laser (QCL), as demonstrated by Faist et al.¹¹ Other important properties of QCL-based MIR spectrometers are based on the typically small footprint of these devices. Among these properties are field portability, high optical power, room-temperature operation⁹, low energy consumption, long-term power stability, and the ability to fine-tune the output frequency,¹² making QCLs useful for many spectroscopic applications, such as remote sensing of environmental gases and pollutants in the atmosphere¹³, and for critical applications in

65 defense and security.¹⁴⁻¹⁹ The relatively high optical power of at least six (6) orders of
66 magnitude larger than global sources (from electrically heated silicon carbide rods) has
67 proven its technological capability for developing a set of varied applications.^{8, 20-34}

68 Quantitative and qualitative spectroscopic analyses have been greatly improved using
69 robust statistical methods. Multivariate analysis methods permit the inclusion of multiple
70 spectral components (wavelengths/wavenumbers), various numbers of samples, very
71 complex data sets contaminated with spectral noise, and spectral overlapping, from which it
72 is possible to predict the sample analyte identities and their concentrations. The diverse
73 multivariate methods available for such tasks, such as partial least squares regression
74 (PLS), PLS coupled with discriminant analysis (PLS-DA), principal component analysis
75 (PCA), and principal component regression (PCR), have surpassed the 50-year lifetime of
76 classical least squares (CLS), which originated as a univariate analysis method but
77 gradually developed into a multivariate regression algorithm. Moreover, the implementation
78 of CLS-based methods in remote multispectral sensing for image generation from satellite
79 data served to demonstrate that the simplicity of CLS algorithm can be used in diverse
80 applications in a modern approach.³⁵ Although in general, it is not straightforward to
81 evaluate the superiority of any given method over another one when analyzing a particular
82 data set, Figueroa-Navedo et al. have recently shown how to establish such comparisons
83 between several multivariate analyses algorithms.³⁶ In their case, the comparisons were
84 based on using laser induced thermal emission (LITE) data of high explosives in a remote
85 sensed scenario.

86 CLS is a well-known regression method that uses the Beer-Bouguer-Lambert linear
87 relation dependence between the absorbance of a chemical species and its molar

concentration and is directly applicable to quantitative spectral analyses. The highest goal of CLS analysis is achieved when a broad spectrum of intensities for several components in a mixture is included in the analysis. This requirement is one of the greatest limitations of CLS: complete knowledge of the individual components in the matrix analyzed is required. Thus, spectra of the mixtures and the spectrum of each neat component are needed to estimate the spectral fraction for each component that is in the composition of the mixture. This is true only when neat components are involved. However, CLS can be considered as the transition state or as a bridge between univariate and multivariate analysis. Accordingly, in CLS, the response at any wavenumber can be considered as a linear combination of the responses of each component that is assumed to be in the mixture. The method also estimates the proportion of each spectrum component in the mixture spectra by minimizing the sum of the squares of the errors. In most of the cases, this spectral proportion is equal to or linearly proportional to the real proportion in the mixture. Following this approach, a CLS analysis is presented and discussed.

In the study, binary, ternary, and quaternary mixtures were generated by four (4) components in the calibration set: three (3) for the HEMs utilized and one (1) for the cotton substrates. A simple implementation of CLS analysis was used for the detection and discrimination analysis of the target HEMs by remote sensing with QCL spectroscopy. The CLS methodology and analysis introduces a statistical experimental design based on reference spectra obtained from the pure components included in the mixtures, establishing a simple technique for data visualization and model interpretation. In comparison, PLS-DA-based calibration models require the development of independent models for each surface, substrate, or type of fabric and are unsuitable for real remote sensing applications. Using

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the proposed method, in-field actualization of the substrates can be performed, and only the spectra of neat HEMs and surfaces/substrates need be included as part of the spectroscopic library.

Experimental

Reagents and Materials

The HEMs used in this work were 2,4,6-trinitrotoluene (TNT), pentaerythritol tetranitrate (PETN), and cyclotrimethylenetrinitramine (RDX). PETN and RDX were synthesized directly in the laboratory. TNT was purchased from Chem Service (West Chester, PA, USA). Cotton fabric (blue jeans) samples were used as non-reflective, matte substrates.

Sample Preparation

The HEMs samples were deposited onto the cotton fiber substrates by direct transfer. Two (2) procedures were evaluated for HEMs deposition. In the first procedure, the desired total amount of HEM or HEMs mix was transferred to a glass Petri dish, and the fabric sample was gently rubbed against the bottom of the Petri dish to transfer the HEMs by thumbprint pressure, this produced a stain on the fabric. The area covered by the HEM was approximately $2.2 \times 1.7 \text{ cm}^2$. This area was larger than the laser spot area ($2 \times 4 \text{ mm}^2$). This guarantees the total area of the substrate investigated was populated with HEMs samples. In the second deposition procedure, small amounts (particles) of the samples were transferred to a stainless-steel applicator tip ($\sim 1 \text{ mm}^2$ tip area) by pressing against a deposit of HEM or mixture of HEMs, followed by direct deposition by pressing with the applicator

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3 133 onto the cotton fabric samples. The area covered by the HEM was approximately 0.8 mm^2 .
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6 134 This area was much smaller than laser spot area. Thus, the laser was aimed at the samples
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8 135 in such a way that the particles were located within laser spot. The fabric was weighed
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10 136 before and after deposition to determine the exact amount of HEM deposited. The weighing
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12 137 was performed on two (2) calibrated scales for appropriate measurement precision. In the
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14 138 first mass determination, a scale with an accuracy of $\pm 0.1 \text{ mg}$ was used for depositions
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16 139 from 0.1 to 3 mg. In the second procedure, a lower mass scale with a precision of ± 0.01
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18 140 mg, a quartz balance from a thermal gravimetric analyzer (TGA) was used for the smallest
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20 141 amounts of particle deposition ($< 0.1 \text{ mg}$). For the two weightings mentioned above, the
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22 142 fabric was weighed before and after of transferring the HEMs samples.
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30 144 *Instrumentation*

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32 145 A MIR pre-dispersive spectrometer (model LaserScan™ Block Engineering, Marlborough,
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34 146 MA, USA) was used for the spectroscopic measurements. This system was equipped with
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36 147 three (3) synchronized, tunable MIR lasers (tuning ranges: 990 to 1111 cm^{-1} , 1111 to 1178
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38 148 cm^{-1} , and 1178 to 1600 cm^{-1}). Each diode was scanned for approximately 0.5 s each for a
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40 149 total scan time of 1.5 s per single, non-co-added run. The average power typically varied
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42 150 from 0.5 to 10 mW across the 600 cm^{-1} tuning range. The other laser parameters were
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44 151 $100:1$ transverse electromagnetic (TEM) polarization and a beam divergence of $< 2.5 \text{ mrad}$
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46 152 on the x-axis and $< 5 \text{ mrad}$ on the y-axis. The instrument was equipped with a 3 in. diameter
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48 153 ZnSe lens, which was used to focus the MIR beam onto the sample and to collect the
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50 154 reflected MIR light and focus it onto the thermoelectrically cooled internal mercury-cadmium-
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52 155 telluride (MCT) detector. The measurement mode was diffuse reflectance in back reflection
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3 156 (180°) with an experimental setup similar to Galan-Freyte, et al.³⁶ (Supplementary Materials
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6 157 section). The wavenumber accuracy and precision were 0.5 cm⁻¹ and 0.2 cm⁻¹, respectively.
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8 158 The best operating working distance from the target was 15 ± 3 cm. Each MIR source
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11 159 produced an elliptical laser spot with dimensions of approximately 4 mm x 2 mm at the
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13 160 working distance of 15 cm due to beam divergence differences in the x-y plane.
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16 161 A Q-500 TGA (TA Instruments - Waters L.L.C., New Castle, DE, USA) was used for the
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18 162 gravimetric measurements, with an accuracy of ± 10 ng and a working temperature range of
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23 164 for 5 min to achieve a thermal stabilization during weighting. This process was carried out
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30 167 *Statistical Model*
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33 168 All spectra were converted to Thermo-Galactic SPC format (Thermo-Fisher Scientific, Inc.,
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35 169 Waltham, MA, USA) and analyzed using a CLS model developed with customized
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37 170 commands in MatlabTM (The MathWorks, Inc., Natick, MA, USA; see Supplementary
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40 171 Materials). Acquired spectra were converted to Thermo-Galactic SPC format (Thermo-
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42 172 Fisher Scientific, Inc., Waltham, MA, USA) and partial least squares (PLS) loadings for PLS-
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44 173 discriminant analysis (PLS-DA) using PLS Toolbox v. 8.1 (Eigenvector Research, Inc.
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47 174 Manson, WA, USA) to generate the matrices for the analyses. Additional statistical analyses
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49 175 were performed using StatgraphicsTM Centurion XV software, version 15.2.05. (Statpoint
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52 176 Technologies, Inc. Warrenton, VA, USA). The proposed linear model, based on CLS, can be
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$$f(\varphi_j, \hat{\beta}_j)_i = \hat{\beta}_0 + \hat{\beta}_1 \varphi_1(\omega_i) + \cdots + \hat{\beta}_j \varphi_j(\omega_i) \quad (1)$$

where $f(\varphi_j, \hat{\beta}_j)_i$ represents the i^{th} normalized intensity of the spectrum [from $-\text{Log}(R)$], calculated from a mixture of several components (j); $\varphi_j(\omega_i)$ is the normalized intensity at each wavenumber (ω_i) of the net spectrum belonging to the j component and $\hat{\beta}_j$ is a parameter that indicates the fraction or proportion of the net spectrum of a certain component in the spectrum of the mixture. The model assumes that there are no binding interactions among the components in the mixture, which implies that the intensity contributions are additive. The $\hat{\beta}_j$ parameters can be calculated by finding the minimum of the square of the difference between the real spectra (RS) and the calculated spectra (CS) as follows:

$$d_i = y_i - \hat{f}(\varphi_j, \hat{\beta}_j)_i \quad (2)$$

The minimum value of the sum of the squares of d_i (residual) with respect to $\hat{\beta}_j$, illustrated above, can be found by equating to zero the first order partial derivatives with respect to $\hat{\beta}_j$ and finding the $\hat{\beta}_j$ values. Because the model contains “n” parameters, this generates n partial derivative equations as follows:

$$\frac{\partial d^2}{\partial \beta_j} = -2 \sum_i d_i \frac{\partial f(\varphi_j, \hat{\beta}_j)_i}{\partial \hat{\beta}_j} = 0, \quad j = 1, 2, \dots, n \quad (3)$$

It is possible to extract the signals of interest for each component of the mixture from the model. For example, if the component of interest is 1, the extracted spectrum ($\hat{\psi}$) is:

$$\hat{\psi}_{1(\omega_i)} = y_i - \hat{\beta}_0 - \hat{\beta}_2 \varphi_2(\omega_i) - \cdots - \hat{\beta}_j \varphi_j(\omega_i) \quad (4)$$

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4 197 **Results and Discussion**

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6 198 Reference spectra of HEMs and cotton were acquired by diffuse reflectance using the QCL
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8 199 spectrometer. Roughened gold substrates were used as background reference for
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10 200 reflectance measurements. Reflectance units were converted to the negative of the
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12 201 logarithm of reflectance. The sample spectra of cotton with the corresponding dosing
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14 202 amounts of HEMs were acquired in the same form (Figure 1). The normalization was
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16 203 performed using standard normal variate (SNV) as a preprocessing step. SNV was applied
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18 204 to the full spectral region of the analyses to eliminate the baseline drift caused by MIR
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20 205 scattering due to the difference in particle size, the topology of the fabric, and inherent scale
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22 206 of the spectra.
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30 208 *Binary Models*

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32 209 Three models of classes were generated: binary class models which consisted exclusively
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34 210 of the combination of cotton substrates and each one of the HEMs. In this case, Eq. 1
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$$f_{cotton}^{HEM} = \hat{\beta}_0 + \hat{\beta}_{cotton} \varphi_{cotton}(\omega_i) + \hat{\beta}_{HEM} \varphi_{HEM}(\omega_i) \tag{5}$$

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43 213 Twenty (20) samples containing various amounts of HEMs ranging from 0.1 to 3 mg were
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45 214 deposited on cotton substrates and the parameters $\hat{\beta}_{HEM}$ were calculated from five (5)
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47 215 replicates. A probability distribution was estimated (additional information included in
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50 216 Supplemental Materials). A binary model for each HEM/cotton combination was generated.
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52 217 These models had high sensitivity and selectivity for the mass range of 0.1 to 3 mg, as
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55 218 illustrated in Table 1. The decision threshold (P) for the model was determined using the
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predicted average value of $\hat{\beta}_{HEM}(\bar{x})$ for the cotton sample (blank) and the standard deviation (s_d):

$$P = \bar{x} + 3.28 \cdot s_d \quad (6)$$

There is a 5% probability of random error. This is based on the definition of the detection limit.³⁷ There will be a high probability that all the clean samples are below this threshold.

This way, it is only necessary to have representative cotton spectra in the database to generate the discrimination. The model was compared with the discriminant analysis (DA).

Results are shown in Table 1, where the value of β_{HEM} was used to generate a model for discrimination. The difference between this model and the proposed model in this contribution is that it must be fed with a spectrum of cotton without HEMs (clean substrate) and the spectra of the neat HEMs. The spectra for the binary models for TNT, RDX, and PETN are shown in Figures 1(a) to 1(c). In each of these figures, the spectra with approximately 0.1 mg of HEM deposited on cotton are shown in blue. The predicted spectra from Equation (5) are shown in red. Reference spectra for the powder form HEM and cotton fiber substrates are shown in black and orange, respectively. The HEM/cotton spectra with the cotton spectra subtracted using the Eq. (5) are shown in green.

The binary model that consisted only of the cotton spectrum and RDX spectrum is given as an example (the other models are discussed in the Supplementary Materials section). The relationship based on Eq. 5 is as follows:

$$f_{cotton}^{RDX} = \hat{\beta}_0 + \hat{\beta}_{cotton} \varphi_{cotton}(\omega_i) + \hat{\beta}_{RDX} \varphi_{RDX}(\omega_i) \quad (7)$$

Figure 2 illustrates the calculation of the probability for RDX in the mass range of 0.1 – 3 mg as a function of $\hat{\beta}_{RDX}$.

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241 *Ternary Models*

242 The equation for ternary models with three (3) components, cotton, TNT, and RDX based on
243 Eq. 1 is as follows:

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$$f_{cotton}^{TNT+RDX} = \hat{\beta}_0 + \hat{\beta}_{cotton} \varphi_{cotton}(\omega_i) + \hat{\beta}_{TNT} \varphi_{TNT}(\omega_i) + \hat{\beta}_{RDX} \varphi_{RDX}(\omega_i) \quad (8)$$

245 Samples of 100% TNT from 0.1 to 3 mg, 100% RDX from 0.1 to 3 mg, and binary mixtures
246 of 50% TNT/RDX with total mass ranging from 0.5 to 3 mg (134 samples), were deposited
247 on cotton. The values of the parameters $\hat{\beta}_{TNT}$ and $\hat{\beta}_{RDX}$ were then calculated, and the
248 distribution values for each sample were plotted from Eq. (6). Figure 3(a) shows that good
249 discrimination of the binary samples was obtained. However, in ternary mixtures, a few
250 samples were classified as binary mixtures composed of TNT/cotton. These samples
251 coincided with the locations on the cotton surface where only small yellow TNT crystals
252 were found when visually inspecting the samples. The sensitivity and specificity are also
253 shown in Table 1. Decision thresholds for the models were determined using the predicted
254 average values of β_{TNT} and β_{RDX} for the cotton samples plus the standard times 3.28. In
255 Figure 3(a) the decision value thresholds are represented by green asterisks and the
256 thresholds lines are represented by black dotted lines. This threshold was labelled “P” in
257 Figure 3(a) to differentiate it from threshold of DA. This is shown for binary models in the
258 Supplementary Materials section.

260 *Quaternary Model*

261 The quaternary model was composed of four (4) components based on Eq. 1: cotton, TNT,
262 RDX, and PETN, was as follows:

$$f_{cotton}^{TNT+RDX+PETN} = \hat{\beta}_0 + \hat{\beta}_{cotton} \varphi_{cotton}(\omega_i) + \hat{\beta}_{TNT} \varphi_{TNT}(\omega_i) + \hat{\beta}_{RDX} \varphi_{RDX}(\omega_i) + \hat{\beta}_{PETN} \varphi_{PETN}(\omega_i) \quad (9)$$

Samples of 100% TNT, 100% RDX, and 100% PETN ranging from 0.1 to 3 mg and samples with of mixtures of 50% TNT/RDX, 50% TNT/PETN, 50% PETN/RDX, and 33.3% TNT/PETN/RDX with total mass ranging from 0.5 to 3 mg were deposited on cotton fiber substrates (252 samples). The values of the parameters $\hat{\beta}_{TNT}$, $\hat{\beta}_{RDX}$, and $\hat{\beta}_{PETN}$ for the mixtures were calculated along with their distribution plot for each sample from the calculated values following Eq. 9 (Figure 3(b)). The sensitivity and specificity are also shown in Table 1. Visualization of the separation of classes is not possible because 3D visualization is difficult. The sensitivity and specificity are also shown in Table 1 together with the comparison with DA.

Tests with Other Substrates

Five other substrates were investigated: white cotton (from a T-shirt), polyester, 65% polyester-35% cotton, 45% polyester-55% cotton, and 84% polyester-16% spandex™. Spectra of neat substrates (HEM free) and spectra of substrates dosed with TNT were acquired and used for the study. Figure 4 shows the QCL spectra of TNT, polyester, and spandex used in models for other substrates. Three models were generated and tested. First, a binary model for TNT based on Eq. 5 was developed. This model was composed of a spectrum for blue jeans cotton and a TNT spectrum. The prediction of samples is shown in Table 2. All substrates contaminated with TNT were correctly predicted. However, the

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3 285 samples consisting of neat polyester and spandex™ substrates (without TNT) were
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6 286 predicted as containing TNT, i.e. false positives (bold red). The $\hat{\beta}_{TNT}$ values were high for all
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9 287 cases, except for the white cotton substrate samples, because the model already included a
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11 288 spectrum of cotton from another substrate (blue jeans). Low amounts of TNT (~ 0.1 mg)
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14 289 predicted high $\hat{\beta}_{TNT}$ values. This is unreasonable because $\hat{\beta}_{TNT}$ values should have been
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16 290 low. However, this can be explained in the case of polyester and spandex™ polymers
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19 291 substrates since both have intense signals in the same spectral window as TNT (see Fig. 4).
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21 292 A second model was built with a spectrum of blue jeans cotton, a spectrum of polyester
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24 293 and a spectrum of neat TNT. When the spectrum of polyester was added to the model, all
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26 294 the samples with this substrate were correctly predicted with values of $\hat{\beta}_{TNT}$ near zero.
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29 295 Only the samples that contained spandex™ fiber were not correctly classified. Finally, a third
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31 296 model was generated by adding the spectrum of spandex™ to the second model. After this,
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34 297 all samples were correctly classified, and the samples with low amounts of TNT (~ 0.1 mg)
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37 298 had a low $\hat{\beta}_{TNT}$ value (see Table 1). Thus, for classifications of samples using CLS and the
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39 299 protocol presented, it is important to include the spectra of all components of the substrate
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42 300 in the model under development to have a good prediction capability. For a practical
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46 302 built must contain the neat spectrum the HEM as well as the spectra for the substrates
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307 *Discriminant analysis*

308 To be able to statistically evaluate the discrimination capabilities statistically of the $\hat{\beta}_j$
309 parameters in the quaternary mixtures and to obtain an improved visualization of the
310 separation of classes, detailed discriminant analysis was performed using the $\hat{\beta}_j$ parameters
311 as variables. Eight (8) groups were used for the discrimination: cotton fiber substrates, TNT,
312 RDX, PETN, TNT-RDX, TNT-PETN, RDX-PETN, and TNT-RDX-PETN. Two (2) highly
313 significant and statistically weighted discrimination functions were obtained. These functions
314 contained nearly all the statistically relevant information because they contributed 95.3% of
315 the discrimination capability of the model. As shown in Table 1, two functions with high
316 eigenvalues values for the discrimination were highly significant ($p < 0.0001$). Per the
317 canonical correlation coefficient, which represents the ability or effectiveness of the
318 discrimination for new samples, the two (2) main functions (F1 and F2) showed excellent
319 discrimination to determine group differences, with 93% and 87% confidence levels,
320 respectively. A third function (F3), with a 56% capacity for determining group differences
321 was less effective than functions F1 and F2 but was highly significant ($p < 0.0001$) in the
322 discrimination model. The null hypothesis that the populations have identical discrimination
323 means was tested by the Wilks lambda test. The small value of Wilks' lambda indicates the
324 acceptance of the null hypothesis. The statistical significance was evaluated by the χ^2 p-
325 value (< 0.0001), as illustrated in Table 3. It is possible to determine to what extent the
326 contribution of the grouping variable to the variance is explained by the predictor using
327 Wilks' lambda values. The first discriminant function (F1) had a very small Wilks' Lambda

value (0.02), indicating that approximately one-fiftieth of the variance is not accounted for by group differences. For F2, the Wilks' Lambda value was larger (0.16), indicating that approximately one-sixth of the variance is not explained by group differences. In addition, the Wilks' Lambda value for F3 was even larger (0.68), indicating that approximately seventeen twenty-fifths of the variance was not explained by differences in-group classification. Figure 5 shows the discriminant plot using the two main functions, F1 and F2. These two principal functions have the capacity to classify the pure HEM components on the cotton fiber substrates as PETN, RDX, and TNT. Moreover, the ternary mixtures of TNT/PETN and TNT/RDX on cotton are located in the middle of the neat HEMs, providing good classification. However, the classification of the ternary mixtures of RDX-PETN/cotton and the quaternary mixtures of TNT-RDX-PETN/cotton could not be accomplished completely by the two main functions F1 and F2. A portion of the RDX-PETN mixtures deposited on cotton substrates were incorrectly classified as having 100% RDX. The same situation occurred for TNT-RDX-PETN mixtures on cotton. A possible explanation for the lack of discrimination of the RDX-PETN/cotton mixtures is that in some subintervals of the spectral range investigated (e.g., from approximately 1340 to 1402 cm^{-1}), there is a lack of strong PETN absorbance bands, allowing the RDX absorbance signals in these intervals to stand out (see Figure 1(d)). Therefore, the classification was performed with respect to the RDX/cotton binary component rather than the ternary mixture. The same result is likely to occur in quaternary mixtures (see Supplementary Materials). Furthermore, with the consideration of F3 in the analysis and by plotting F1 vs. F3 and F2 vs. F3, improved classification was achieved for mixtures of RDX/PETN and TNT/RDX/PETN. In this case, the 50% RDX/PETN is located in the middle of the two pure components constituting the

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3 351 mixture, and the mixtures of TNT/RDX/PETN are better distributed (see Supplementary
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6 352 Materials).

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8 353 To determine the sensitivity and selectivity values with respect to cotton, TNT, RDX, and
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10 354 PETN, a binary discriminant analysis (with and without) was performed of each material for
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13 355 the binary, ternary and quaternary models (see Table 1). For the binary models, the
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15 356 sensitivity and selectivity were exact (100%), whereas, for the ternary model, these
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18 357 parameters were good, except for TNT/RDX mixtures, which should have been classified as
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20 358 containing only RDX and TNT but were ultimately classified as containing TNT only or as
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22 359 containing RDX only. This could be attributed to a lack of sample homogeneity. Similar
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25 360 results were obtained for the quaternary model.

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27 361 The $\hat{\beta}_j$ values are considered linear proportions of the spectral components in the
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30 362 prediction but no linear behavior is present. However, they are proportional to the
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32 363 concentration of j^{th} component and this is not affected in the detection. The spectra of
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35 364 mixtures are spectra for the amounts of HEM on surface sampled. The intensity of the
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37 365 signals of the HEM depend on the area that the analyte covers on the surface which in turn
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40 366 depends on the amount deposited and on the form in which the material was transferred
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42 367 onto the surface. In the case of HEM formulations (two HEMs 50% each; three HEMs
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44 368 33.33% each), when the samples are deposited on the fibers, it is possible to have some
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47 369 fibers with more amount of one component than of the others, because it is not possible
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49 370 have a homogenous mixture of the materials. This leads to the situation that some parts of
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51 371 the spectra for the formulations is predicted containing only one material in a binary
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54 372 formulation of HEMs or one or two material in a ternary formulation of HEMs.

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375 *Limits of detection (LODs)*

376 The limit of detection (LOD) for RDX was determined from measurements of several spectra
377 at low analyte amounts (< 0.1 mg). The characteristic RDX MIR vibrational signatures stood
378 out when applying Eq. 4 to the spectra. Figure 6(a) shows typical RDX spectra recorded for
379 different masses on the cotton substrates. The reference spectrum of neat RDX (pellet)
380 acquired in reflectance mode and converted to the negative of the logarithm of reflectance
381 (solid black line), was used to identify the RDX characteristic bands and to emphasize the
382 relative signal increase when more amount analyte was deposited on the cotton surfaces.
383 New bands were observed at 1080, 1063, 1484, 1249 cm^{-1} . This can be attributed to
384 interactions of RDX with the cotton substrate. The signal-to-noise ratios (S/N) were
385 calculated for the 1040 cm^{-1} and 1463 cm^{-1} bands at each of the nominal deposited RDX
386 masses, as shown in Figure 4(b). The improvement of S/N is illustrated for the two RDX
387 vibrational bands selected as a function of the mass deposited (μg). A S/N value of 3 was
388 found for a mass of $22 \pm 6 \mu\text{g}$, which based on the IUPAC recommendation, corresponds to
389 the LOD.

390 The $\hat{\beta}_{RDX}$ parameter was plotted against the nominal RDX surface mass to find the
391 relationship shown in Figure 4(c). The assumption of a linear dependence was rather poor
392 ($R^2 = 0.80$) in the range 20 to 100 μg . A power fit resulted in a significantly improved
393 representation of the data ($R^2 = 0.94$). If the range was further reduced from 20 to 75 μg , an
394 improved linear dependence ($R^2 = 0.92$) was found. The threshold value P is also illustrated
395 in Figure 4(c). This was calculated from the values of the $\hat{\beta}_{RDX}$ parameters for 3 spectra of

the cotton substrates (used as blank), the value for the average ($\bar{x}$) and the value for the standard deviations s_d calculated by means of Eq. 6. The P value obtained for RDX (22 ± 6 μg) coincides with the LOD, but in statistical jargon, they are the same or statistically equal. This can be well visualized in Figure 4(d), where S/N and $\hat{\beta}_{RDX}$ are plotted, a low linear dependence is observed. The S/N = 3 and the threshold P cross in the surface mass of 22 ± 6 μg .

Conclusions

In this work, the detection capability of the CLS method for binary, ternary, and quaternary mixtures of HEMs deposited on non-MIR reflective (mate) substrates, such as cotton fabrics, was demonstrated. The reconceptualization of the least squares algorithm in combination with the remote sensing by QCL spectroscopy results in the development of an effective methodology for detection of HEMs and mixtures of HEMs on fabrics. In addition, if neat components spectra of the HEMs of interest (RDX, TNT, and PETN) are present in the calibration set (or spectroscopic library), it is possible to perform discrimination on any surface or substrate by updating the model with the spectra corresponding to the new surface/substrate where the detection would be conducted. Five other substrates: white cotton, polyester, 65% polyester 35% cotton, 45% polyester 55% cotton, and 84% polyester 16% spandex™ neat (HEM free) and dosed with TNT were investigated.

The CLS algorithm facilitates the discrimination process upon HEM detection and provides a better understanding and better control of the spectral visualization of vibrational signals of interest. There is, a priori, no linear dependence between the mixture spectrum

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and the neat components spectra. Rather, with the methodology developed it is not possible to quantify the components but, this nonlinear relationship does not affect the detection.

Acknowledgments

This project was part of the outcomes of a Research Experiences for Undergraduates (REU) summer research internship and the 2015 Department of Homeland Security (DHS) Summer Research Teams Programs for Minority Serving Institutions. The REU summer research internship was sponsored by the DHS ALERT Center of Excellence for Explosives Research, home based at Northeastern University, Boston, MA and its R3-C research, development, and education component at the University of Puerto Rico – Mayagüez Campus.

Conflict of Interest

The authors report there are no conflicts of interest.

Funding

This material is based upon work supported by the U.S. Department of Homeland Security, Science and Technology Directorate, Office of University Programs, under Grant Award 2013-ST-061-ED0001. The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the U.S. Department of Homeland Security.

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CAPTIONS FOR TABLES AND FIGURES

TABLES CAPTIONS

Table 1. Sensitivity and specificity values for binary discriminant models

Table 2. Prediction of β_{TNT} parameters for the three models developed

Table 3. Statistical values for functions derived from β parameters for the DA for the quaternary mixture

FIGURES CAPTIONS

Figure 1. (a-c) Spectra of approximately 0.1 mg of HEMs (TNT, RDX, and PETN) deposited on cotton are shown as blue traces; predicted spectra from Equation (5) are shown as red traces; cotton spectra are shown in orange traces; subtraction of cotton spectra from HEM/cotton spectra calculated using Eq. 4 are shown as green traces; reference HEM spectra are shown as black traces. (d) Comparison of reference spectra for individual HEM and a typical spectrum for the quaternary mixture: TNT-RDX-PETN/cotton.

Figure 2. Probability distribution for the $\hat{\beta}_{RDX}$ parameter for in the RDX/cotton binary mix.

Figure 3. (a) β_{TNT} and β_{RDX} parameters samples distribution. (b) β_{TNT} , β_{RDX} , and β_{PETN} samples distribution parameters.

Figure 4. QCL reflectance spectra of components used in the additional tests of the methodology proposed based on CLS: TNT, polyester and spandex.

Figure 5. Plot of functions F1 and F2 used in the discriminant analysis.

Figure 6. (a) Spectra of RDX particles at various surface masses on cotton substrates; (b) Plot of S/N vs. mass for two RDX signals; (c) Plot β parameter for RDX vs. masses; (d) Plot of S/N vs. β parameter for RDX.

FIGURE 1

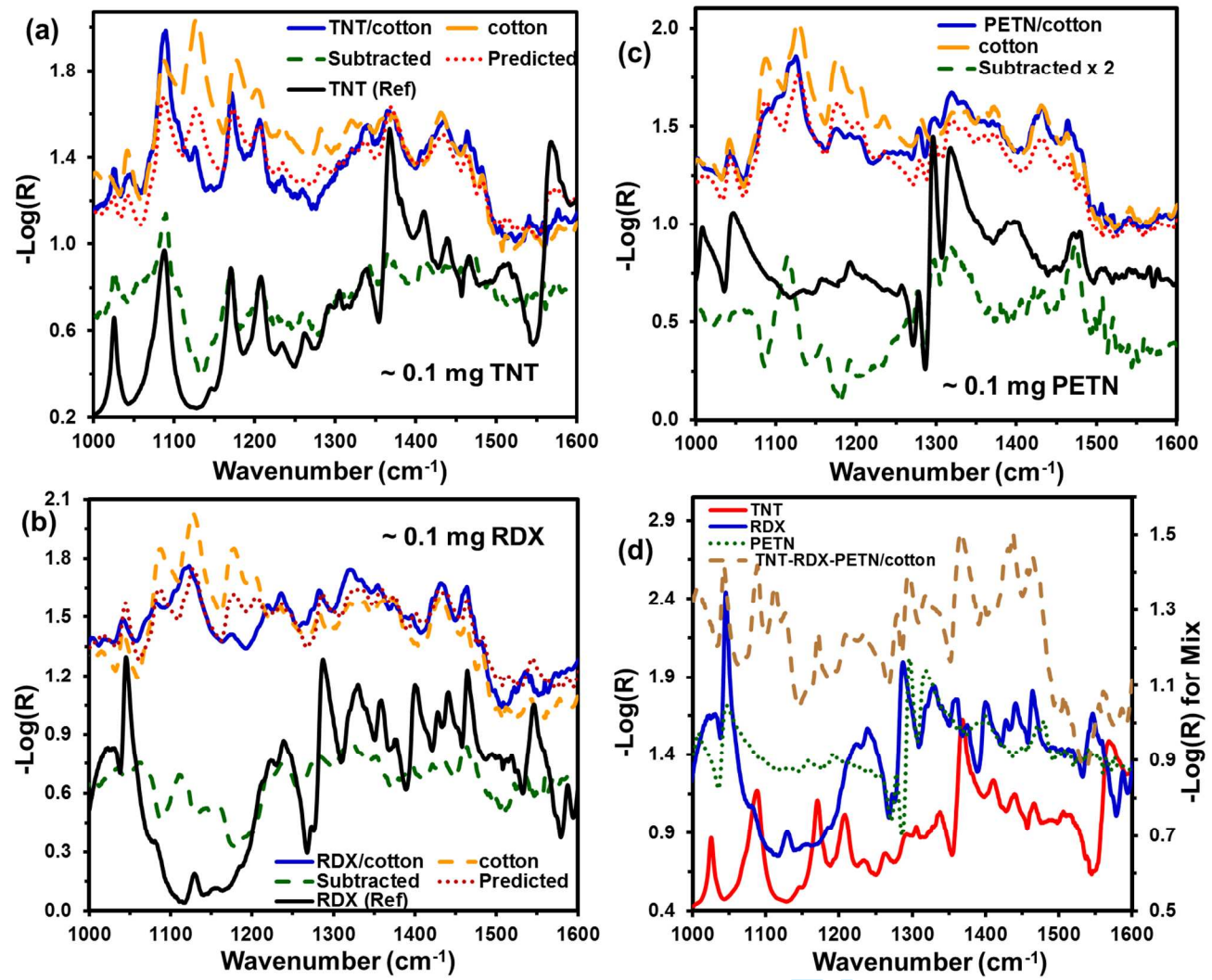


FIGURE 2

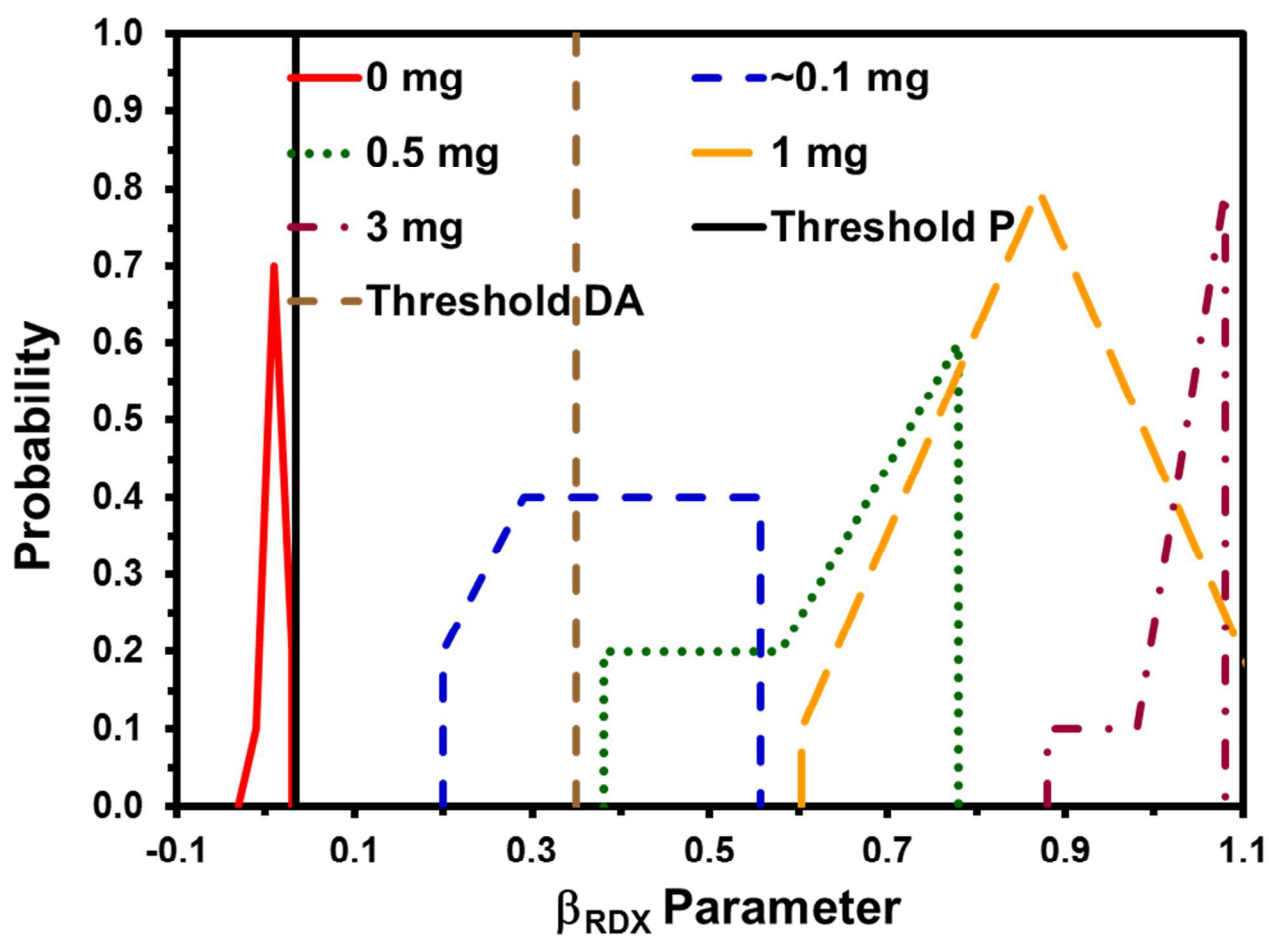


FIGURE 3

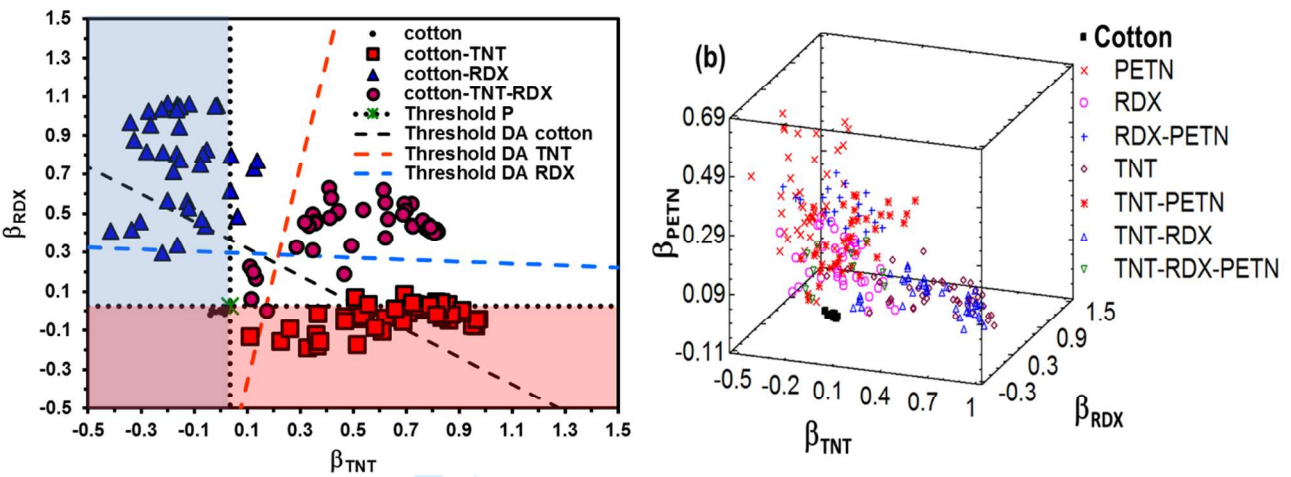


FIGURE 4

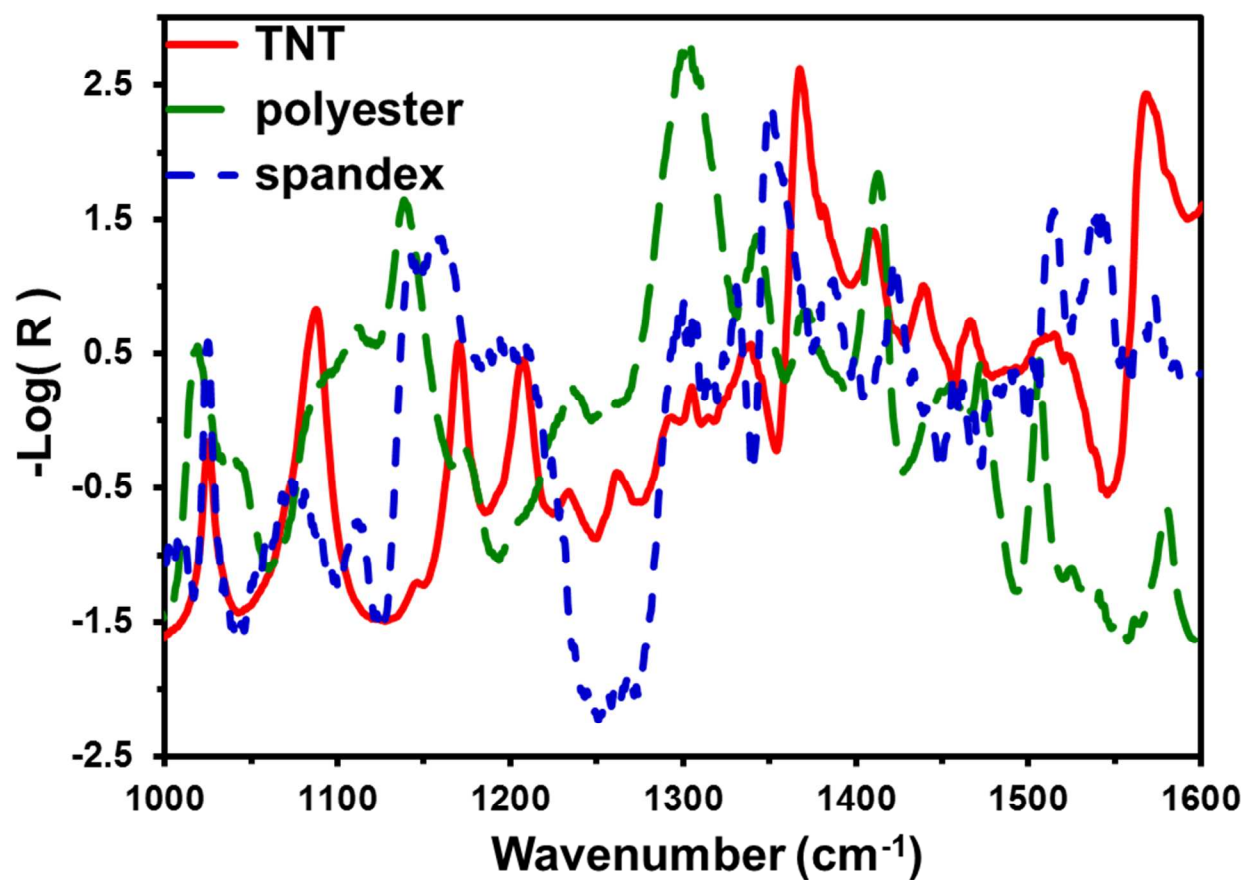


FIGURE 5

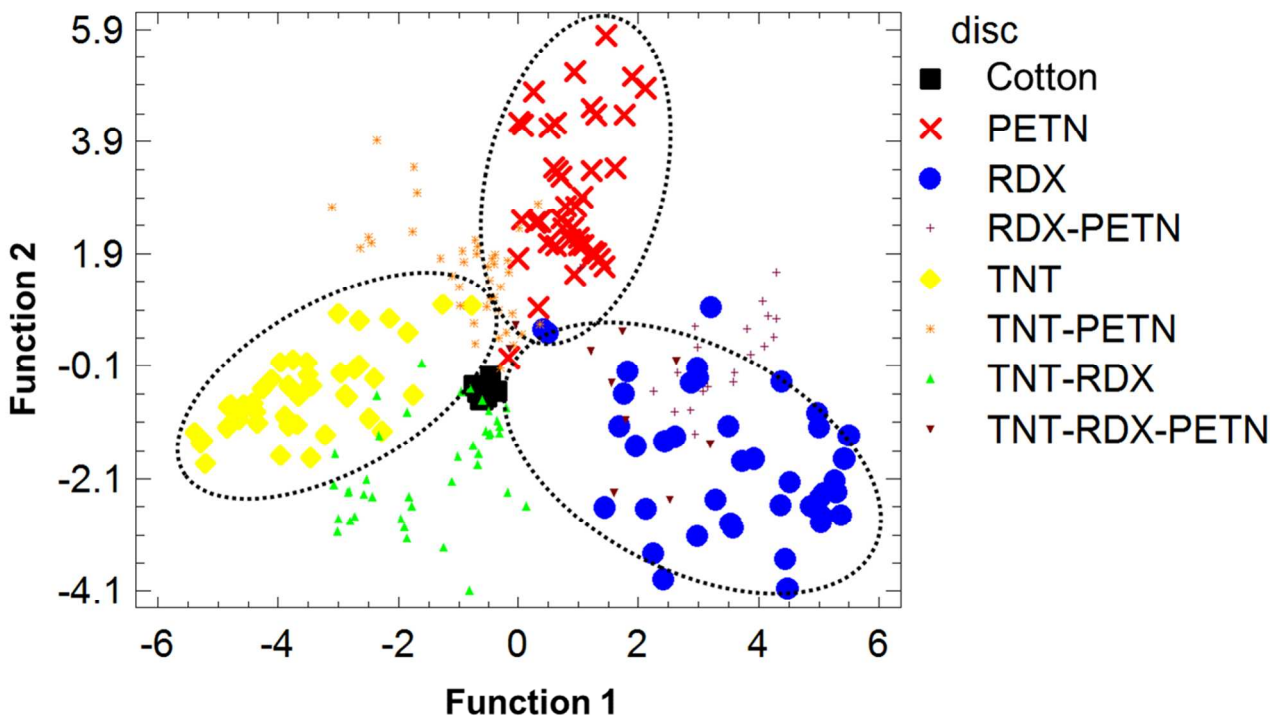
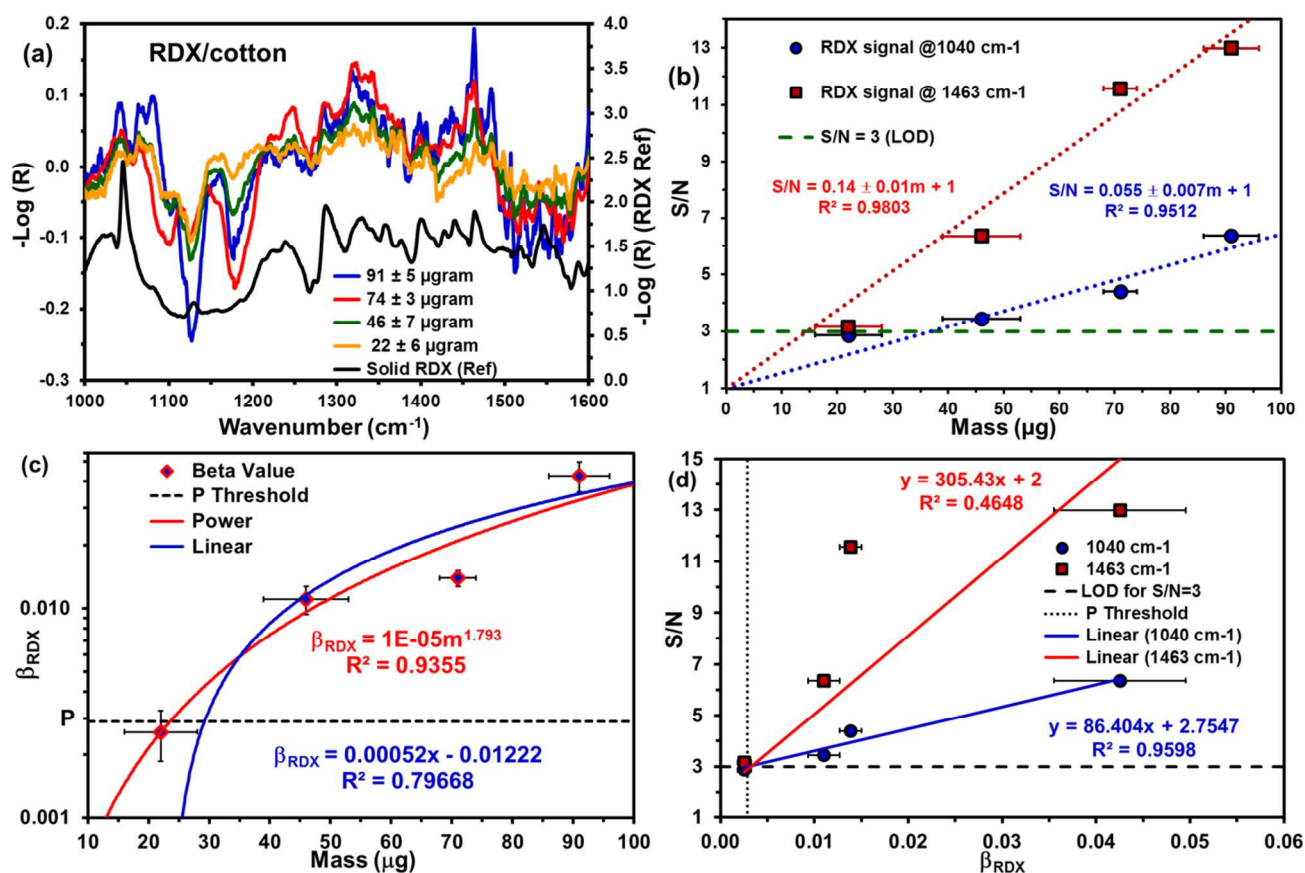


FIGURE 6



Model			Discriminant Model	
	Sensitivity	Specificity	Sensitivity	Specificity
Binary			Binary	
Cotton	100%	100%	100%	89%
TNT	100%	100%	89%	100%
Binary			Binary	
Cotton	100%	100%	100%	85%
RDX	100%	100%	85%	100%
Binary			Binary	
Cotton	100%	100%	100%	95%
PETN	100%	100%	95%	100%
Ternary			Ternary	
Cotton	100%	100%	100%	86%
TNT	100%	97%	94%	100%
RDX	99%	88%	91%	100%
HEM	100%	100%	86%	100%
Quaternary			Quaternary	
Cotton	100%	100%	100%	88%
TNT	89%	94%	86%	90%
RDX	95%	84%	86%	100%
PETN	99%	67%	86%	91%
HEM	100%	100%	88%	100%

Sample	Model 1 (mg TNT)	Model 2 (mg TNT)	Model 3 (mg TNT)
white cotton	-0.05 ± 0.01	-0.07 ± 0.01	-0.06 ± 0.01
polyester	0.15 ± 0.05	-0.01 ± 0.03	0.00 ± 0.02
65% polyester 35% cotton	0.15 ± 0.03	-0.05 ± 0.03	-0.01 ± 0.03
45% polyester 55% cotton	0.04 ± 0.04	-0.03 ± 0.03	-0.07 ± 0.03
84% polyester 16% spandex	0.31 ± 0.03	0.17 ± 0.03	0 ± 0.03
2 mg TNT 65% polyester 35% cotton	0.83 ± 0.04	0.78 ± 0.04	0.68 ± 0.05
0.5 mg TNT 65% polyester 35% cotton	0.5 ± 0.1	0.4 ± 0.1	0.3 ± 0.1
2 mg TNT 45% polyester 55% cotton	0.72 ± 0.08	0.67 ± 0.09	0.58 ± 0.09
0.5 mg TNT 45% polyester 55% cotton	0.38 ± 0.02	0.31 ± 0.02	0.27 ± 0.03
4 mg TNT on 84% polyester 16% spandex	0.9 ± 0.1	0.9 ± 0.1	0.9 ± 0.1
2 mg TNT on 84% polyester 16% spandex	0.3 ± 0.1	0.3 ± 0.2	0.5 ± 0.2
0.8 mg TNT on 84% polyester 16% spandex	0.3 ± 0.2	0.2 ± 0.2	0.3 ± 0.2
0.5 mg TNT on 84% polyester 16% spandex	0.4 ± 0.1	0.3 ± 0.1	0.2 ± 0.2
~0.1 mg TNT on 84% polyester 16% spandex	0.25 ± 0.01	0.12 ± 0.01	0.05 ± 0.01

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Table 3. Statistical values for functions derived from β parameters for the DA for the quaternary mixture

Discriminant functions	1	2	3
Eigenvalue	6.2	3.2	0.5
Relative %	63%	32%	5%
Canonical Correlation	0.93	0.87	0.56
Wilks Lambda	0.02	0.16	0.68
Chi-squared	901.9	431.7	90.6
p-value	< 0.0001	< 0.0001	< 0.0001

FIGURES AND CAPTIONS

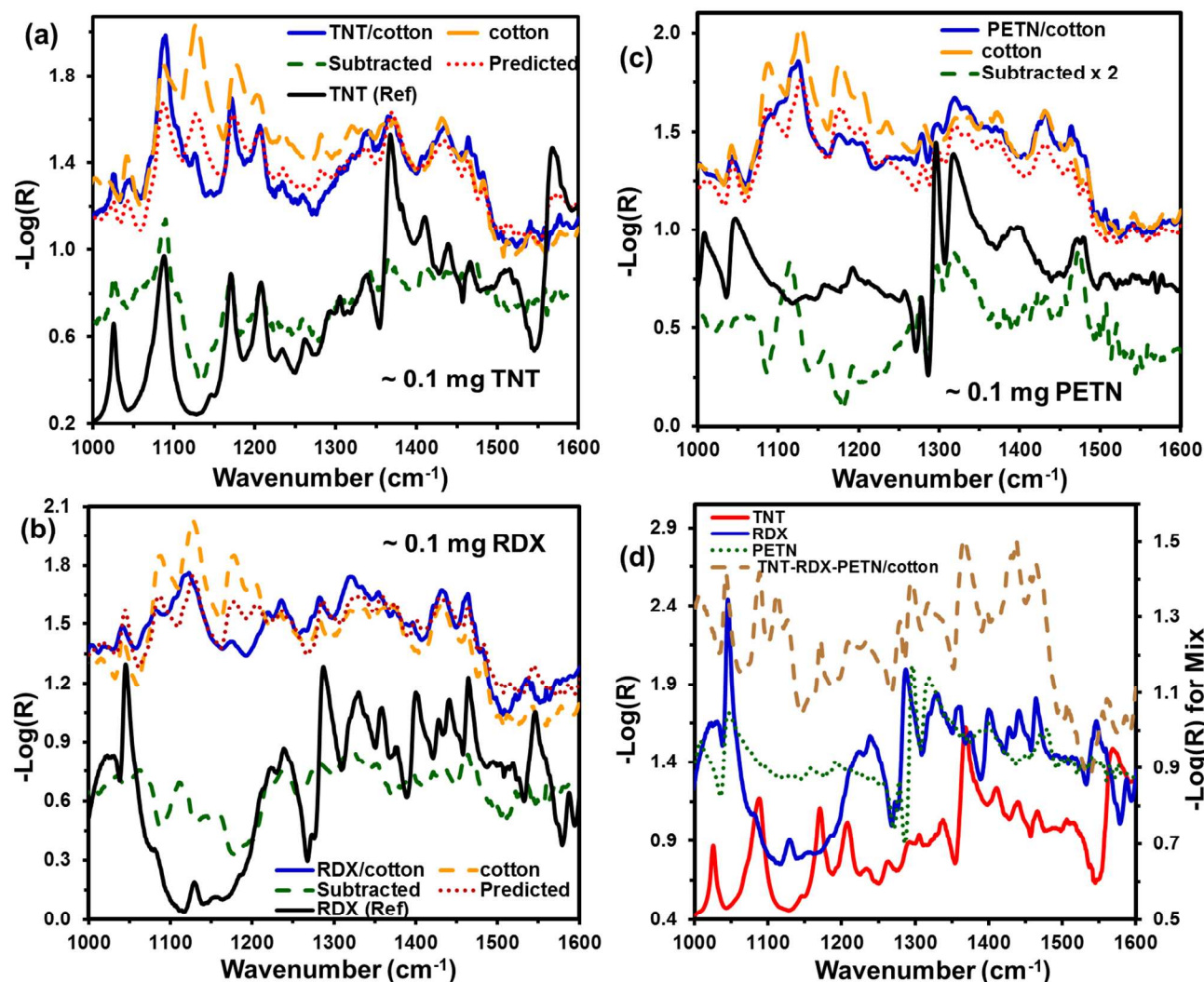


Figure 1. (a-c) Spectra of approximately 0.1 mg of HEMs (TNT, RDX, and PETN) deposited on cotton are shown as blue traces; predicted spectra from Equation (5) are shown as red traces; cotton spectra are shown in orange traces; subtraction of cotton spectra from HEM/cotton spectra calculated using Eq. 4 are shown as green traces; reference HEM spectra are shown as black traces. (d) Comparison of reference spectra for individual HEM and a typical spectrum for the quaternary mixture: TNT-RDX-PETN/cotton.

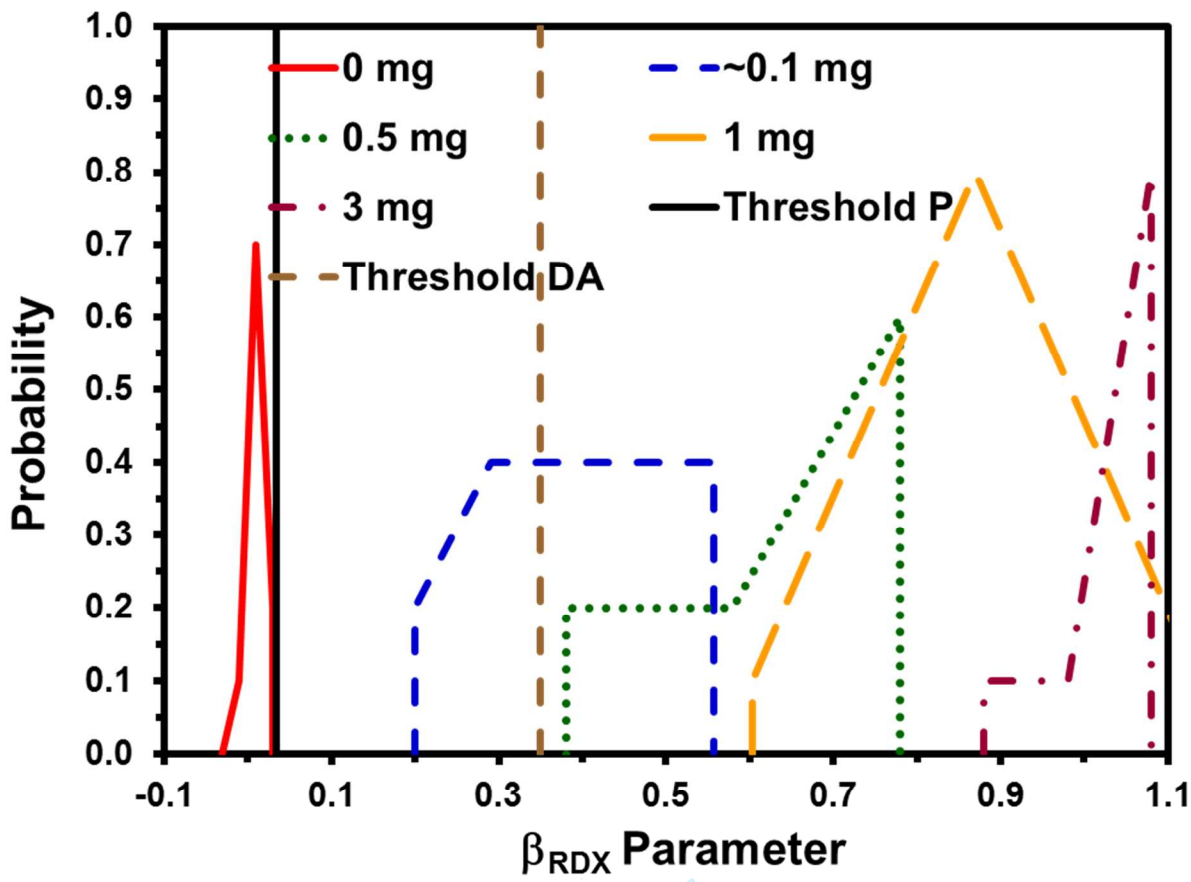


Figure 2. Probability distribution for the $\hat{\beta}_{RDX}$ parameter for in the RDX/cotton binary mix.

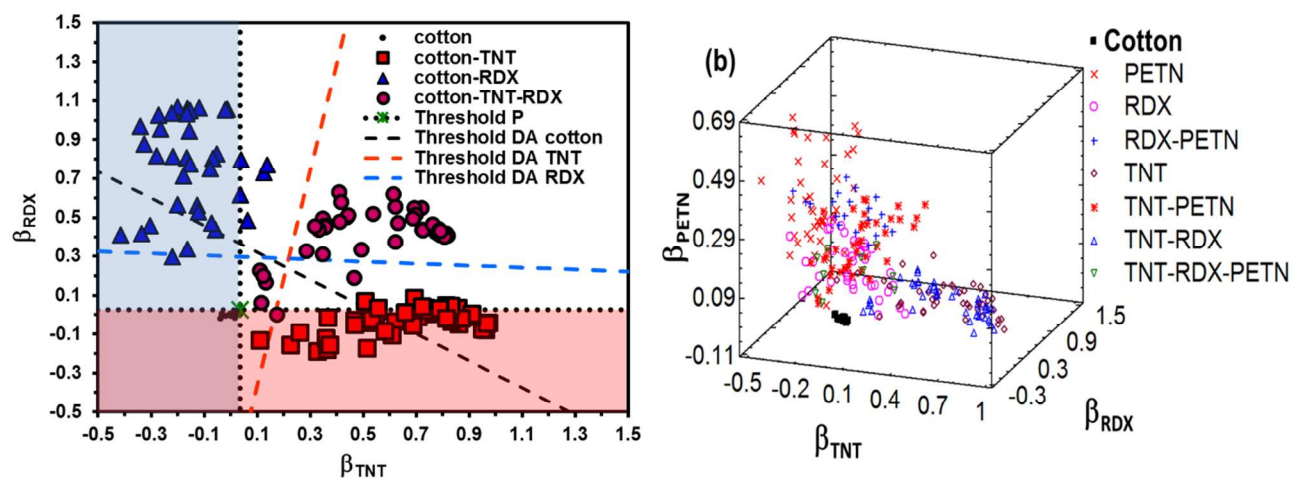


Figure 3. (a) β_{TNT} and β_{RDX} parameters samples distribution. (b) β_{TNT} , β_{RDX} , and β_{PETN} samples distribution parameters.

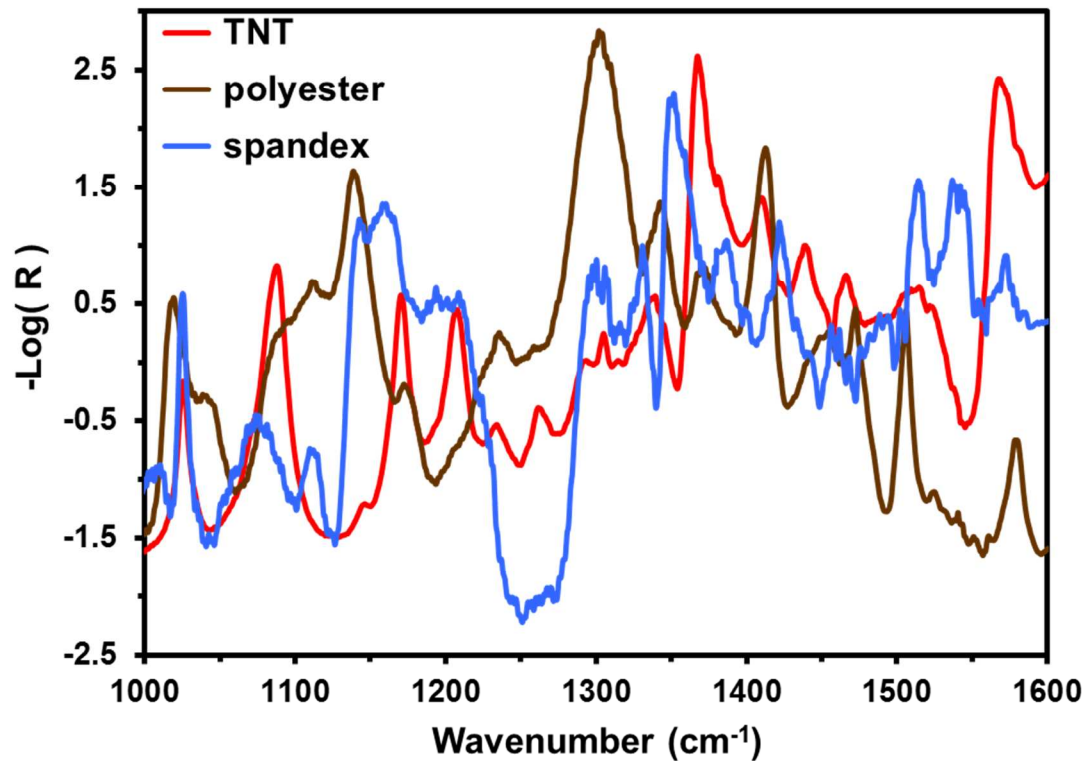


Figure 4. QCL reflectance spectra of components used in the additional tests of the methodology proposed based on CLS: TNT, polyester and spandex.

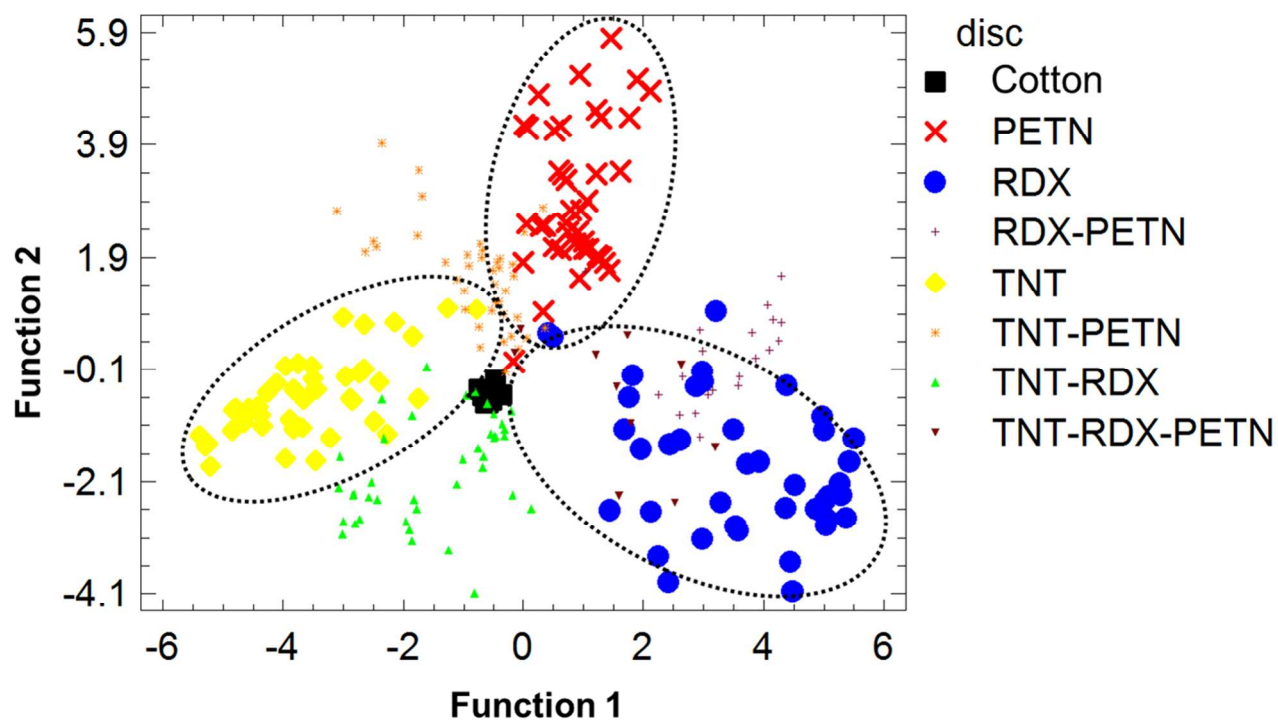


Figure 5. Plot of functions 1 and 2 used in the discriminant analysis.

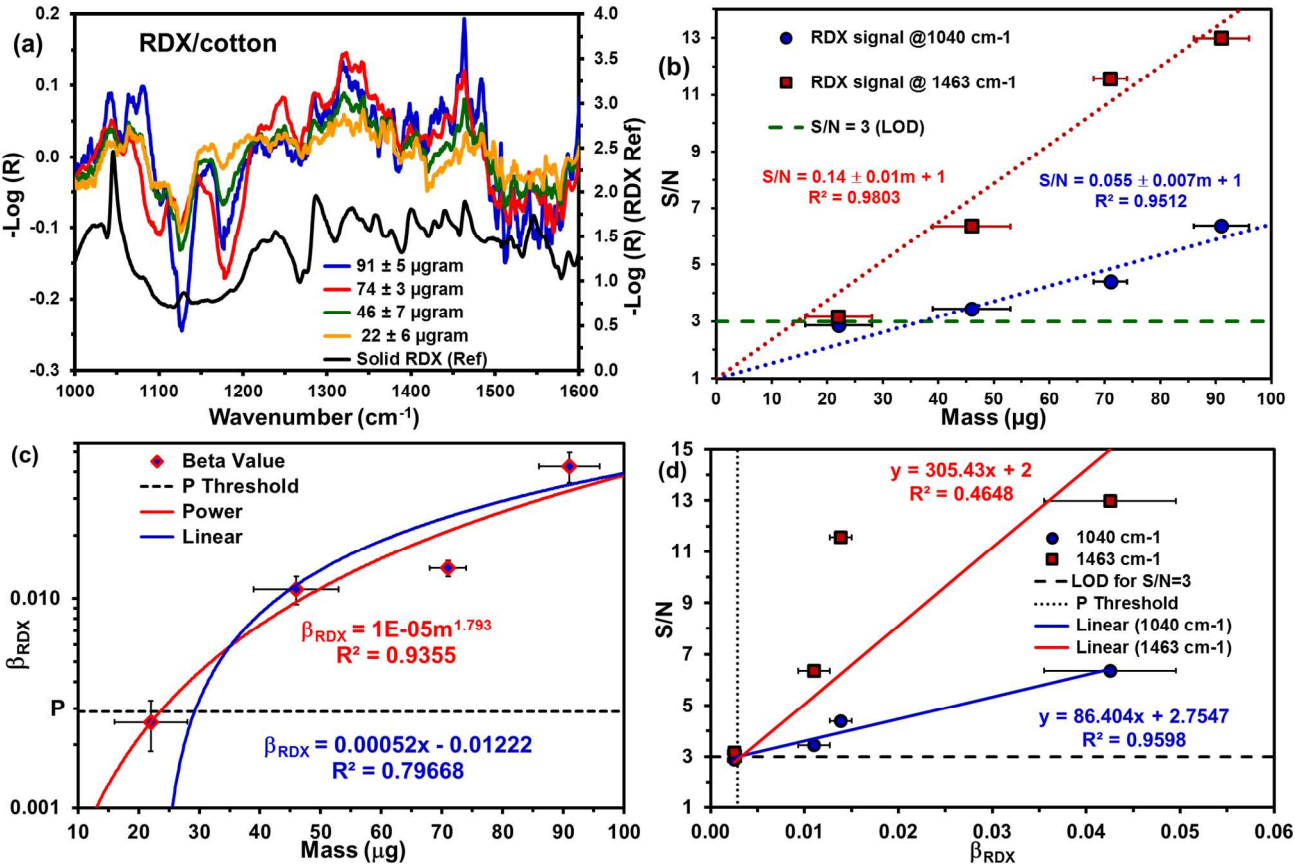


Figure 6. (a) Spectra of RDX particles at various surface masses on cotton substrates; (b) Plot of S/N vs. mass for two RDX signals; (c) Plot β parameter for RDX vs. masses; (d) Plot of S/N vs. β parameter for RDX.

Discriminant functions	1	2	3
Eigenvalue	6.2	3.2	0.5
Relative %	63%	32%	5%
Canonical Correlation	0.93	0.87	0.56
Wilks Lambda	0.02	0.16	0.68
Chi-squared	901.9	431.7	90.6
p-value	< 0.0001	< 0.0001	< 0.0001

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Classical Least Squares Discriminant Analysis of High Explosives Detected on Cotton Fabrics by Quantum Cascade Laser Spectroscopy

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Supplementary Materials

1. Experimental setup used in the investigations

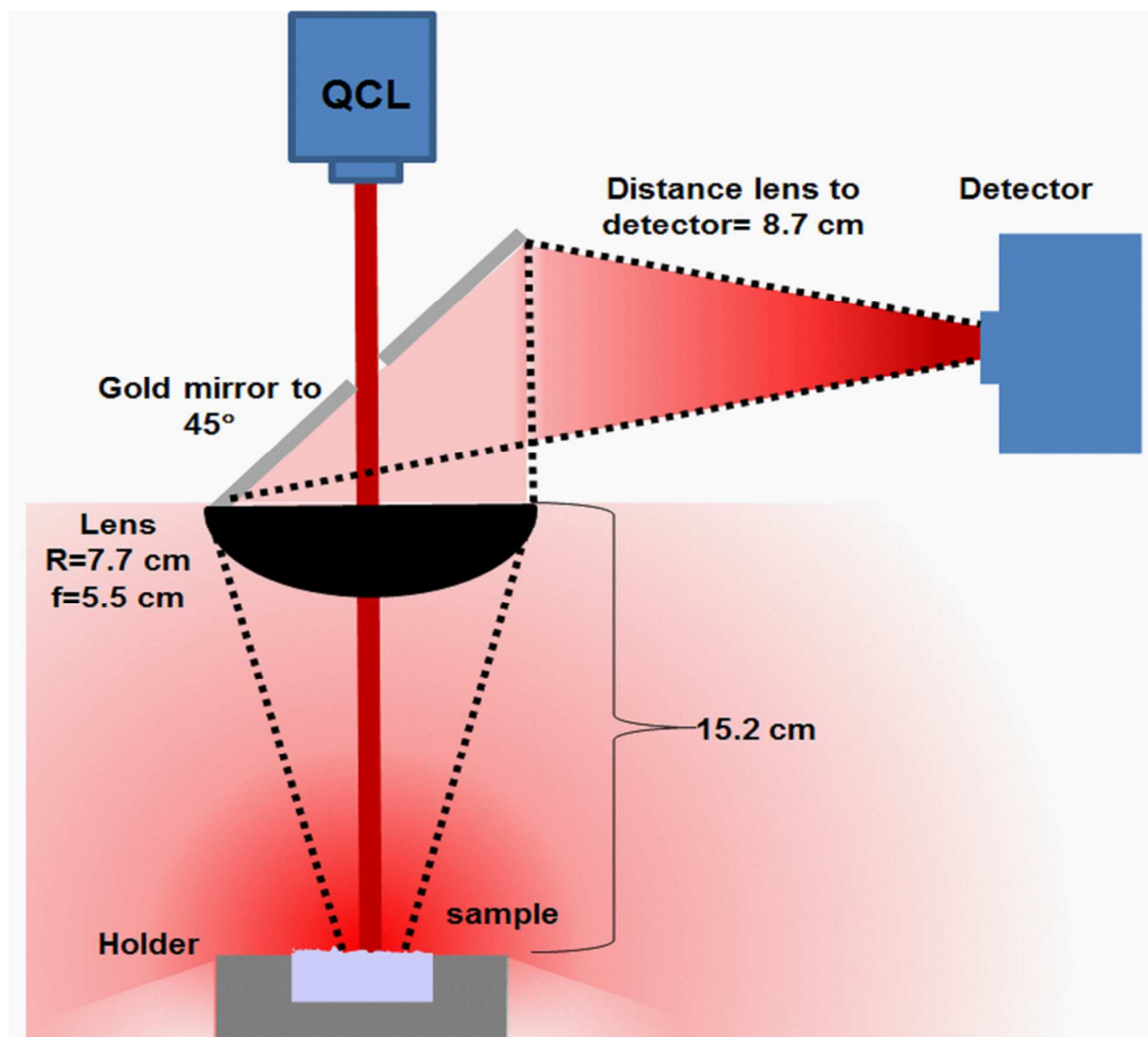


Figure SM-1. Experimental setup used for the QCL based reflectance measurements.

Figure SM-2 shows the details of the weighting procedure using the quartz balance of a TGA system.

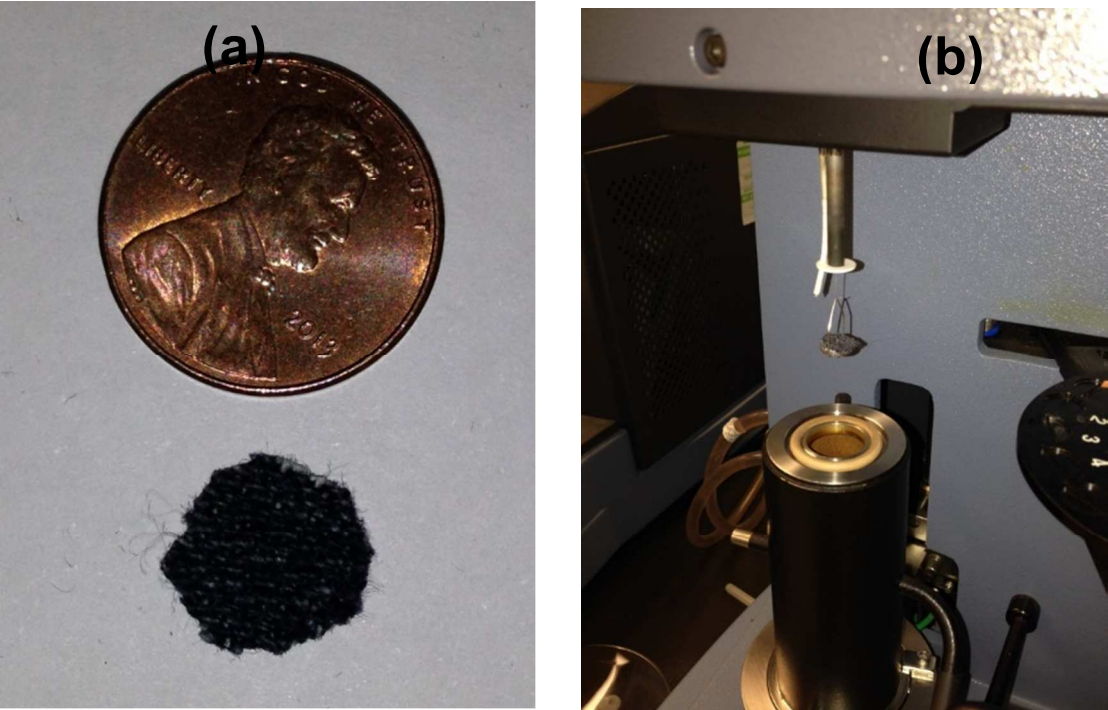


Figure SM-2. (a) Photograph of cotton fabric from jean used in the experiment; (b) weighting in TGA balance.

2. TNT Binary Model

The binary models consisted only in spectra of cotton and cotton with TNT. The equation is as follows:

$$f_{cotton}^{TNT} = \hat{\beta}_0 + \hat{\beta}_{cotton}\varphi_{cotton}(\omega_i) + \hat{\beta}_{TNT}\varphi_{TNT}(\omega_i) \tag{SM 1}$$

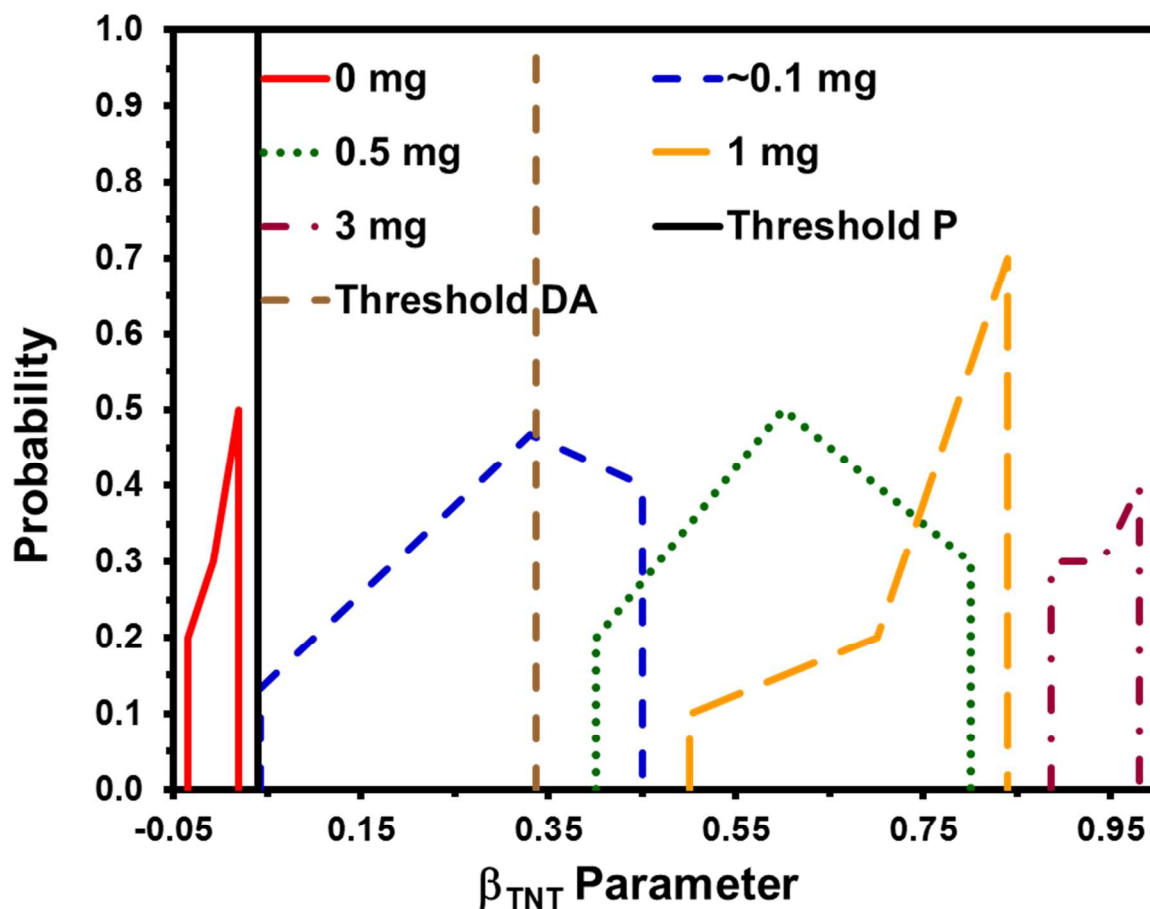


Figure SM-3. Probability distribution for β parameter of TNT.

3. PETN Binary Model

The binary models consisted only in cotton spectra and cotton with PETN. The equation is as follows:

$$f_{cotton}^{PETN} = \hat{\beta}_0 + \hat{\beta}_{cotton} \varphi_{cotton}(\omega_i) + \hat{\beta}_{PETN} \varphi_{PETN}(\omega_i) \quad (\text{SM } 2)$$

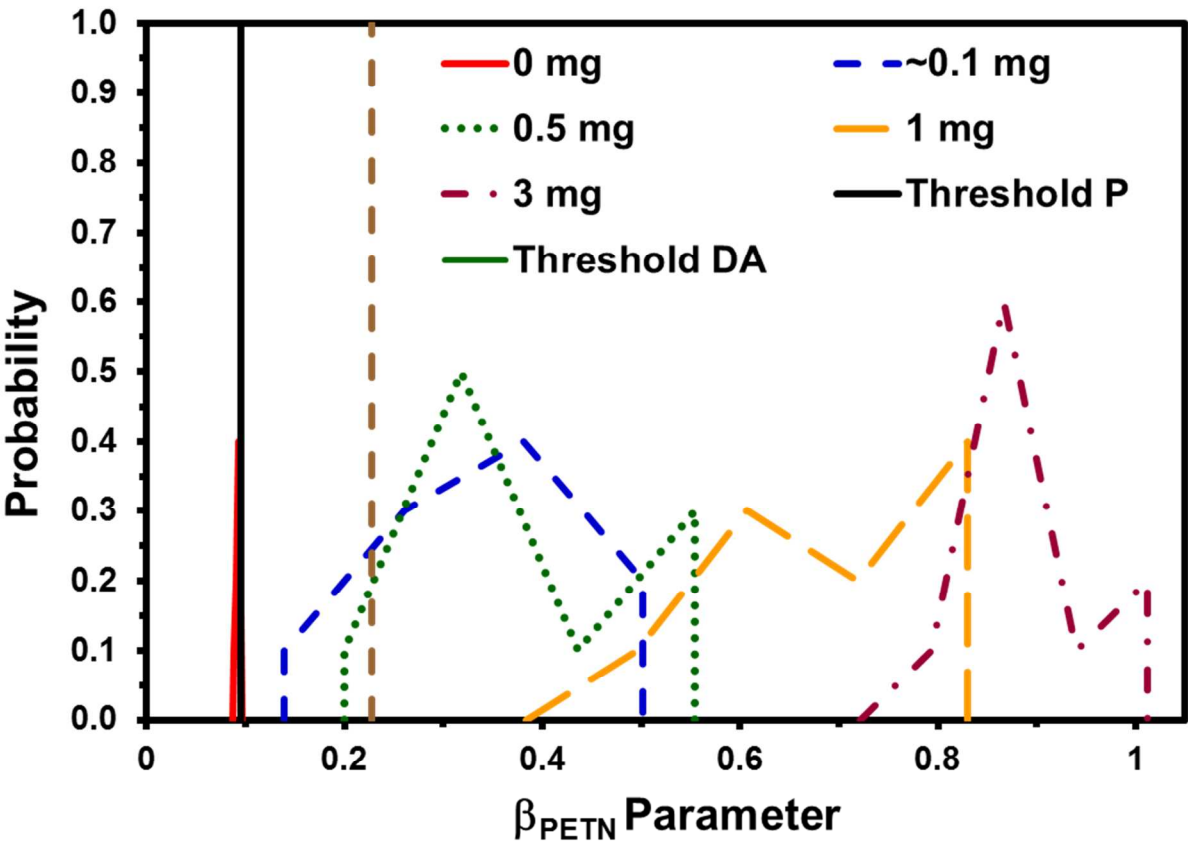


Figure SM-4. Probability distribution for $\hat{\beta}_{PETN}$ parameter.

4. Second Model: Three (3) components for testing:

$$f_{cotton}^{TNT+RDX} = \hat{\beta}_0 + \hat{\beta}_{cotton}\varphi_{cotton}(\omega_i) + \hat{\beta}_{TNT}\varphi_{TNT}(\omega_i) + \hat{\beta}_{RDX}\varphi_{RDX}(\omega_i) \quad (SM\ 3)$$

Various amounts from 0.1 to 3 mg (134 samples) of TNT, RDX, and a mixture of 50% TNT and RDX were deposited on cotton. The β_{TNT} and β_{RDX} parameters were calculated, and the distribution values for each sample was plotted from equation 4 (see Figure SM-4).

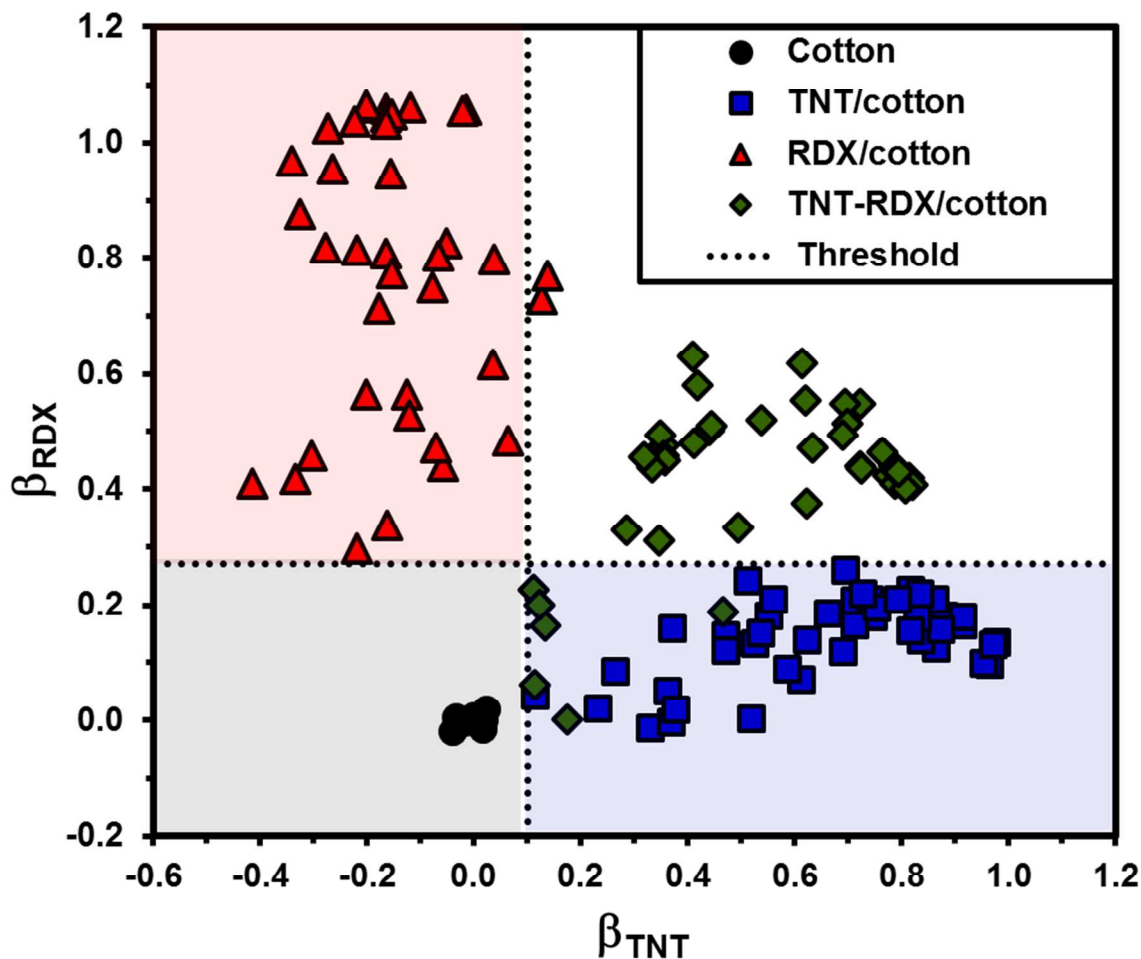


Figure SM-5. Samples distribution for $\hat{\beta}_{TNT}$ and $\hat{\beta}_{RDX}$ parameters.

5. Third Model: Four (4) components for testing:

$$f_{cotton}^{TNT+RDX+PETN} =$$

$$\hat{\beta}_0 + \hat{\beta}_{cotton}\varphi_{cotton}(\omega_i) + \hat{\beta}_{TNT}\varphi_{TNT}(\omega_i) +$$

$$\hat{\beta}_{RDX}\varphi_{RDX}(\omega_i) + \hat{\beta}_{PETN}\varphi_{PETN}(\omega_i) \quad (\text{SM 4})$$

Several amount combinations from 0.1 to 3 mg (252 samples) of TNT, RDX, PETN, and a 50% mixture of TNT with RDX (TNT-RDX), 50% TNT with PETN (TNT-PETN), 50%

PETN with RDX (RDX-PETN), and a mixture of 33.3% of TNT, PETN, and RDX (TNT-RDX-PETN) were deposited on the cotton substrates. The $\hat{\beta}_{TNT}$, $\hat{\beta}_{RDX}$, and $\hat{\beta}_{PETN}$ parameters values were calculated along with their distribution plots for each sample from the calculated values following Eq. SM 5 (see Figure SM 5).

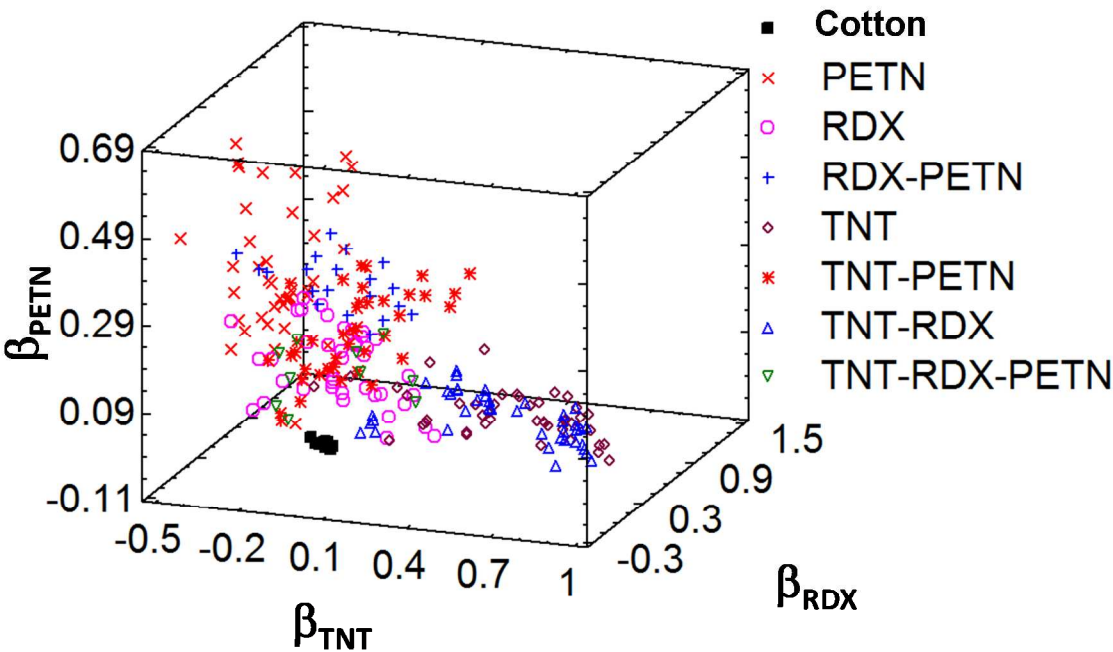


Figure SM-6. The $\hat{\beta}_{TNT}$, $\hat{\beta}_{RDX}$, and $\hat{\beta}_{PETN}$ parameters samples distribution.

6. Spectra for each HEM and the quaternary mixture is illustrated in Figure SM-8

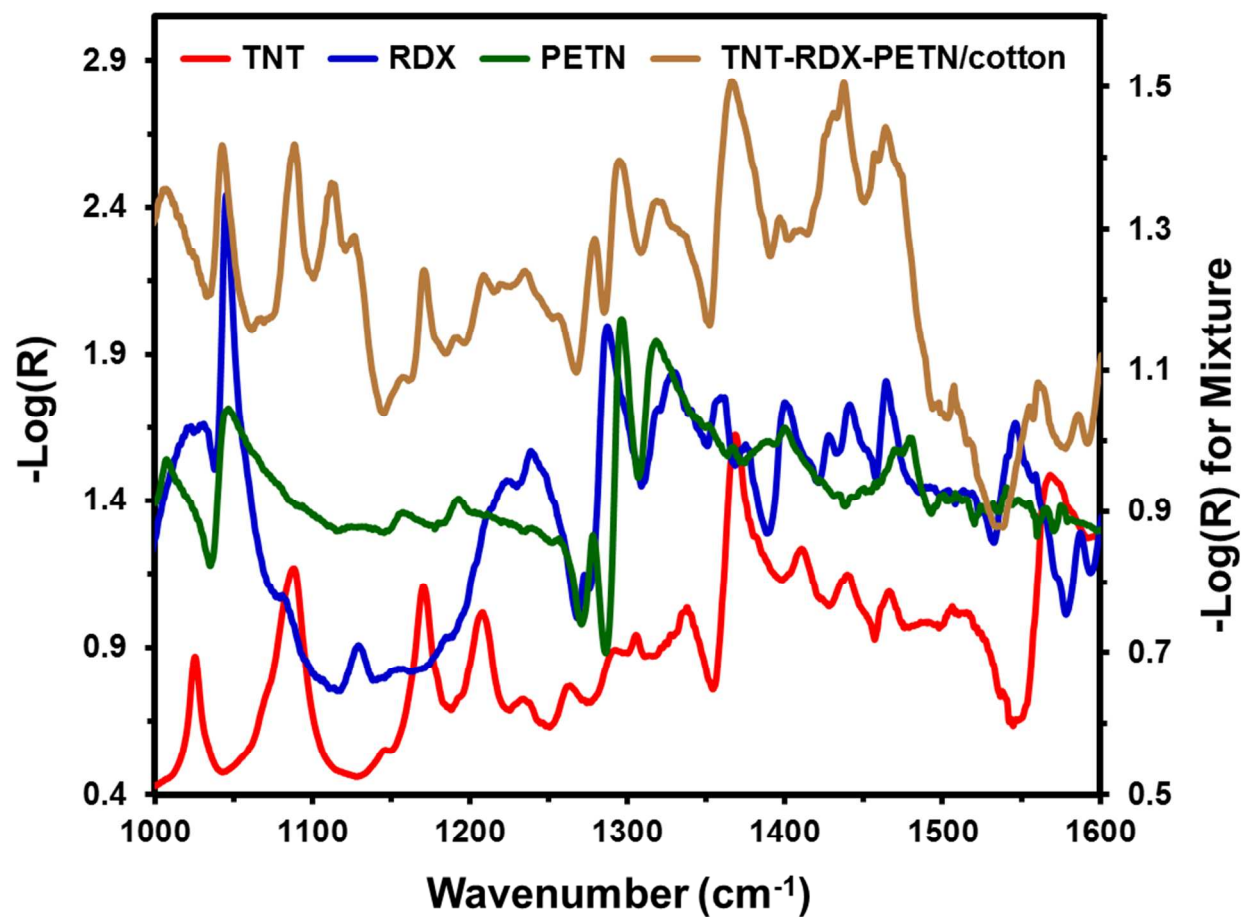
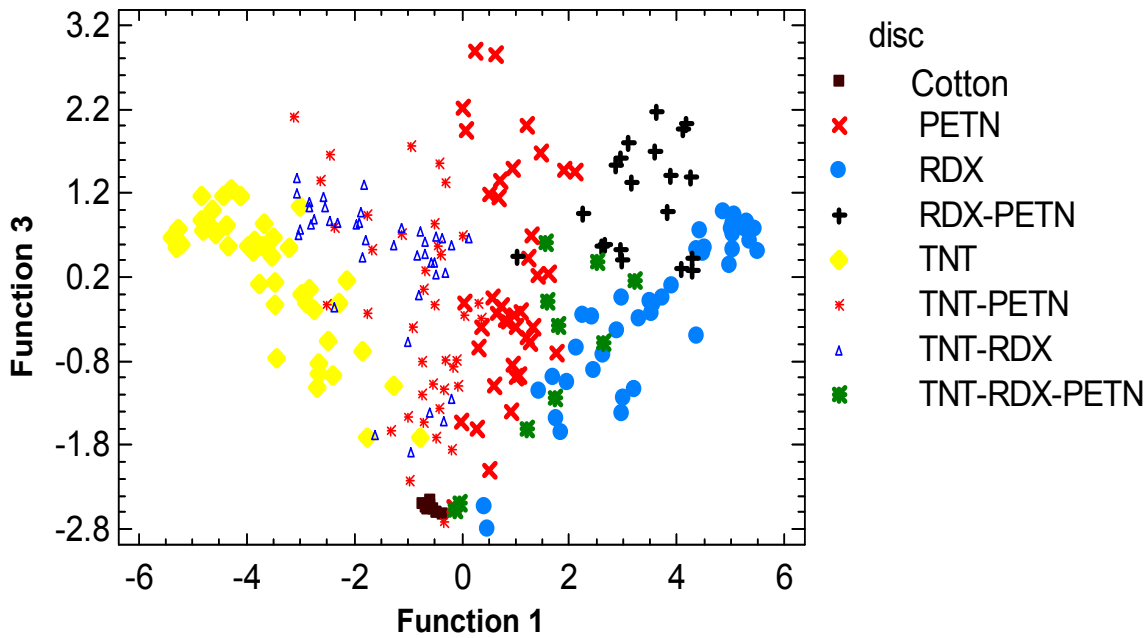


Figure SM-7. Comparison among HEM spectra and the quaternary mixture spectra.

7. Discriminant Functions Plots



8. **Figure SM-8.** Plot of Discriminant Function 1 vs. 3.

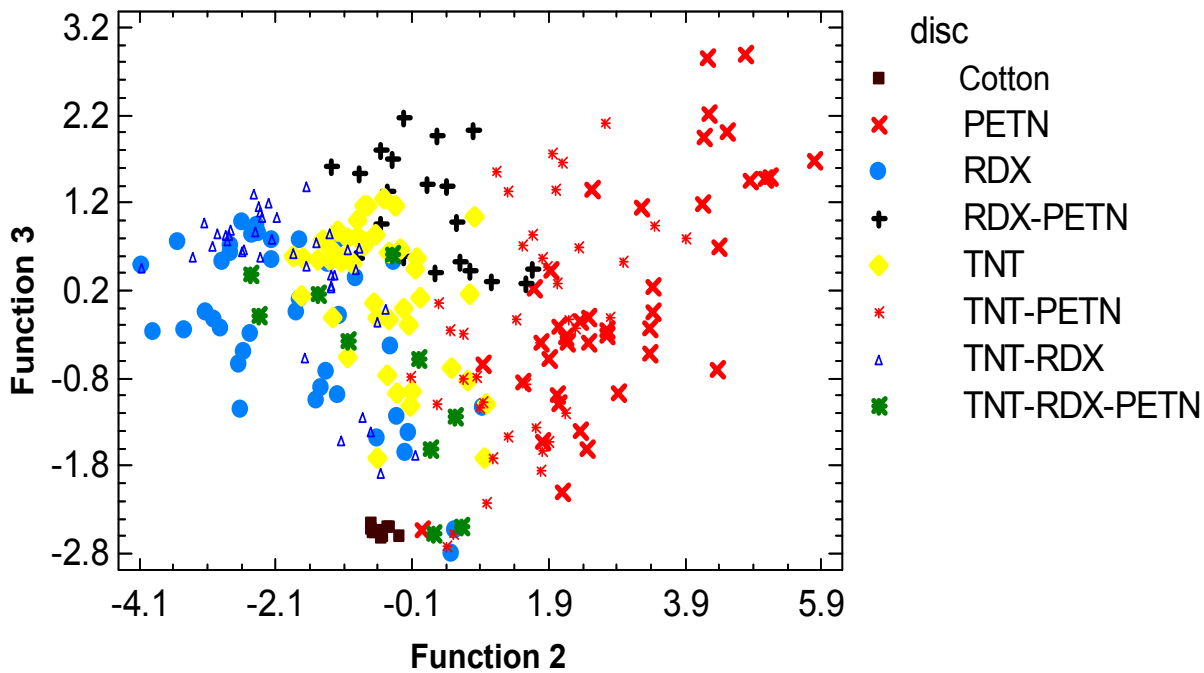


Figure SM-9. Discriminant Function 2 vs. 3.

9. Customized Matlab program to obtain the β parameter for the mixture spectra

```

A = full(file matrix net component); % Loading of matrix of net component
T=full(file mixture);% Loading of matrix of mixture spectra
specwidth=size(A,2); % Number of wavenumber
Ncom=size(A,1); % Number of components
nummix=size(T,1); % Number of mixture
i=1;
X=zeros(Ncom,nummix);% X matrix of fraction for each component for each mixture
mixp=zeros(nummix,specwidth);
while(i<nummix+1) % Calculate the fraction
    C= T(i,:)*A';
    B = A*A';
    p =C/B;
    X(:,i) = p;
    i=i+1;
end
%extract component signals of interest in this case 1 component
for h= 1:nummix
    mix=zeros(1,specwidth);
    for j=2:Ncom
        dumin=X(j,h).*A(j,:);
        mix=mix+dumin;
    end
    mixp(h,:)=mix;
end
D=T-mixp; % extracted matrix

```