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Enhanced RDX Detection Studies on Various Types of Substrates via Tunable Quantum Cascade Laser Spectrometer Coupled with Grazing Angle Probe

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Abstract. Owing to scientific advances in the field of materials sciences and engineering, researchers have developed new energy sources used for spectroscopic applications and measurements of properties resulting from the interaction of matter and electromagnetic radiation in the mid-infrared (MIR) region. MIR lasers, such as quantum cascade lasers (QCLs), used for spectroscopy have quickly found numerous applications in a wide cadre of IR techniques. This provides the opportunity to study properties of highly energetic materials (HEM), among many other applications. MIR laser spectroscopy based detection experiments of HEMs were carried out using a QCL optically coupled to compact grazing angle probe mount (QCL-GAP) enabling reflection-absorption infrared spectroscopy (RAIRS) measurements of thin films of HEMs. A saturated solution of RDX in acetone was prepared, and aliquots of subsequent dilutions of the stock solutions were transferred to test surfaces for QCL-GAP back-reflectance measurements. RDX reflectance signals were monitored as function as the decreasing surface concentration until the signal/noise was ~ 3 . Stainless steel (SS) plates were used as reflective substrates, and anodized aluminum (AN-Al), cardboard, and Teflon were used as non-reflective (matte) substrates. Using generated calibration curves a low limit of detection (LOD) of 1.7 ng/cm^2 for RDX/SS and $95 \text{ } \mu\text{g/cm}^2$ for RDX/AN-Al were found. Based on the area of laser spot (0.3 cm^2) we conclude the minimum masses detected were 490 pg (RDX/SS) and $28 \text{ } \mu\text{g}$ (RDX/AN-Al).

1. Introduction

As part of contingency preparations for awareness and localization of explosives-related threats (ALERT), we have expanded our studies to gain a deeper knowledge about the diverse ways for depositing explosives on substrates for preparing samples and standards used in the remote detection program of highly energetic materials (HEMs). In this regard, it has been a continuous growth of knowledge using various technologies available for preparing test samples. We have explored techniques that include spin coating [1-5], smearing [6], and drop-cast [7] as part as the methodologies used to simulate real-world scenarios of sample preparation and subsequent detection. This part of the



remote detection program is important because the surfaces that come in contact with explosives that are left as residues can evidence potential terrorist acts. [8] Targets include car-bomb surfaces, cardboard substrates evidencing package and letters bombs, clothes and backpacks (or baggage) and other surfaces that may have come in contact with HEM handled in the processes. [9]

In recent years, detection of explosives has become an issue of high importance, particularly in Homeland Security and National Defense applications. This has led to developments in instruments and methods for detection of HEM which includes mass spectrometry [10], vibrational spectroscopy [11], standoff detection [12-13], other sensing schemes [14-15], and trace detection. [16-17] An efficient detection and identification method that provides the low limits of detection (LODs) of HEM on substrates when exposed to different explosives types are always on demand. Developed methodologies would be highly beneficial to airport security, border controls, and military operations, among others.

This work centers on the use of mid-infrared (MIR) quantum cascade lasers (QCLs) which can be tuned to strong absorption bands of HEM such as 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) deposited on substrates for target (analyte) detection, discrimination, and quantification. QCLs are unipolar semiconductor injection lasers that are based on sub-interband transitions in a multiple quantum-well heterostructure. This type of laser has various advantages over other types of lasers. As a semiconductor laser it can produce varying wavelengths and operate at various temperatures. QCLs can produce from a few tens to hundreds of milliwatts of continuous or pulsed mode power under ambient conditions. [18-21] The beam size can be as small as $2 \times 4 \text{ mm}^2$ at the sample, which corresponds to the average beam size at the sample focus of standard laboratory (FT-IR) instruments. [22] The need to develop more powerful MIR sources that enable reflection-absorption infrared spectroscopy (RAIRS) data when a target chemicals or microorganisms are present on a substrate at low surface concentration levels suggests the use of collimated, coherent, and polarized sources [1]. A new setup developed in our laboratory, in which a tunable QCL spectrometer was coupled to a grazing angle probe (QCL-GAP) has provided improvements including the beam size change to $24 \times 4 \text{ mm}^2$. This arrangement consists of using a mirror to direct the IR beam to hit the sample at an angle of 82° with respect to the normal vector (Figure 1). [1] This application of QCL spectroscopy presents certain advantages, such as a low limit of detection (LOD) values ranging from 10 to 50 ng/cm^2 of HEM. [9, 23] In another improvement is in acquisition time (10-15 s per scan) whereas typical RAIRS measurements are highly time-consuming (min to h). [18] If a thin film or coating of some sort exists on a smooth surface, the light beam passes through the coating, reflects off the smooth substrate and passes through the coating for the second time. This phenomenon is called double transmission RAIRS. [1, 23] The best experimental conditions for obtaining RAIRS grazing angle ($\geq 80^\circ$) incidence, with the radiation, polarized parallel to the plane of incidence (p-polarization). It is seen that s-polarized light is almost canceled by reflection at grazing angle (GA). P-polarized light is almost intensity doubled at grazing incidence. Under such conditions, the surface electric field of the resulting stationary wave is normal to the metal plane and represents an enhanced intensity due to constructive interference. [1]

Since the objective of this investigation was to enhance the detection of HEMs, the substrates studied were divided into two classes (a) highly reflective substrates that in token are poor absorbers of the incident electromagnetic radiation (i-EMR) in the MIR region, and (b) non-reflective or matte substrates which are high absorbers of i-EMR. The first class of substrates used are highly reflective metallic substrates such as stainless-steel (SS), gold, highly polished aluminum, and other metals. The second class of substrates used are non-reflective or matte and include Teflon, anodized aluminum (AN-AL), and cardboard. Teflon substrates have an absorption band in the spectroscopic window used in the analyses, but it still allows us to follow other important bands of RDX in the spectral window of $1173 - 1428 \text{ cm}^{-1}$. This research was intended to expand on the results obtained in previous investigations by determining the limits of detection (LOD) for methodologies QCL-based spectrometers for RDX deposited on the mentioned substrates [9] and to test if the QCL based methodology can be used effectively in the field for detecting HEMs on these substrates at low concentration levels.

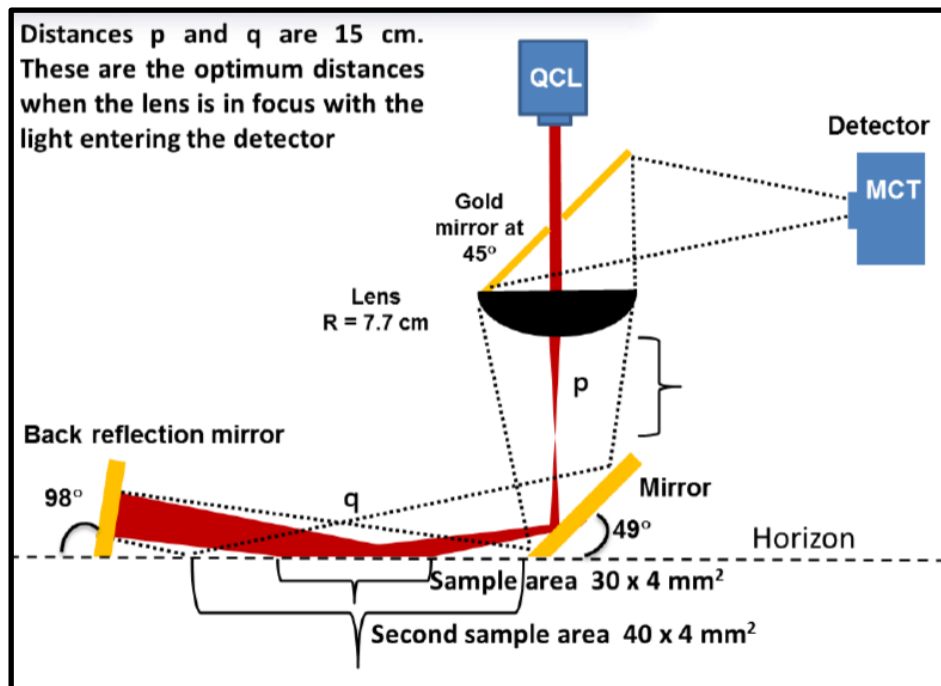


Figure 1. Optical layout for coupling a QCL spectrometer to the GAP.

Ideally, to achieve the purpose, the instrument would have to scan the substrates to detect whether it is contaminated with HEMs or not. If the surface is smooth and reflective, the reflection angle is the same as the incidence angle, and no signal is lost, provided the reflected beams are collimated and directed towards the detector. If the surface is rough and non-reflective, the laser reflection could be lost nearly completely depending on the surface if an integrating sphere is not used to collect all reflection angles. This effect is called diffuse reflectance as shown in Figure 2. The amount of signal loss depends on the deposition method, how homogenous the HEM is and the type of substrate under analysis. The secondary aim of this research is to see how much the LOD is affected by the effect above and if an alternative can be found to optimize the analysis in these conditions. This is particularly important when using AN-AL, Teflon, and cardboard substrates.

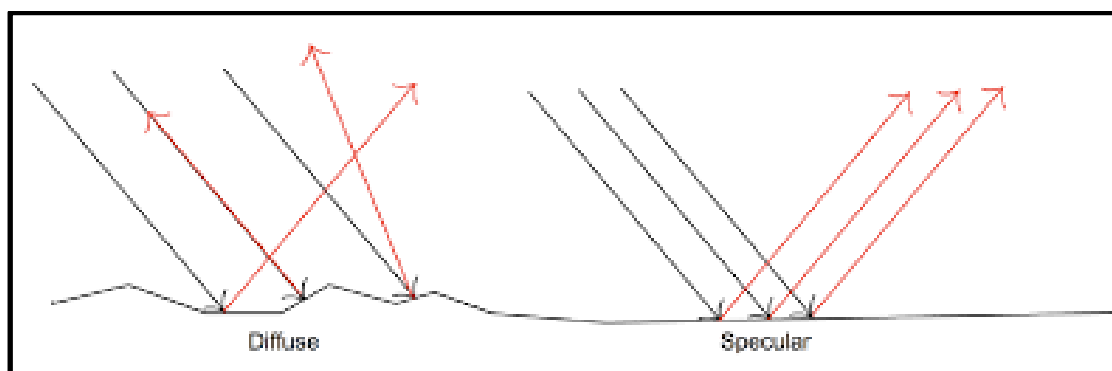


Figure 2. Diffuse vs. specular reflectance.

Deposition methods are a key part of this research. Finding the best way to reproduce real samples such as the case when a terrorist cleaning his hands contaminated with HEMs by wiping them with his clothes, contaminated hair, and fingerprints can prove to be a difficult task. [22] As deposition methods go the following methods have been previously used: spin coating deposition [1-5], smearing, and drop

cast. [24] While spin coating was effective in generating a nearly homogenous film on the substrate, the way about the deposition is done a large part of the deposited solution could be lost thus creating a problem in quantifying the amount that was deposited. Sample smearing and drop cast are easy to quantify how much is deposited, but the films obtained are not homogenous throughout the substrate, both leading to errors in the analysis. To solve this situation, an alternative methodology consisting of air spray of solutions of HEM was implemented. The first step of the effort was to guarantee that the right volume of spray is deposited only on the entire substrate. [1]

This report intends to expand the knowledge in the field of preparation of RDX samples and standards based on thin films, for both basic and applied research by depositing traces of target analytes on substrates of high interest using any technique such as smearing, spray deposition and injection methodology to develop the sought HEM/substrates assemblies. The primary goal is to develop methodologies capable of producing solid samples deposited on substrates in controlled size and distribution modes deposited on selected surfaces to generate specimens that would reproduce real contamination samples. Finally, the applications of these well-characterized samples include use in experiments that require fine control of the distribution of loadings of analytes on surfaces.

2. Experimental

2.1. Reagents

Acetone (C_3H_6O , HPLC grade), methanol (CH_4O , HPLC grade), isopropyl alcohol (C_3H_8O , HPLC grade), acetonitrile (C_2H_3N , HPLC grade) were acquired from Sigma-Aldrich (Sigma-Aldrich Corp., Millipore-Sigma, St. Louis, MO, USA) RDX was synthesized according to the Bachmann method with certain modifications [25]. Reagent and methodologies used in the synthesis of the HEMs used are described in detail in previous reports. [1-3, 26-28]

2.2. RDX Samples Prepared by Spin Coating Deposition on Three Substrates Types

RDX was dissolved in acetone to make a saturated solution (stock solution). Dilutions of the stock solution were prepared by dividing in half of the original solution and diluting in acetone, making a solution with half the concentration of the initial one. This process was repeated until the solution showed no appreciable reflectance signals on the QCL-GAP setup. The substrate was placed on the spin coater, and 30 μ L of the RDX test solution was transferred. Then assembly was spun at 3000 rpm for 30 s so that the substrate would have enough time to generate a uniform layer of RDX. [1-3] The substrates with RDX crystal films on them were analyzed with the tunable QCL-GAP setup. The process was repeated until the substrate showed no reflectance signal of explosive. The same procedure was performed on the following substrates: SS plates with 26.01 cm^2 areas, An-Al of 1.00 in^2 , and Teflon of 1.00 in^2 .

2.3. Samples Prepared by Immersion of Cardboard (bottom side) on RDX Solutions

Using the same RDX solutions described in the last section, cardboard substrates (19.74 cm^2) were placed in a 250 mL beaker and immersed in 30 μ L of the solution to be transferred and left absorbing until dried. Spectra were acquired as described before.

2.4. Quantum Cascade Laser Setup Overview

This arrangement consists of using a gold-coated mirror to direct the IR-beam to hit the sample at 82° with respect to the surface normal. This enables acquiring spectra under RAIRS conditions. The main objective of the study was to compare the different types of surfaces, their reflectance, and the LOD value for the various types of HEMs. This application of QCL-GAP spectroscopy presents certain advantages, such as a lower LOD of RDX on certain substrate materials. This could be added as another benefit in the optics array and the time-consuming analysis. RDX was used as the target explosive for the experiment since it has been previously studied, its polymorphism is well known, and as it is easy to synthesize. [1-3, 5, 9]

3. Results and Discussion

3.1. RDX Deposited on SS substrates by spin coating

As mentioned before in the experimental section, RDX sample concentrations prepared by spin coating deposition on SS substrates are shown in Table 1. The table also includes the calculations of signal-to-noise relationship which is used to determine the LOD values. These quantities were obtained from spectra similar to the ones shown in Figure 3.

Table 1. Mass deposited at different concentrations on SS and their average

Concentration				Signal to Noise Relationship		
mol/L	$\mu\text{g}/\text{cm}^2$	ng/cm^2	cm^2/ng	Signal (S)	Noise (N)	S/N
1.00E-01	25.62	25620	3.90E-05	1.113	0.006	175.64
5.00E-02	12.80	12810	7.81E-05	0.784	0.006	125.65
2.50E-02	6.405	6405	1.56E-04	1.012	0.009	116.97
1.25E-02	3.202	3202	3.12E-04	1.015	0.011	93.83
6.25E-03	1.601	1601	6.25E-04	0.448	0.006	77.51
3.13E-03	0.801	801	1.25E-03	0.161	0.007	21.57
1.56E-03	0.400	400	2.50E-03	0.155	0.010	15.72
7.81E-04	0.200	200	5.00E-03	0.094	0.006	14.86
3.91E-04	0.100	100	9.99E-03	0.077	0.005	14.97
1.95E-04	0.050	50.0	2.00E-02	0.049	0.005	9.65
9.77E-05	0.025	25.0	4.00E-02	0.047	0.008	5.95

With respect to Figure 3, many depositions of RDX solutions by spin coating stimulated the formation of polymorph β -RDX crystal deposits. RDX polymorphism was something expected since it was documented before by FTIR analysis [1–3]. The spectra represented with red and black dashes lines have been included for purposes of comparison. They correspond to reference spectra of β - and α -RDX, respectively. Spectral signatures from the tunable QCL-GAP setup in reflectance units (R) were obtained in ThermoGalactic Grams/Al "spc" file format. For quantitative analysis, reflectance (R) were changed to $\log(R)$ which is proportional to absorbance and can be used for Chemometrics analyses. [29]. The rectangular blue frames illustrate the range used to calculate the signal and noise values by integration of peak areas. The β - and α -RDX were acquired using bulk quantities using a 532 nm diode laser as the excitation source (green line) by Raman Microspectroscopy (InVia™, Renishaw PLC, West Dundee, IL, USA). The spectra were adapted to the scales of Figure 3 to illustrate polymorphism of the RDX deposits on SS by this deposition technique. This confirms that RDX deposited on SS at low surface concentration exhibits β -RDX spectral signatures with red-shift of peaks at $\sim 1226\text{ cm}^{-1}$, $\sim 1277\text{ cm}^{-1}$, and $\sim 1328\text{ cm}^{-1}$. The observation of polymorphism confirms previously published findings within the research group [1-2, 22-24, 26-27].

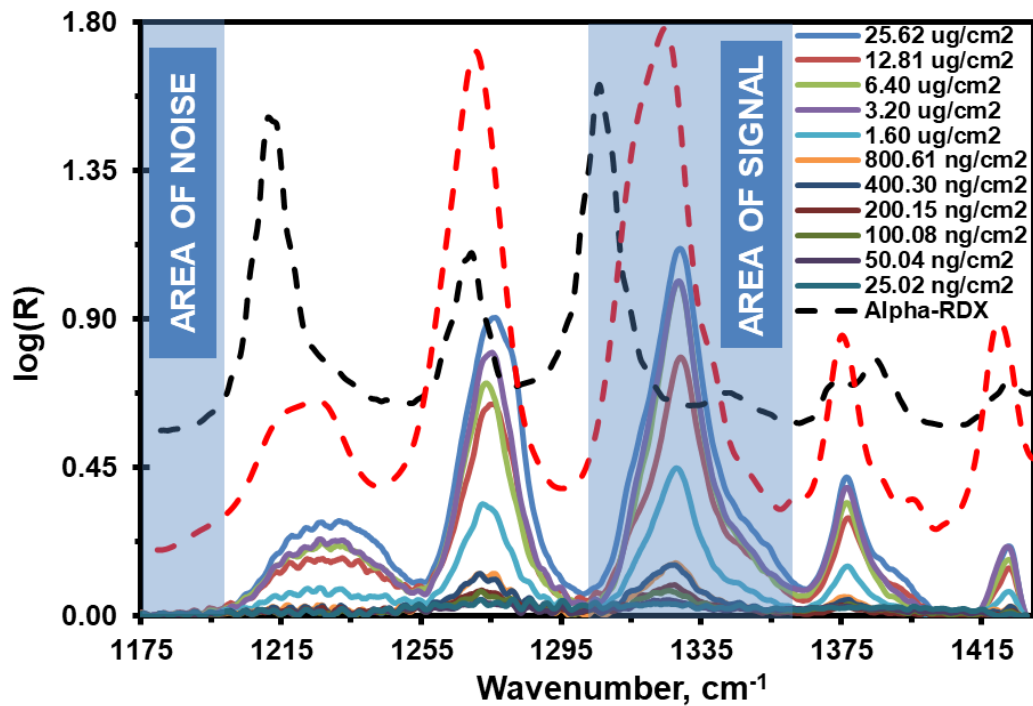


Figure 3. QCL reflectance spectra of RDX on SS at various surface concentrations

Figures 3 and 4 provide the data needed to establish that the LOD value for RDX/SS was 1.64 ng/cm². This was obtained by curve fitting the ratio of S/N dependence on the reciprocal of the surface concentration. The lowest quantity of RDX that can be distinguished from the absence of himself comes when the signal raises 3 times the noise. Assuming (S/N) = 3 then the surface concentration (C_s) becomes LOD which it results to be 1.64 ng/cm².

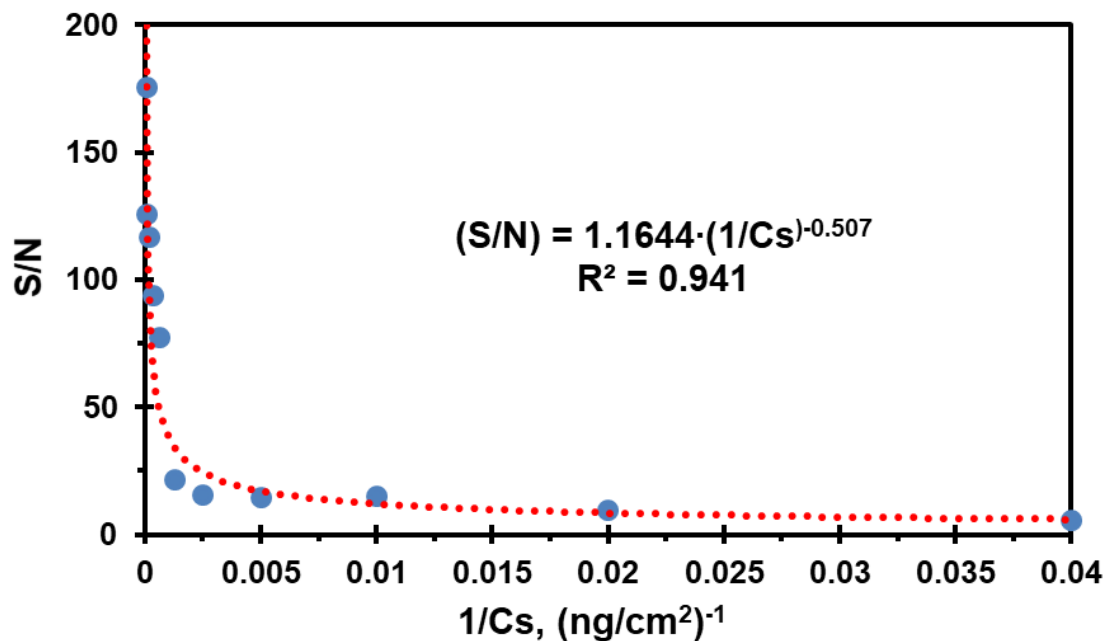


Figure 4. S/N as function of the reciprocal of the surface concentration for RDX/SS samples.

3.2. RDX Deposited on AN-AL Substrates by Spin Coating

Similar experiments were done using the same RDX solutions prepared before but changing the SS substrates to AN-AL substrates of areas 1.00 in². Good results were obtained using spin coating technology and acquiring reflectance spectra with QCL-GAP setup. The results are summarized in Figure 5. This spectral window enclosed both the characteristic strong signatures of RDX. Comparing Figure 3 with Figure 5, the reflectance signal was plotted using the unprocessed raw data (no Log(R)) because in this way it was possible to interpret the results directly as they were acquired. LOD values were obtained using the methodology employed before. A blue rectangular frame delimits the area used to find the S/N values. An interesting observation was readily available from Figure 5 by comparing the QCL-GAP reflectance spectra of AN-AL with the FTIR reference spectra of the polymorphic phases of the RDX (in red and black dotted lines). All the acquired spectra at the various surface concentrations studied indicate that the α -RDX polymorph is favored. The important fact is based on the similarity with the peaks at 1330 cm⁻¹ and the doublet that forms in the range 1360 – 1395 cm⁻¹. However, our most recent findings published (Figueroa et al., 2016 [2]) confirm that there is a coexistence of both polymorphs on the substrate studied in that project (SS). A key aspect of the spectra taken with the GA arrangement is that these polymorphs which have collinearity with the electric field vector of a polarized source (thermal or laser) will be favored. This feature was confirmed by recent work (Ruiz et al., 2017 [1]) where the optical properties of the polymorph β -RDX follow the selection rules according to the orientation of the electric field vector from the source of excitation. These orientations of the can be directed perpendicular or parallel to the normal surface vector and can be achieved using a field-polarizer (for a non-polarized, thermal source).

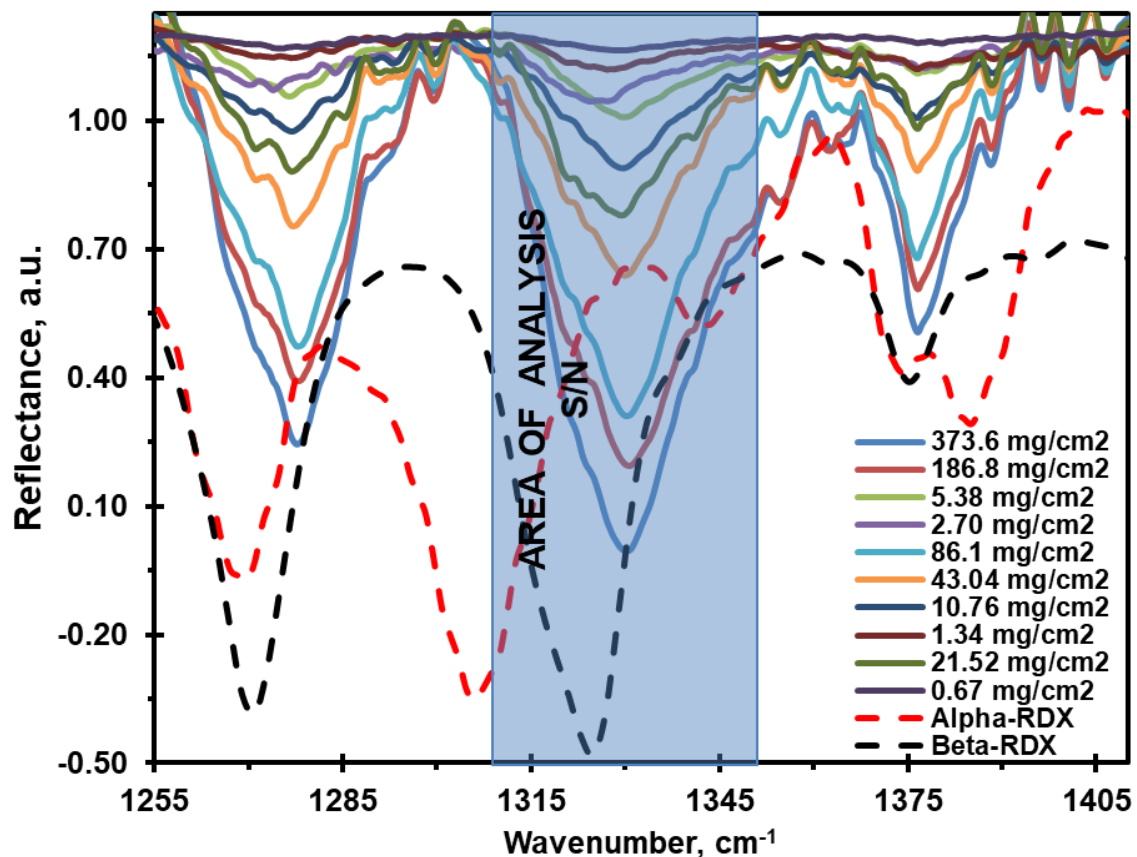


Figure 5. Reflectance spectra of RDX/AN-AL samples at various surface concentrations.

Figures 5 and 6 provide the data needed to establish that the LOD for RDX/AL-AN samples: is $94.7 \mu\text{g}/\text{cm}^2$. Comparing limit of detection between stainless-steel (SS) and anodized-aluminum (An-Al) substrates, the AN-AL is 215 times larger. In fact, β -RDX is favored by stainless-steel and α -RDX is favored by anodized-aluminum. This could be explained regarding porosity of the anodized aluminum. The cavities of the AN-AL substrates could generate a greater amount of solid deposited (\sim bulk concentrations) and in those conditions the α -RDX is the favored conformation. This is an important finding because to be prepare standards against terrorism attack; all databases should include those RDX polymorphs.

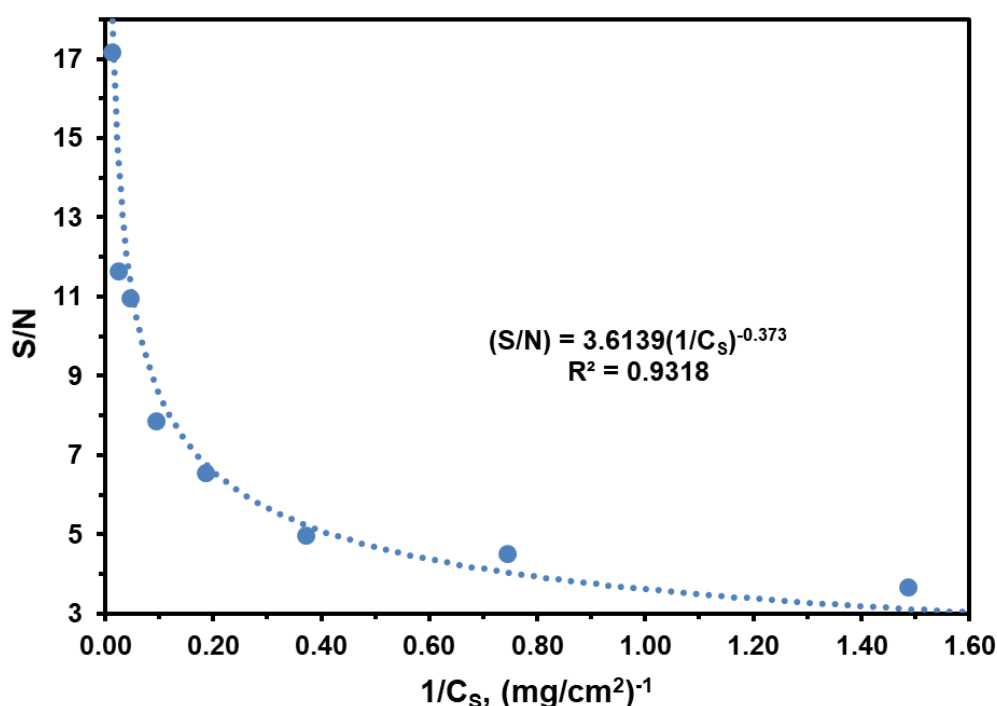


Figure 6. Signal/Noise vs. of reciprocal of RDX surface concentration on AN-AL.

3.3. RDX deposited on Teflon Substrates by Spin Coating

Similar to the previous procedures, experiments were done on Teflon substrates, In this case, RDX deposited on the Teflon substrates using spin coating technology represent largest source of interference to the RDX signal, when compared the other substrates (see Figures 3, 5, and 7). For this reason, the LOD values were not calculated. In agreement with the objective of generating a database that registers substrates with interferences, this information is very important.

3.4. RDX Deposited on Cardboard Substrates by Immersion

From the procedure described in the Materials and Methods section, is important to highlight that the RDX/cardboard samples were prepared by immersing the substrates into a beaker-flask with a fixed volume of a saturated RDX solution. This action was the best way to prepare RDX samples on cardboard. MIR laser reflectance spectra shown in Figure 8 were acquired by the QCL-GAP setup. Spin coating technology was inappropriate because the cardboard absorbed on both layers (front and back) and retained the solvent longer. Also, when using the drop-casting method, a similar situation occurred. However, the cardboard immersed in a beaker allowed controlling that the front layer retained the RDX and assured that the lower layer did not lodge RDX particulates. The problem faced was that it was not possible to quantify the amount accurately absorbed. Only estimated values using the amount transferred

to the beaker-flask by gravimetric analysis were available. Table 2 shows relevant information for the experiments. The injection volume for each sample was of 30 μL .

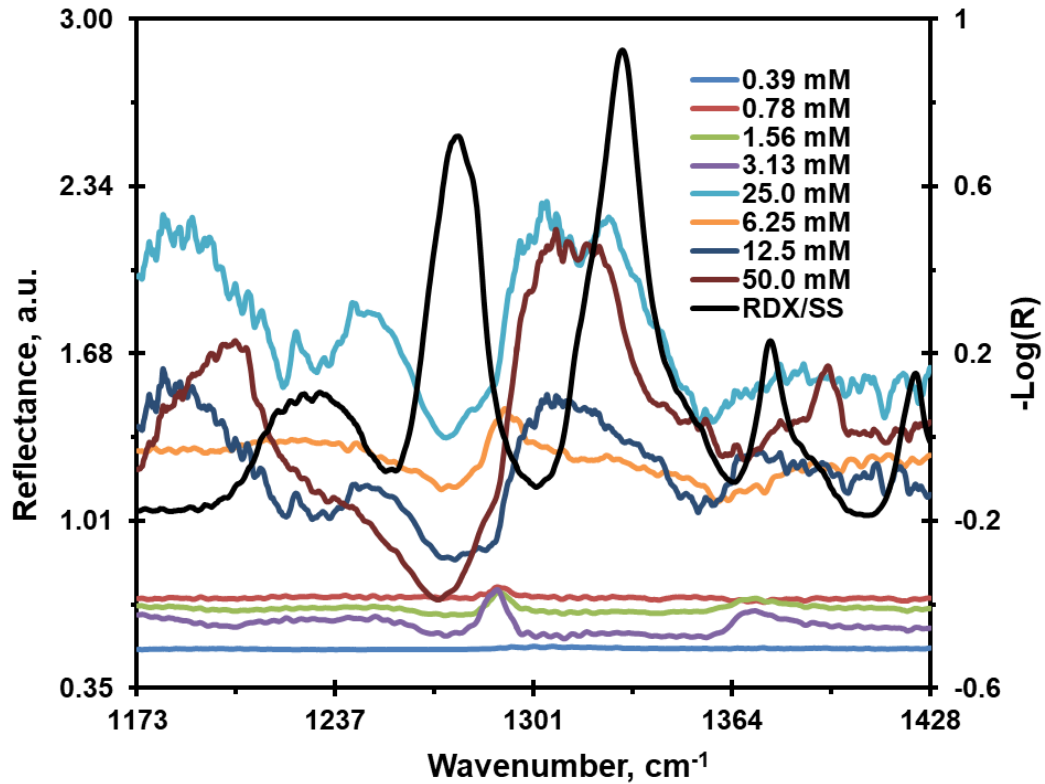


Figure 7. QCL-GAP reflectance spectra for of RDX/Teflon at various surface concentrations.

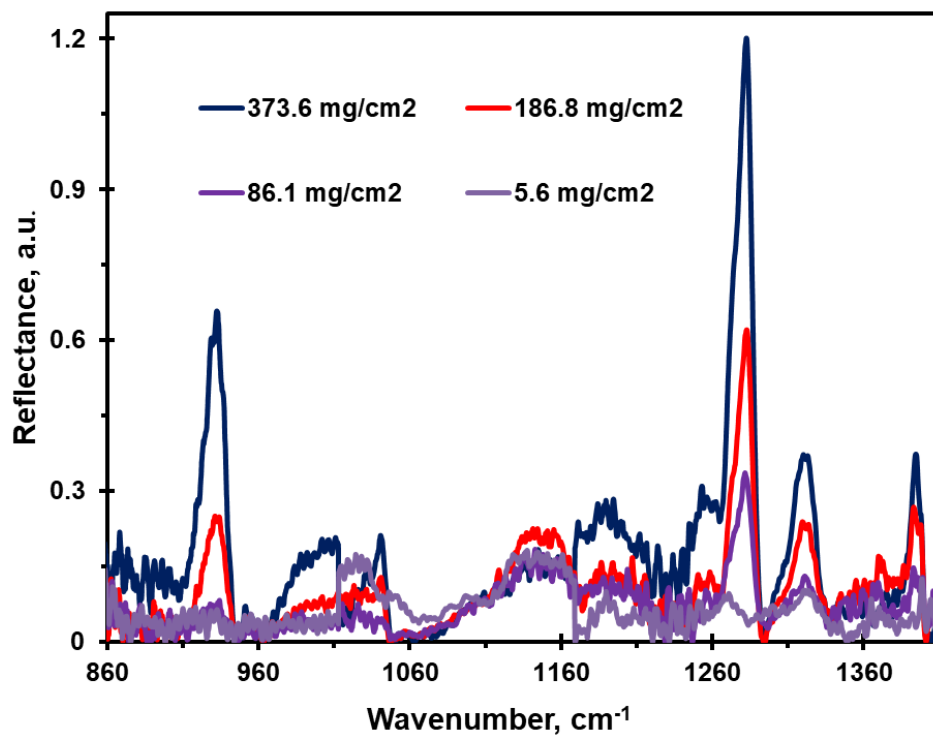


Figure 8. QCL-GAP reflectance spectra of RDX/cardboard at various surface concentrations.**Table 2.** Masses of RDX deposited on cardboard substrates

M (mol/L)	mg/cm ²	Area	1/Cs	Signal (S)	Noise (N)	S/N
2.17E-01	3.74E+02	1.97E+01	2.68E-03	1.20E+00	9.85E-03	1.22E+02
1.09E-01	1.87E+02	1.00E+01	5.35E-03	6.21E-01	8.37E-03	7.41E+01
5.00E-02	8.61E+01	5.66E+00	1.16E-02	3.36E-01	1.40E-02	2.41E+01
2.50E-02	5.55E+00	4.52E-01	1.80E-01	7.01E-02	6.52E-03	1.08E+01

LOD values could not be determined because the amount of RDX absorbed on cardboard as a substrate could not be quantified. Similar to Teflon substrates, interferences are present in those signature signals. To solve the problem of quantifying the amount and the homogeneity of RDX deposited over cardboard, we suggest using other methodology named direct-Spray. This improves deposition in a better way. [30-31]

4. Conclusion

The deposition of RDX solutions by spin coating technology predominantly stimulates the formation of β -RDX polymorph crystal deposits. However, results depend on second order on the substrate properties. For example, β -RDX is favored in depositions on SS to 100%; α -RDX is favored in depositions on AN-AL substrates. Roughness and micro cavities of AN-AL seem to generate a greater amount of solid deposits (quasi-bulk concentration), and under these conditions, the formation of α -RDX is favored as expected. LOD values for stainless steel resulted in 1.6 ng/cm². LOD for AN-AL substrates resulted in 94.7 μ g/cm². LOD for the immersion of cardboard in the saturated solution of RDX could not be determined accurately. As future work, we suggest using the spray deposition methodology. This methodology favors solvent evaporation very quickly and the deposition of the analyte on the surface in a controlled manner.

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Conflict of Interest.

The authors report there are no conflicts of interest.

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