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Detection of High Explosives Using Reflection Absorption Infrared Spectroscopy with Fiber Coupled Grazing Angle Probe/FTIR

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Abstract Fiber Optic Coupled Reflection/Absorption Infrared Spectroscopy (RAIRS) has been investigated as a potential technique for developing methodologies of detection and quantification of explosive residues on metallic surfaces. TNT, DNT, HMX, PETN, and Tetryl were detected at loading concentrations less than 400 ng/cm^2. Data were analyzed using Chemometrics statistical analysis routines. In particular, partial least squares multivariate analysis (PLS) was used for quantification studies. Peak areas were also used for data analysis to compare with linear multivariate analysis. The measurements resulted in intense absorption bands in the fingerprint region of the infrared spectrum that were used to quantify the target threat chemicals and to calculate the limit of detection for each compound. Micro-RAIRS vibrational imaging was also used for characterization of the distribution and form of layers of explosives deposited on stainless steel sheets. The degree of homogeneity depended strongly on the method of deposition. The images were generated by calculating the area under vibrational signals of 15 μm × 15 μm grids with a separation of 15 μm. Histograms of the maps were generated and the homogeneity was evaluated by using standard deviations, mean kurtosis, skewness, and moments of distributions obtained. Methanol solutions of High Explosives (HE) resulted in the optimum distributions on the stainless steel surfaces tested and therefore, Methanol selected as the preferred solvent for the Fiber Optics Coupled-RAIRS experiments.

Keywords Grazing angle FTIR · RAIRS · Fiber optics · Nitroexplosives

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1 Introduction

The methodology for the detection of trace amounts of explosives developed in this work is based on the phenomenon of specular reflectance: a non-destructive, non-contact technique particularly useful for film thickness and refractive index measurements and for recording spectra of thin films on metallic substrates [1]. In the phenomenon of specular reflectance, light is reflected from a smooth, mirror-like sample. If there is a film, coating, or residue on the surface, an infrared beam that passes through the coating, reflects off the smooth substrate and passes through the coating again. This process is termed double transmission or Reflection/Absorption Infrared Spectroscopy (RAIRS) [1]. When a true specular reflectance takes place off the first surface of the sample, the resultant spectrum may contain derivative-like shaped bands due to the dependence of the real part of the refractive index of the material ($Re\{n\}$) on the frequency where the sample absorbs radiation. Typical RAIRS spectra are reported in terms of the measured absorbance defined as:

$$A = \mathrm{Log}(R_\mathrm{r}/R_\mathrm{s}) \tag{1}$$

where, R_r is the reflectance of the surface (substrate) and R_s is the reflectance of sample–substrate composite. Fourier Transform (FT)-RAIRS, when measured close to the grazing angle (>80° with respect to the surface normal), is one of the most sensitive optical absorption techniques available for measuring low concentrations of chemical compounds present in trace amounts and thin films adhered to reflective surfaces such as metals [2–4].

The disadvantage of conventional reflectance spectroscopic techniques for applications such as explosives detection on surfaces is that readily available reflectance measurements must be performed by physically placing the sample within the spectrometer's sample compartment for the desired measurements. However, FT-RAIRS, when combined with an optically coupled grazing angle probe, can be used outside of the sample compartment. Fiber optic cables (FOC) that transmit in the mid-infrared (MIR) range have enabled the development of such spectroscopic probes for in situ analysis outside the traditional sample compartment [5, 6].

The features of this technique that make it attractive for field work include: portability, simple and rugged design, high sensitivity, and short cycle time. These important attributes of FOC-FT-RAIRS pave the way for a potential use of the method to be an excellent alternative for sensing explosives and other threat chemicals of interest in national defense and security applications. For example, the technology could be used as an alternative for airport screening for explosive compounds including homemade explosives (HMEs) such as triacetone triperoxide (TATP) and its formulations and mixtures and ANFO (94% ammonium nitrate prills in 6% absorbed fuel oil), among other explosives employed by terrorists in Improvised Explosives Devices (IED). Also, the proposed methodology can be applied in post production of explosives to determine the cleanliness of reactors during batch production changeover. Thus, FOC-GAP-FTIR could also be used in decontamination verification of surfaces that come in contact with HEs and their formulations in many military and civilian operations.

2 Experimental

2.1 Reagents

In order to demonstrate the detection and quantification capabilities for explosives of the developed methodology, five high explosives (HE) were selected: 2,4,6-trinitrotoluene (TNT), 2,6-dinitrotoluene (DNT), tetryl, octogen (HMX), and pentaerythritol tetranitrate (PETN). Reagents used included solvents, energetic materials and metal substrates cleaning agents. Acetonitrile (CH_3CN, HPLC grade), acetone (CH_3COCH_3, HPLC grade, ACS specifications), methanol (99.9%, CH_3OH, HPLC grade), ethanol (CH_3CH_2OH, 99.5%, anhydrous, 200 proof, Acros Organics) and isopropanol ((CH_3)$_2$CHOH, anhydrous 99.8+%, Acros Organics) were purchased from Fisher Scientific Int., Chicago, IL. PETN was synthesized according to the method described by Urbanski [7]. 2,4,6-TNT, 2,6-DNT, tetryl and HMX were purchased from ChemService, Inc., West Chester, PA.

2.2 Instrumentation

The experimental setup for the FOC-RAIRS equipment is presented in schematic form in Fig. 1. The spectra were collected using a Bruker Optics Vector 22 FTIR spectrometer. A Remspec grazing angle probe (GAP) was externally interfaced to the spectrometer by a 1 m long, 3 mm outer diameter, 19 chalcogenide glass optical fiber bundle. The As–Se–Te based fiber system used transmits IR signals throughout the mid-infrared region (MIR), with the exception of a strong H–Se absorption band centered approximately at 2,200 cm^{-1}. The GAP head had carefully aligned off-axis gold parabolic mirrors that were used to collimate the IR beam exiting the
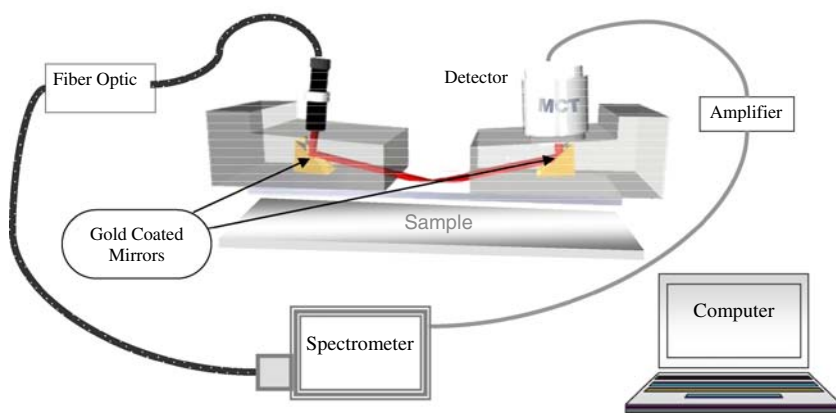

Fig. 1 Experimental setup: samples were deposited on SS plate. Gold coated elliptical mirrors direct IR light to and from the samples. Grazing angle probe (GAP) was fiber coupled to FTIR spectrometer. IR signal was detected by MCT sensor, amplified and sent to interferometer. Data collection and analysis was controlled by PC

interferometer and direct it to the sampling surface near the grazing angle ($\sim 80°$ from test surface normal); the reflected beam was then collected and returned to a mid-IR detector. External, liquid nitrogen cooled, mercury–cadmium–telluride (MCT) detector was used to detect the reflected MIR light in the wavenumber range of 650–4,000 cm^{-1}. The GAP head illuminated a large spot on the sample surface, forming an ellipse, 1 inch by 6 inches, whose intensity profile decayed outward, from the center to the edges.

Micro-RAIRS, operating in vibrational mapping mode, was used for characterization of the morphology and sample distributions of the layers of HE deposited by sample smearing on the stainless steel test surfaces. Micro-FTIR equipment used for the IR imaging experiments included Bruker Optics IFS 66v/S spectrometer coupled to a Hyperion II IR microscope equipped with $15\times$ magnification, grazing angle objective, and a computer controlled motorized stage. For the experiments described, the system was equipped with a cryocooled MCT detector and a potassium bromide (KBr) beamsplitter. Some of the samples were first run in micro-RAIRS vibrational mapping for generation of vibrational images and then run in FOC-RAIRS.

2.3 Sample Preparation and Solvent Selection

Samples and standards preparation are a critical step for the development of analytical methodologies. The central idea in chemical sensing applications is to generate a set of standards and build a response calibration in order to use it for detection and quantification of unknown samples. Standards were prepared using a previously developed sample "smearing method'' [8, 9]. Stainless steel metal sheets (SS type 316, non-magnetic) with an effective area of 46.3 cm^2 (3.0 cm $\times$ 15.4 cm) were used as test substrates.

Stock solutions of high explosives were prepared from either neat crystalline forms or GC/MS standard solutions (1 mg/mL) obtained from ChemService, Inc., West Chester, PA. Solutions were then diluted in the used solvent. After taking into account the surface area to be covered by the sample after evaporation, the amount of each compound (or solution) was measured and diluted in order to have the desired loading.

In order to select the most appropriate solvent that would best distribute the HE samples on the test surfaces forming nearly uniform distributed coatings, analytes were dissolved in the following solvents: methanol, isopropanol, acetone, ethanol, and acetonitrile. They were used as transfer solvents for "smearing" the analytes on the stainless steel surfaces. A rectangular piece of Teflon sheet (3 cm width and 0.04 cm thick) was used to smear a fixed volume (20 μl) of the solutions containing the analytes onto the metal surface. The Teflon sheet was inclined towards the right or left and the smearing was done quickly in a single pass operation. Assuming minimum adhesion of the sample solution to the Teflon sheet, the resulting average surface concentrations of explosives ranged from 100 ng/cm^2 to 15 μg/cm^2. Spectroscopic parameters for micro-RAIRS (IR mapping mode) were 650–3,600 cm^{-1} wavenumber range, average of 32 scans at 4 cm^{-1} resolution within a 1 mm $\times$ 1 mm grids separated by 100 μm.

2.4 RAIRS Experiments

As explained before, a 20 μL aliquot of a standard solution of HE in each of the solvents tested was dispensed on the SS plate and spread on by smearing (see Sect. 2.3) using a Teflon sheet. The solvent was allowed to evaporate and FOC-RAIRS spectra were collected. Plates were cleaned with HPLC grade methanol and air-dried at room temperature before measurements.

Since RAIRS is a single beam technique, a background spectrum was collected using a clean test plate (R_r) under the same conditions as the sample spectrum measurement. The spectral range used was $1{,}000$–$3{,}600$ cm^{-1} at 4 cm^{-1} resolution. A minimum of 10 RAIRS spectra (R_s) were acquired for each loading concentration using 20 scans. Bruker Optics OPUS^{TM} software package was used for data collection. RAIRS spectra were calculated using Eq. 1.

3 Results and Discussion

3.1 Sample Preparation: Solvent Selection

Samples were prepared by using smearing transfer method. The amount of HE deposited could be readily determined without the need of an independent analysis. Vibrational images were generated from vibrational maps acquired using peak areas. Histograms of the images were generated and the homogeneity of the distributions of the target compounds on the test surfaces was evaluated by using the standard deviations (SD). A fundamental task in many statistical analyses is to characterize the location and variability of a data set. Parameters such as the SD are important to describe the distributions obtained, since they are good measures of degree of homogeneity. Additional parameters used were: the mean, the kurtosis, and the skewness of the distributions. These parameters are customarily calculated for a distribution and are used to determine the deviation from a "normal" or Gaussian distribution. A further characterization of the data includes skewness and kurtosis. Skewness is a measure of symmetry, or more precisely, the lack of symmetry. A distribution or data set is symmetric if it looks the same to the left and right of the center point. Kurtosis is a measure of whether the data are peaked or flat relative to a normal distribution. That is, data sets with high kurtosis have peaks near the mean and are characterized by heavy tails. Data sets with low kurtosis tend to have a flat top near the mean rather than a sharp peak, in contrast to normal distributions.

The spectral images of TNT deposits on SS metal substrates using different solvents are shown in Fig. 2a–e. Images and data for distributions of other HEs have been omitted. The asymmetric stretching vibration of the nitro group [$v_{as}(NO_2)$] was used for the generation of TNT vibrational images. Peak areas in the wavenumber range of $1{,}473$–$1{,}569$ cm^{-1} for TNT vibrational images are represented in rainbow contour scale and x–y axes are spatial dimensions (μm). The spatial distributions are based on the variations or contrasts in pixel intensities. The image contrasts are due, primarily, to differences in the intensities of the FTIR spectra at a specific
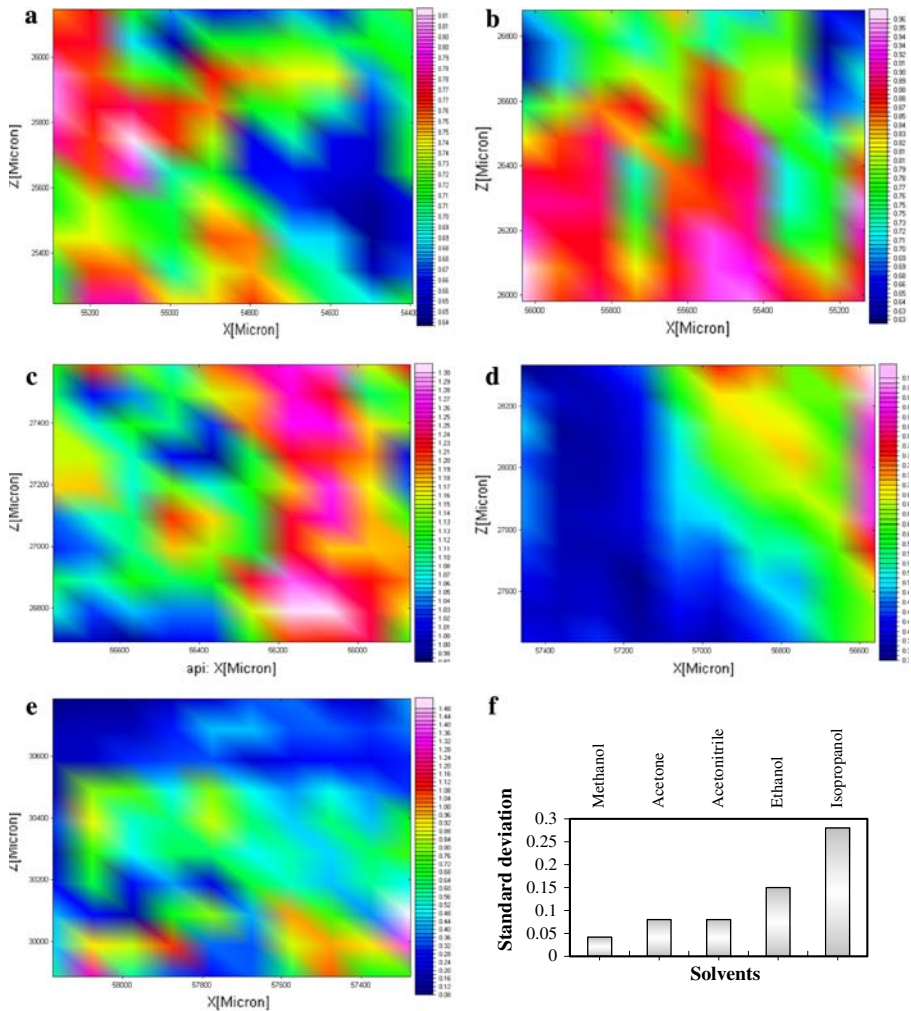
Fig. 2 Infrared spectroscopic images of ∼10 μg/cm² of TNT deposited for different solvent: **a** methanol; **b** acetone; **c** acetonitrile; **d** ethanol; **e** isopropanol; **f** plot of standard deviations of the peak areas in the images for each solvent

wavenumber; specifically, variations in the intensity of a the absorption band which represents a particular chemical component of the HE. Each pixel of the image contains spectral information of the HE analyzed. The three red spectra are generated from the highest intensity pixels and the three blue spectra from the lowest intensity pixels in the image field. Therefore, the red pixels are enriched in HE surface concentration. In contrast, the blue pixels indicate a diminished target compound surface loading. A color that tends to red indicates a higher concentration of the HE and one that tends to blue represents lower concentration of the HE. The relative homogeneity of distributions of the same loading concentrations in different solvents can be estimated by comparing their standard deviations.

PLS-1 regression algorithm from Quant2 software of Bruker Optics OPUS^{TM} (version 4.2) was used to find the best correlation function between the spectral matrices and the concentration matrices. Quant2 uses a Partial Least Squares (PLS-1) fit method. Calibrations were performed using PLS-1 in which only one component can be analyzed separately instead of simultaneously analyzing multiple components as in PLS-2 routine of Chemometrics. PLS-1 was used for the generation of all the HE calibrations.

Peak areas were calculated by integration using, as baseline, straight lines that connected the wavenumber limits of the peak envelopes. Resulting SD values plotted as histograms for the solvents used are shown in Fig. 2f. The analysis of distributions gave kurtosis and skewness with normal values for all the solvents. These values were in the range of -2 to $+2$, indicating statistical significance when compared to a normal distribution. Because all the distributions were considered as normal, the standard deviations could be used as parameters for establishing the relative homogeneities of the distributions.

Methanol was considered the best solvent for the studies based on the low SD values found in the samples prepared for all HE loading concentrations. To determine if there were significant differences between SD values, F-tests at a 99% confidence level were performed. Significant differences were found for all the SD values for the distributions except for acetonitrile and acetone. The lowest standard deviations were obtained for methanol for all HE (data shown only for TNT, 2.0–10.0 $\mu g/cm^2$ surface loading range). This was the rationale used for selecting methanol as the solvent for the FOC-RAIRS experiments. However, the SD values of the rest of the solvents used improved when the loading concentrations ranges were limited to low loading values (<3 $\mu g/cm^2$). A likely explanation for this finding is based on the solubility of HEs in the solvents used. Solvents in which nitroexplosives are slightly soluble (such as acetone and acetonitrile) resulted in more uniformly distributed surfaces when they were deposited on the stainless steel surfaces. However, during the solvent evaporation stage, parts of the material tended to aggregate with the escaping solvent, forming island-type structures and generating surface concentration gradients (hills and valleys). Solubility in methanol is generally lower and when the solvent evaporated, samples exceeded solubility limits at much lower surface loadings. This in turn limited the formation of aggregates and crystallization seeds and the sample remained more uniform at solvent evaporation stage. At low surface concentrations, isopropanol and ethanol resulted in better SD values, most likely due to higher surface tensions than acetone or methanol that resulted in the same effect as the one discussed for methanol at higher surface loadings. At high concentrations, the crystallization processes begin before all the solvent evaporates.

3.2 FOC-RAIRS Spectra

As shown in Fig. 1, FOC-RAIRS is an open path method due to the fact that the IR beam passes through the atmosphere before and after the interaction with the sample. Thus the methodology is prone to interferences from highly absorbing atmospheric constituents. Some absorption bands from water vapor (3,800–3,400 cm^{-1}) and CO_2
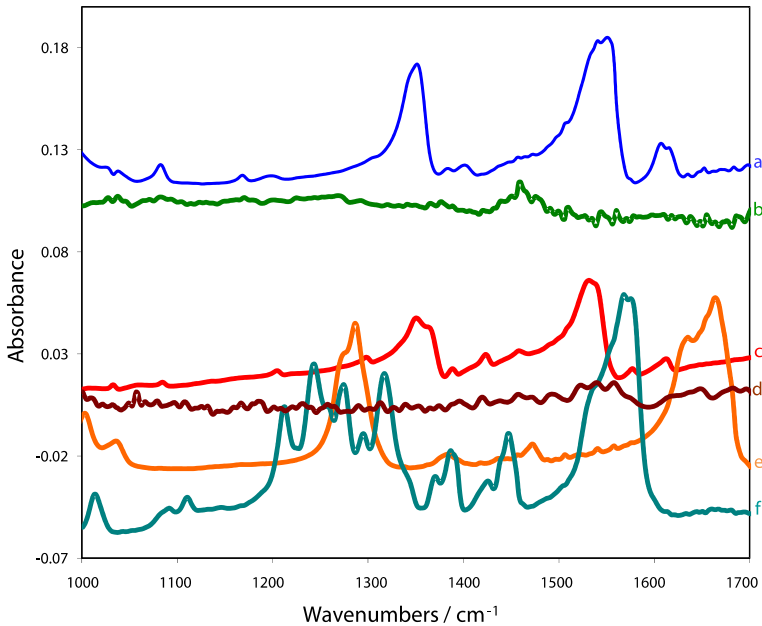
Fig. 3 RAIRS spectra of nitroexplosives at different loading concentrations: **a** TNT, 5.0 μg/cm^2; **b** Tetryl, 8.1 μg/cm^2 (3×); **c** DNT, 10.0 μg/cm^2; **d** SS blank or background (100×); **e** PETN, 8.5 μg/cm^2; **f** HMX, 7.2 μg/cm^2

($\sim$2,350 cm^{-1}) are indeed observed. To avoid this problem, a single channel background spectrum (blank) was recorded before each sample run. This way interferences related to the IR absorbance of air components were minimized.

The NO$_2$ MIR bands can be used for nitroexplosives detection since they act as vibrational signatures for several classes of explosives: nitroaromatic (TNT, DNT, Tetryl), nitroaliphatic (PETN, HMX), nitramines (HMX, Tetryl) and nitrate esters (PETN). Figure 3 shows the prominent signals of some nitroexplosives deposited on SS test surfaces. A typical blank (SS plate) spectrum is also included (multiplied by 100-fold). Any IR signal observed in the blank can be adequately subtracted from the IR signal of the HE. Only one HE IR signal in the range 1,200–1,400 cm^{-1} was highly significant for quantitative analysis. This band can be attributed to nitro symmetric stretch vibration. In PETN this band appears in the 1,250–1,320 cm^{-1} region. For explosives such as TNT, HMX, and DNT, the band appears at 1,320–1,360 cm^{-1} [10]. In the case of Tetryl, the CH symmetric stretch was used.

3.3 Calibration: Partial Least Squares and Single Peak Area

It has been demonstrated in our lab using active pharmaceutical ingredients (APIs), that Chemometrics modeling based on Partial Least Squares analysis can be used to correlate the loading concentration with the RAIRS spectra [6]. The advantages of using Chemometrics for quantification of organic compounds on glass and

aluminum surfaces are well discussed in the literature [9]. Statistically based, multivariate calibrations use spectral features over a wide spectroscopic range. Information from a calibration spectral set (training set) is compared to independently determined concentration data using PLS regression. The method is based on the assumption that systematic variations in the spectra are a consequence of concentration changes. PLS is a spectral decomposition technique that is closely related to principal component analysis (PCA). However, in PLS, the decomposition is performed in a slightly different way. Instead of first decomposing the spectral matrix into a set of eigenvectors and scores and then performing a regression against the concentrations as a separate step, PLS actually uses the concentration information during the decomposition process [11]. PLS-1 regression algorithm from Quant2 software for OPUS^{TM} version 4.2 was used to find the best correlation function between the spectral information and the loading masses. PLS-1 was used to generate all HE calibrations. Cross validations were performed and the root mean square errors of cross validations (RMSECV) and root mean square errors of estimations (RMSEE) were used as criteria to evaluate the quality of the correlations obtained.

Measuring surface concentrations using peak areas is simple and easy to use but it has some limitations. The method is univariate since the concentration is determined with only one peak, and there is a direct linear correlation between the concentration and the peak areas. Perturbations such as fluctuations caused by detector noise, temperature variations or molecular interactions are undetermined. The method is in agreement with Beer's Law. Taking into account the advantages of the PLS-1 routine of Chemometrics, a calibration was generated using this method.

Grazing angle FTIR spectra of freshly prepared samples were collected for a series of different surface loadings. A PLS-1 model was built from spectra of all the explosives studied which have different spectroscopic ranges, rank (number of PLS1), RMEE, and RMSECV. Standard "leave-out-one" cross validations were constructed in which each spectrum is omitted from the training set and then tested against the model built with the remaining spectra. Figure 4 shows the results of a "leave-one-out" cross validation for each of the nitroexplosives studied and the model parameters obtained are shown in Table 1. The low RMSECV values in the cross validations indicate that good Chemometrics models were obtained and could be used for predicting loading concentrations of unknown explosives samples on metallic surfaces. Current efforts are focused on developing data bases for explosives detection and to quantify explosives mixtures using the present methodology combined with Chemometrics PLS-1 calibrations. The spectral range of the Chemometrics models built cover the fingerprint region where the nitro symmetric stretch vibration is located, except for the case of the nitroexplosive Tetryl for which the region used was 3,024–2,810 cm^{-1}, which corresponds to the aromatic CH region. The cross validations for each explosive exhibit low ranks (ranging from 3 to 10), indicating that satisfactory models were obtained. First derivative spectroscopic preprocessing was applied to PETN and DNT in order to build a better calibration model, reducing the values of RMSECV. For the rest of explosives the calibrations were constructed without any preprocessing.
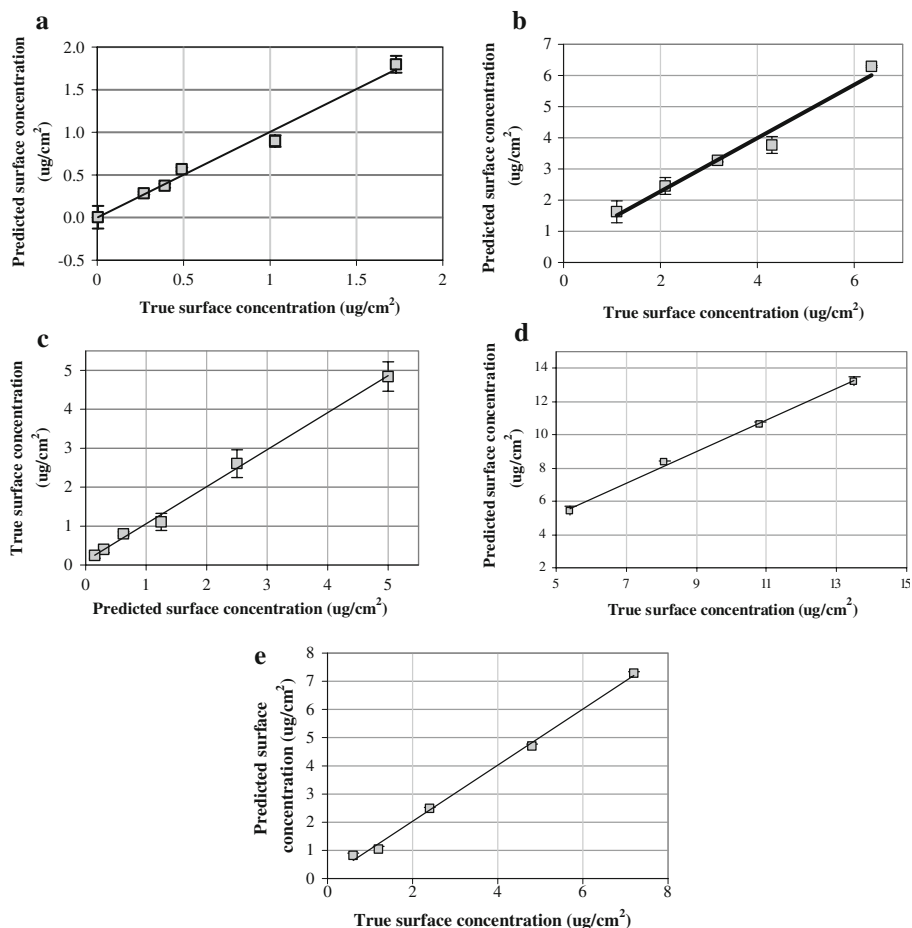
Fig. 4 Predicted versus true surface loading concentrations for the studied nitroexplosives from a "leave-one-out" cross validation using Quant2. **a** TNT; **b** PETN; **c** DNT; **d** Tetryl; **e** HMX

Table 1 PLS-1 calibration parameters for the chemometrics models

	2,4,6-TNT	PETN	2,6-DNT	HMX	Tetryl
Loading concentration (μg/cm^2)	0.005–1.73	0.3–6.5	0.15–5.00	0.6–7.2	5.4–13.5
Spectral range (cm^{-1})	1,028–1,713	1,878–1,088	1,057–1,979	1,632–968	3,024–2,810
Preprocessing	No	First derivative	First derivative	No	No
Rank (PLS)	3	10	9	8	7
RMSECV (μg/cm^2)	0.258	0.498	0.398	0.42	0.78
RMSEE	0.18	0.37	0.19	0.27	0.58
R^2	0.996	0.914	0.946	0.97	0.934
Number of samples	84	72	22	60	48

All the HE calibration runs were generated for concentrations lower than 14 μg/cm². Attempts to build calibration runs of higher surface loadings were unsuccessful. This may be attributed to the change in the nature of the surface coating at high surface loadings: from a thin film capable of generating a double-pass transmission or transflectance spectra; to a nearly bulk material generating diffuse surface reflectance spectra, independent of the coating thickness. A true transflectance experiment is possible only when the layer of organic material is very thin, so that the IR radiation can pass all the way through it to be reflected from the substrate (i.e., the metal surface). If the coating is thicker than about 1 or 2 μm, the IR radiation does not reach the substrate and is reflected from the top surface of the organic material (as if it were a bulk sample of the organic material) originating a diffuse reflectance optical effect. This situation changes the spectra that are obtained from the organic material from the transflectance spectrum to a diffuse reflectance spectrum. The diffuse reflectance spectrum is not affected by the thickness of the coating, since the diffused IR signal does not come from the whole coating but only from the top layer, therefore, it does not contribute to a useful calibration because of the loss of concentration information.

3.4 Detection Limits

A common misconception is that the Limit of Detection (LOD) is the smallest concentration that can be measured. Instead, it is the concentration at which we can decide whether an element or compound is present or not. Specifically, it is the point where we can just distinguish a signal from the background [12]. Quantification is generally agreed to begin at a concentration equal to 10 standard deviations of the blank. This is called the limit of quantification (LOQ) or limit of determination. Therefore, LOQ is equal to 3.3 × LOD.

As the concentration of the sample decreases, the precision, expressed as the relative standard deviation degrades. Quantitatively speaking, the RSD is 10% at the limit of quantification and 33% at the limit of detection ($k = 3$ in IUPAC definition or three detection limits) [13]. After generating the PLS-1 model for each HE (in terms of predicted loading concentration vs. true loading concentration), the standard deviation of the intercept (SDI) was calculated. SDI values were divided by three times the slope and the detection limits were calculated as shown in Eq. 2 [14].

$$\text{RSD} = \frac{\text{SDI}}{\text{SLOPE}} \times 3 \tag{2}$$

Results for the regression statistics and classical LOD for the nitroexplosives studied are shown in Table 2. The LOD values were in the range of 160–400 ng/cm². The developed methodology offers advantages to Ion Mobility Spectroscopy (IMS) for detecting explosives on surfaces. In particular, IMS is limited in linear dynamic range and it cannot be used for quantitative analysis [15, 16]. Moreover, since the technique under development is based on IR spectroscopy in the fingerprint region, the methodology offers near unambiguous identification, particularly when Chemometrics routines are coupled to linear discriminating functions.

Table 2 Limit of detection (LOD) of the study explosives and location of the symmetric stretch nitro vibration

Explosive	Slope	Standard deviation of the intercept	LOD (ng/cm^2)^a	Significance P value
2,6-DNT	1.05	0.075	220	5.67×10^{-6}
2,4,6-TNT	1.00	0.05	160	7.5×10^{-5}
PETN	0.86	0.31	220	2.0×10^{-3}
HMX	0.99	0.13	400	7.61×10^{-5}
Tetryl	1.05	0.39	160	1.4×10^{-3}

^{a} With PLS-1

4 Conclusions

FOC-FTIR spectroscopy has been shown to provide a useful framework for method development of in situ detection of explosives traces on metallic surfaces. Very low limits of detection (~ 160–400 ng/cm^2) were found for nitroexplosives. This study was limited to highly reflective metallic surfaces. However, since it is based on a GAP head that is sensitive to adsorbates deposited on substrates regardless of the nature of the surface (at least to first order), the methodology should be applicable for trace detection of explosives on other types of surfaces (including glasses and plastics). Detection of target molecules using this technique was found to be limited by the residence time of the substance on the surface. At low loading concentrations, high vapor pressure explosives quickly escape to the vapor phase by sublimation, limiting the low limit of detection achievable. This is the case of transparent or peroxide based explosives, such as triacetone triperoxide (TATP) which has very high sublimation rates at close to ambient temperatures and pressures.

The smearing deposition method used was excellent for depositing explosive on surfaces studied, because nearly normal distributions were consistently obtained. The errors or fluctuations in IR absorbance obtained from different samples of a given surface concentration are smaller than other factors that may influence the distributions. These other factors are most likely causing the observed variations.

The proposed methodology for High Explosives detection and quantification based on Fiber Optic Coupled Grazing Angle Probe-FTIR promises to be an excellent alternative for sensing explosives and other threat chemicals of interest in national defense and security applications. For example, the technology could be used as an alternative for airport screening for explosive compounds including homemade explosives (HMEs) and formulations and mixtures. The proposed methodology could also be applied in post production of threat chemical and toxic compounds to determine the degree of cleanliness of chemical processes reactors and other surfaces that come in contact with these agents during batch production and changeover. Thus, FOC-GAP-FTIR could also be used in decontamination verification of surfaces that come in contact with HEs in many military and civilian operations. Other field applications include use in environmental analysis of pollutants present at trace levels on surfaces. More sensitivity and selectivity studies

as well as discrimination analysis should follow in order to establish more firmly the proposed methodology based on RAIRS.

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