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# Interpreting the near infrared region of explosives

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## ABSTRACT

The NIR spectra from 1000 to 2500 nm of 18 different explosives, propellant powders and energetic salts were collected and interpreted. NIR spectroscopy is known to provide information about the combination bands and overtones of highly anharmonic vibrations as those occurring in X-H bonds (C-H, N-H and O-H). Particularly intense and complex were the bands corresponding to the first combination region (2500–1900 nm) and first overtone stretching mode ( $2\nu$ ) of C-H and N-H bonds (1750–1450 nm). Inorganic oxidizing salts including sodium/potassium nitrate, sodium/potassium chlorate, and sodium/potassium perchlorate displayed low intense or no NIR bands.

**KEYWORDS:** Explosives; Energetic powders; Near infrared spectroscopy; Combination region; Overtone

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## 1. Introduction

Every fundamental vibrational mode that is active in the midinfrared region (MIR) from 4000 to 400  $\text{cm}^{-1}$  (i.e. 2500–25,000 nm), have different overtones and combination bands at higher energies (lower wavelengths). Among those IR active vibrations, the fundamental vibrations whose overtones and combination bands lie on the nearinfrared (NIR) region from 1000 to 2500 nm (i.e. 12,500–4000  $\text{cm}^{-1}$ ), are those belonging to highly anharmonic vibrations [1, 2]. In fact, although overtones and combination bands are theoretically forbidden for harmonic oscillators, they are usually observed in real anharmonic molecular vibrations. In general, these anharmonic vibrations involve the stretching vibrations of strong short bonds, as those occurring between small atoms and hydrogen (X-H). Most of the X-H stretching fundamental vibrations absorb at wavenumbers above 2000  $\text{cm}^{-1}$  (MIR) so that their first overtones appear in the NIR region [1, 2]. These chemical bonds usually prevail in organic molecules including C-H, O-H and N-H. In fact, there is such a common prevalence of C-H, O-H and N-H bonds in organic molecules that the selectivity of NIR spectroscopy has been traditionally questioned. However, according to the high number of combination bands that may exist for a certain number of fundamental vibrations, it is even possible (for some molecules) that the combination bands will provide a more specific profile of identification than the fundamental IR spectrum or IR fingerprint [3].

A large number of explosive compounds contain C-H and/or N-H bonds in their structure, including not only organic explosives, such as 2,4,6-trinitrotoluene (TNT) and triacetone-triperoxide (TATP); but also smokeless gun-powders and propellants (composed of nitrocellulose (NC), nitroglycerine (NG) and nitroguanidine (NQ)); and also ammonium nitrate (AN) based explosives, such as dynamite or ammonium nitrate fuel oil (ANFO). An extensive literature can be found for most common explosives and energetic salts about the chemical fundamental vibrations occurring in MIR and Raman spectroscopy [3–11]. However, the analysis and vibrational interpretation of explosives using NIR spectroscopy is very limited (almost missing) in literature. Most of the studies in which NIR spectroscopy has been tested for the analysis of explosives [12–20], usually involve the employment of hyperspectral imaging (HSI) in very short NIR range (800–1700 nm) with the aim of detecting explosive residues on different matrixes such as clothing or fingerprints [15–20]. Advanced pre-processing and classification chemometric models are

performed in order to discriminate the explosive residues over the background [15–20]. However, the fundamental chemical interpretation of the NIR spectra of explosives is not usually reported.

In order to reduce this lack of knowledge, this study focuses on the comprehensive study and interpretation of the NIR spectra displayed by 18 different explosives commonly used in the manufacture of commercial explosives, commercial ammunition and homemade improvised explosive devices (IEDs).

## **2. Experimental Section**

### *2.1. Explosives*

In this study, 18 different explosives, propellant powders and energetic salts were analysed. They are summarized in Table 1. Explosives and propellant powders were provided by Spanish Explosive Ordnance Disposal (EOD). Energetic salts were purchased anhydrous at ACS grade (purity over 98%) from Sigma-Aldrich (St. Louis, MO, USA).

### *2.2. Instrumentation for Near Infrared Analysis*

A NIRS XDS™ Rapid Content Analyzer spectrometer from Metrohm AG (Herisau, Switzerland) working in the range 400–2500 nm and controlled through the Vision Spectral Analysis Software developed by Foss NIRSystems Inc. (Hilleroed, Denmark) was used for characterizing the NIR spectra of explosives. Around 0.5 g of explosive was placed onto the sampling cell to be analysed. NIR spectra were collected from 1000 to 2500 nm, with a spectral resolution of 2 nm (data spacing of 0.5 nm) and 32 scans. Three replicate spectra were collected per explosive by analysing three different sample portions. The NIR spectra displayed in Results section is the spectral average of the three replicates. No further pre-processing was performed.

### 3. Results and Discussion

As preliminarily explained in the introduction, NIR spectra of organic explosives were dominated by those bands corresponding to the overtones and combination bands of the vibrational modes of C-H bonds.

**Table 1**

Explosives, propellant powders and energetic salts included in this study. Their chemical composition (provided by EOD) is summarized in column 2. Regarding explosive mixtures, only major components whose mass percentage is over 10% are indicated.

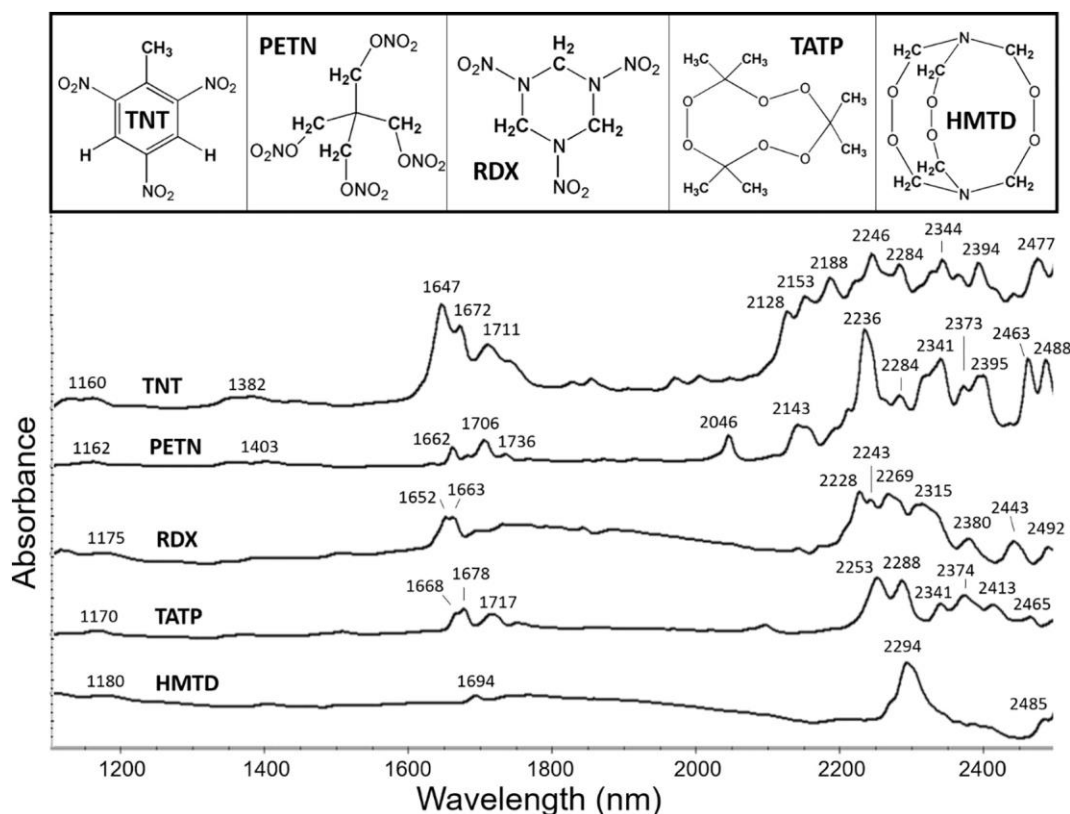
Explosives/energetic salts	Chemical composition (mass percentage)	Type
TNT	2,4,6-Trinitrotoluene (100%)	Nitroaromatic explosive
RDX-plastic explosive	Cyclotrimethylene trinitramine (91%)	Nitramine explosive
PETN	Pentaerythritol tetranitrate (100%)	Nitrate ester
TATP	Triacetone triperoxide (100%)	Peroxide explosive
HMTD	Hexamethylene triperoxide diamine (100%)	Peroxide explosive
Powder 1 (NC + NQ + NG)	Nitrocellulose (19%) + nitroguanidine (55%) + nitroglycerine (18%)	Triple-base smokeless gunpowder
Powder 2 (NC + DNT)	Nitrocellulose (85%) + dinitrotoluene (10%)	Double-base smokeless gunpowder
Powder 3 (NC + NG)	Nitrocellulose (71%) + nitroglycerine (25%)	Double-base smokeless gunpowder
Powder 4 (NC)	Nitrocellulose (94%)	Single-base smokeless gunpowder
Dynamite	Ammonium nitrate (66%) + ethylene glycol dinitrate (29%)	AN-explosive
ANFO	Ammonium nitrate (90%) + diesel (10%)	AN-explosive
NH <sub>4</sub> NO <sub>3</sub>	Ammonium nitrate (100%)	Nitrate salt
NaNO <sub>3</sub>	Sodium nitrate (100%)	Nitrate salt
KNO <sub>3</sub>	Potassium nitrate (100%)	Nitrate salt
NaClO <sub>3</sub>	Sodium chlorate (100%)	Chlorate salt
KClO <sub>3</sub>	Potassium chlorate (100%)	Chlorate salt
NaClO <sub>4</sub>	Sodium perchlorate (100%)	Perchlorate salt
KClO <sub>4</sub>	Potassium perchlorate (100%)	Perchlorate salt

Thus, in order to facilitate their interpretation, the chemical structure of explosives is displayed in Fig. 1 above their NIR spectra.

As a summary of C-H bonds, TNT has one methyl group (CH<sub>3</sub>) linked to the aromatic ring and two C-H aromatic bonds. PETN has four CH<sub>2</sub> groups equally bonded to nitrate ester groups {-C-CH<sub>2</sub>-ONO<sub>2</sub>}. RDX has three CH<sub>2</sub> groups equally bonded to nitramine groups {(O<sub>2</sub>N)N-CH<sub>2</sub>-N(NO<sub>2</sub>)-}. TATP has six methyl groups equally bonded to quaternary carbons bonded to two peroxides {(CH<sub>3</sub>)<sub>2</sub>-C-(OO)<sub>2</sub>}. HMTD has six CH<sub>2</sub> groups equally bonded to nitrogen (amine) and peroxide {-N-CH<sub>2</sub>-OO-}. In the knowledge of the theoretical NIR bands expected from those C-H bonds (revised in literature [2]), the experimental NIR bands of explosives were assigned to their respective vibrations (overtones or combination bands).

As expected, most organic explosives displayed multiple bands within the region 2500–2100 nm,

which corresponds to the CH/CH<sub>2</sub>/ CH<sub>3</sub> first combination region. The specific values of all these bands are indicated in Fig. 1 and their interpretation is summarized in Table 2. In brief, each explosive provided selective bands, which were different from each other as expected from their different C-H bonds. Furthermore, even the NIR bands of PETN, RDX and HMTD, which are due to CH<sub>2</sub> groups, were different (according to the different chemical environment of CH<sub>2</sub> groups in each explosive molecule). From the interpretation point of view, this region (2500–2000 nm) is extraordinarily complex and, at the time of this publication, there is not a comprehensive assignment for each particular band. Only a few bands were assigned, based on the NIR assignments reported in literature for very similar molecules. For instance, the interpretation of the NIR bands previously reported for toluene [2] was very helpful in the interpretation of TNT spectrum. Thereby, the bands located at 2477 and 2394 nm were assigned to the combination of aromatic C-H stretching with C-C bending ( $\nu\text{ArCH} + \delta\text{CC}$ ). The band located at 2344 nm was assigned to the combination of aromatic C-H stretching with C-H bending ( $\nu\text{ArCH} + \delta\text{ArCH}$ ). The bands located at 2284 and 2246 nm were assigned to the combination of CH<sub>3</sub> symmetric/antisymmetric stretching with CH<sub>3</sub> bending ( $\nu\text{CH}_3 + \delta\text{CH}_3$ ). Finally, the bands located at 2188, 2153 and 2128 nm were assigned to the combination of aromatic C-H stretching with C-C stretching ( $\nu\text{ArCH} + \nu\text{ArCC}$ ). Regarding PETN, RDX and HMTD, no chemically similar molecules have been reported by NIR, thus the interpretation of their spectra within 2500–2000 nm range was not specifically assigned band by band, but a general assignment was performed instead. The most intense bands located within 2350–2200 nm theoretically correspond to the combination of symmetric/antisymmetric CH<sub>2</sub> stretching with CH<sub>2</sub> bending ( $\nu\text{CH} + \delta\text{CH}$ ), as previously reported for methylene group (CH) in literature [2]. The rest of the bands within the combination region (2500–2000 nm) might be due to the second overtone of CH<sub>2</sub> bending ( $3\delta\text{CH}_2$ ) and the combination of CH<sub>2</sub> stretching with C\C/C\C/O\C\N bending/stretching ( $\nu\text{CH}_2 + \delta\text{CC}/\text{CO}/\text{CN}$  /  $\nu\text{CH}_2 + \nu\text{CC}/\text{CO}/\text{CN}$ ) depending on the explosive (see Table 2). TATP displayed two highly intense bands located at 2288 and 2253 nm that respectively correspond to the combination of symmetric and antisymmetric CH<sub>3</sub> stretching with CH<sub>3</sub> bending ( $\nu\text{sCH}_3 + \delta\text{CH}_3$  and  $\nu\text{aCH}_3 + \delta\text{CH}_3$ ), as previously reported for methyl group [2]. The bands of TATP located above 2300 nm are probably due to the second overtone of CH<sub>3</sub> bending ( $3\delta\text{CH}_3$ ) and the combination of CH<sub>3</sub> stretching with C\C/C\C/O bending/stretching ( $\nu\text{CH}_3 + \delta\text{CC}$  /  $\nu\text{CH}_3 + \delta\text{CO}$  /  $\nu\text{CH}_3 + \nu\text{CC}$  /  $\nu\text{CH}_3 + \nu\text{CO}$ ) though the specific assignment is unclear.



**Fig. 1.** Near infrared spectra (1100–2500 nm) of TNT, PETN, RDX, TATP and HMTD explosives. Each spectrum is the average of three replicates. In addition, the chemical structure of explosives is displayed

above their NIR spectra.

Besides the first C\H combination region, organic explosives also displayed bands within the range 1750–1600 nm corresponding to the first overtone of CH/CH<sub>2</sub>/CH<sub>3</sub> stretching vibrations. In the case of TNT, the three bands located at 1647, 1672 and 1711 nm are likely assigned to the first overtones of C-H aromatic stretching, antisymmetric CH<sub>3</sub> stretching and symmetric CH<sub>3</sub> stretching (2νArCH/2νaCH<sub>3</sub>/ 2νsCH<sub>3</sub>). Among the multiple bands that PETN displayed in this region, the two most intense bands were those located at 1662 and 1706 nm, which are probably due to the first overtones of antisymmetric and symmetric CH<sub>2</sub> stretching modes (2νaCH<sub>2</sub>/2νsCH<sub>2</sub>). Similarly, the bands of RDX located at 1652 and 1663 nm are theoretically assigned to the first overtones of antisymmetric and symmetric CH<sub>2</sub> stretching modes (2νaCH<sub>2</sub>/2νsCH<sub>2</sub>). These two vibrations should be also present in HMTD molecule (since it only contains methylene groups), however, a unique weak band located at 1694 nm was observed in the NIR spectrum of HMTD (2νCH<sub>2</sub>). The bands of TATP located at 1678 and 1717 nm are likely assigned to the first overtone of antisymmetric and symmetric CH<sub>3</sub> stretching modes (2νaCH<sub>3</sub>/2νsCH<sub>3</sub>), though the first band split into two bands.

**Table 2.** Summary of X-H NIR active groups contained in the pure organic explosives under study (TNT, PETN, RDX, TATP and HMTD); the experimental band obtained for each explosive and their assignment to the specific vibration (overtone or combination region) according to the literature [2].

Explosive	X-H NIR active groups	Experimental NIR bands (nm)	NIR bands assignment
TNT	1 CH <sub>3</sub> 2 ArCH	2477, 2394	νArCH+δCC (1 <sup>st</sup> comb ArCH/CH <sub>3</sub> )
		2344	νArCH+δArCH (1 <sup>st</sup> comb ArCH/CH <sub>3</sub> )
	2284, 2246	νCH <sub>3</sub> +δCH <sub>3</sub> (1 <sup>st</sup> comb ArCH/CH <sub>3</sub> )	
	2188, 2153, 2128	νArCH+νArCC (1 <sup>st</sup> comb ArCH/CH <sub>3</sub> )	
	1711, 1672, 1647	2νArCH / 2ν <sub>a</sub> CH <sub>3</sub> / 2ν <sub>s</sub> CH <sub>3</sub>	
	1382 1160	2 <sup>nd</sup> comb ArCH/CH <sub>3</sub> 3νArCH / 3νCH <sub>3</sub>	
PETN	4 CH <sub>2</sub>	2488, 2463, 2395, 2373, 2143, 2046	(2500-2000) νCH <sub>2</sub> +δCC / νCH <sub>2</sub> +νCC / νCH <sub>2</sub> +δCO / νCH <sub>2</sub> +νCO / 3δCH <sub>2</sub> (1 <sup>st</sup> comb CH <sub>2</sub> )
		2341, 2284, 2236*	*(2350-2200) ν <sub>s</sub> CH <sub>2</sub> +δCH <sub>2</sub> , ν <sub>a</sub> CH <sub>2</sub> +δCH <sub>2</sub> (1 <sup>st</sup> comb CH <sub>2</sub> )
		1736, 1706, 1662	2ν <sub>s</sub> CH <sub>2</sub> / 2ν <sub>a</sub> CH <sub>2</sub>
		1403	2 <sup>nd</sup> comb CH <sub>2</sub>
		1162	3νCH <sub>2</sub>
RDX	3 CH <sub>2</sub>	2492, 2443, 2380	(2500-2000) νCH <sub>2</sub> +δCC / νCH <sub>2</sub> +νCC / νCH <sub>2</sub> +δCN / νCH <sub>2</sub> +νCN / 3δCH <sub>2</sub> (1 <sup>st</sup> comb CH <sub>2</sub> )
		2315, 2269, 2243, 2228*	*(2350-2200) ν <sub>s</sub> CH <sub>2</sub> +δCH <sub>2</sub> , ν <sub>a</sub> CH <sub>2</sub> +δCH <sub>2</sub> (1 <sup>st</sup> comb CH <sub>2</sub> )
		1663, 1652	2ν <sub>s</sub> CH <sub>2</sub> / 2ν <sub>a</sub> CH <sub>2</sub>
		1175	3νCH <sub>2</sub>
TATP	6 CH <sub>3</sub>	2465, 2413, 2374, 2341	νCH <sub>3</sub> +δCC / νCH <sub>3</sub> +νCC / νCH <sub>3</sub> +δCO / νCH <sub>3</sub> +νCO / 3δCH <sub>3</sub> (1 <sup>st</sup> comb CH <sub>3</sub> )
		2288, 2253*	*ν <sub>s</sub> CH <sub>3</sub> +δCH <sub>3</sub> , ν <sub>a</sub> CH <sub>3</sub> +δCH <sub>3</sub> (1 <sup>st</sup> comb CH <sub>3</sub> )
		1717, 1678, 1668	2ν <sub>s</sub> CH <sub>3</sub> / 2ν <sub>a</sub> CH <sub>3</sub>
		1170	3νCH <sub>3</sub>
HMTD	6 CH <sub>2</sub>	2485	νCH <sub>2</sub> +δCC / νCH <sub>2</sub> +νCC / νCH <sub>2</sub> +δCO / νCH <sub>2</sub> +νCO / νCH <sub>2</sub> +δCN / νCH <sub>2</sub> +νCN / 3δCH <sub>2</sub> (1 <sup>st</sup> comb CH <sub>2</sub> )
		2294*	*νCH <sub>2</sub> +δCH <sub>2</sub> (1 <sup>st</sup> comb CH <sub>2</sub> )
		1694	2νCH <sub>2</sub>
		1180	3νCH <sub>2</sub>

**Abbreviations:** comb (combination region), 2ν (first overtone of stretching fundamental vibration), 3ν (second overtone of stretching fundamental vibration), 3δ (second overtone of bending fundamental vibration), νa (antisymmetric stretching), νs (symmetric stretching), ν (stretching), δ (bending).

In addition, a wide weak band within the range 1430–1360 nm, assigned to the CH/CH<sub>2</sub>/CH<sub>3</sub> second combination region, was observed for most organic explosives. Despite of also being an incredibly complex region, a unique wide weak band was observed, probably because of the low intensity of these bands. Likewise, explosives displayed very weak bands within the range 1200–1150 nm attributed to the second overtone of CH/CH<sub>2</sub>/CH<sub>3</sub> stretching vibrations (3νCH/3νCH<sub>2</sub>/3νCH<sub>3</sub>). As theoretically predicted [1], the intensity of overtones/combination bands strongly decreases with the number of vibrational levels transgressed: first overtone (0 → 2) (i.e. transition from fundamental to second vibrational level) was much more intense than second overtone (0 → 3).

After interpreting the NIR spectra of organic explosives, the NIR spectra of smokeless gunpowders were studied. According to the chemical structure of the components of smokeless gunpowders (see Fig. 2), nitroglycerine (NG) has two CH<sub>2</sub> groups and one CH group, the three of them bonded to nitrate ester groups. DNT has one methyl group (CH<sub>3</sub>) linked to the aromatic ring and three C–H aromatic bonds. Nitroguanidine (NQ) has no CH bonds, but NH bonds, including one imine group (–NH), one nitramine group (–NH–NO<sub>2</sub>) and one primary amine group (–NH<sub>2</sub>). Finally, nitrocellulose (NC) has one CH<sub>2</sub> group and five

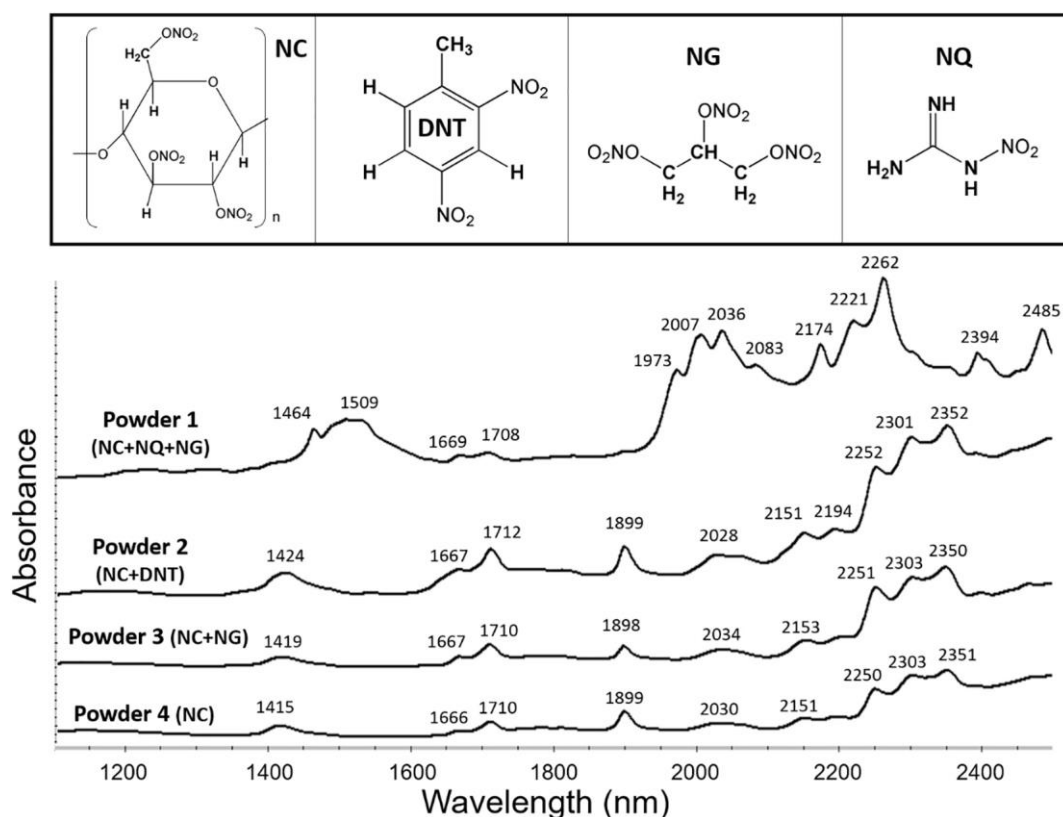


different CH groups per monomer of glucose. CH<sub>2</sub> group and two CH groups are bonded to nitrate ester groups whereas three CH groups are linked to oxygen (ether). It should be noted that NC structure displayed in Fig. 2 corresponds to NC with the maximum nitrogen content theoretically possible (14%), which results from the replacement of all hydroxyl groups of cellulose by nitro groups. However, in the real synthesis of highly-nitrated NC, the nitrogen content never reaches the maximum, but usually varies between 12 and 13.5% [21]. This means that some hydroxyl groups (around one OH group per two monomers of glucose) have not been replaced by nitro groups, and consequently, the NIR bands of OH might be also observed.

Regarding the C–H first combination bands of smokeless powders, powders 2, 3 and 4 (whose major component is NC (N70%)) displayed intense bands located at 2351, 2303 and 2250 nm. These bands are likely assigned to the second overtone of CH/CH<sub>2</sub> bending ( $3\delta\text{CH}/3\delta\text{CH}_2$ ) and the combination of CH/CH<sub>2</sub> stretching with CH<sub>2</sub> bending ( $\nu\text{CH} + \delta\text{CH}_2 / \nu\text{CH}_2 + \delta\text{CH}_2$ ), as previously reported in literature for cellulose [2].

In addition, the two bands located at 1667 and 1710 nm displayed by NC (as evidenced in the NIR spectrum of powder 4 (94% NC)) might be assigned to the first overtone of either CH, antisymmetric CH<sub>2</sub> or symmetric CH<sub>2</sub> stretching modes ( $2\nu\text{CH}/2\nu_a\text{CH}_2/2\nu_s\text{CH}_2$ ), as summarized in Table 3.

Besides the C–H bands, additional bands due to N–H/O–H vibrations were observed in smokeless gunpowders. For instance, triple-base smokeless powder (composed of 55% NQ) displayed multiple bands within the region 2300–1900 nm (assigned to the NH/NH<sub>2</sub> first combination region) and a wide doublet located at 1509 and 1464 nm (assigned to the first overtones of symmetric NH<sub>2</sub>, antisymmetric NH<sub>2</sub> and amine/imine NH stretching vibrations ( $2\nu_s\text{NH}_2/2\nu_a\text{NH}_2/2\nu\text{NH}$ )). As occurred for C–H first combination region, the N–H first combination region (2300–1900 nm) of NQ was extraordinarily complex and the particular assignment of each band to the respective NH stretching-bending combination mode was unfeasible. As a general assignment, the bands located at 1973, 2007, 2036 and 2083 nm were tentatively assigned to a combination of NH stretching with NH bending vibrations ( $\nu\text{NH} + \delta\text{NH}$ ), based on the available literature reported for amines [2]. The bands above 2100 nm (2174, 2221 and 2262 nm) might be due to second overtones of N–H bending vibrations ( $3\delta\text{NH}$ ) and the combination of NH stretching with N–N stretching/bending vibrations ( $\nu\text{NH} + \nu\text{NN} / \nu\text{NH} + \delta\text{NN}$ ). Finally, the NIR spectrum of single-/double-base smokeless powder (NC) displayed additional bands located at 2151, 2030 and 1899 nm. This region (2200–1850 nm) is clearly assigned to OH first combination region. This outcome was not unexpected since, as previously explained, NC usually contains remaining hydroxyl groups that have not been completely replaced by nitro groups.



**Fig. 2.** Near infrared spectra (1100–2500 nm) of smokeless powders: powder 1 (NC + NQ + NG), powder 2 (NC + DNT), powder 3 (NC + NG) and powder 4 (NC). Each spectrum is the average of three replicates. In addition, the chemical structure of their explosive components is displayed above their NIR spectra.



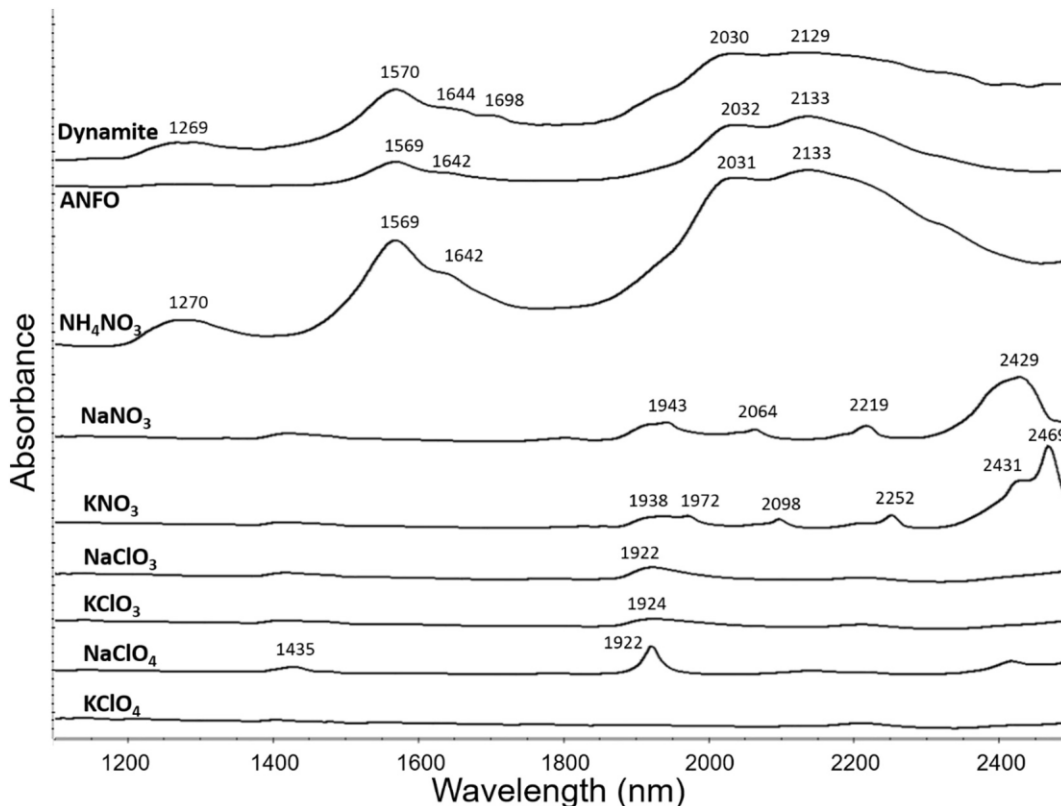
**Table 3.** Summary of X-H NIR active groups contained in the smokeless powders under study; the experimental bands obtained for each explosive; and their assignment to the specific vibration (overtone or combination region) according to the literature [2].

Explosive	X-H NIR active groups	Experimental NIR bands (nm)	NIR bands assignment
<b>Powder 1</b> <b>(triple base)</b>	1n CH <sub>2</sub> (NC)	2485, 2394	$\nu\text{CH}+\delta\text{CH}_2 / \nu\text{CH}_2+\delta\text{CH}_2 / 3\delta\text{CH} / 3\delta\text{CH}_2$ (1 <sup>st</sup> comb CH/CH <sub>2</sub> )
	5n CH (NC)	2262, 2221, 2174	$\nu\text{NH}+\nu\text{NN} / \nu\text{NH}+\delta\text{NN} / 3\delta\text{NH}$ (1 <sup>st</sup> comb NH/NH <sub>2</sub> )
	0.5n OH (NC)	2083, 2036, 2007, 1973	$\nu\text{NH}+\delta\text{NH}$ (1 <sup>st</sup> comb NH/NH <sub>2</sub> )
	2 CH <sub>2</sub> (NG)	1708, 1669	$2\nu\text{CH} / 2\nu_a\text{CH}_2 / 2\nu_s\text{CH}_2$
	1 CH (NG)	1509, 1464	$2\nu_s\text{NH}_2 / 2\nu_a\text{NH}_2 / 2\nu\text{NH}$
	1 =NH (NQ)		
	1 NH (NQ)		
<b>Powder 2</b> <b>(double base)</b>	1n CH <sub>2</sub> (NC)	2352, 2301, 2252	$\nu\text{CH}+\delta\text{CH}_2 / \nu\text{CH}_2+\delta\text{CH}_2 / 3\delta\text{CH} / 3\delta\text{CH}_2$ (1 <sup>st</sup> comb CH/CH <sub>2</sub> )
	5n CH (NC)	2194, 2151, 2028, 1899	$\nu\text{OH}+\delta\text{OH} / \nu\text{OH}+\nu\text{CO} / \nu\text{OH}+\delta\text{CO} / \delta\text{OH}+\nu\text{CO} / 3\delta\text{OH}$ (1 <sup>st</sup> comb OH)
	0.5n OH (NC)	1712, 1667	$2\nu\text{CH} / 2\nu_a\text{CH}_2 / 2\nu_s\text{CH}_2$
	1 CH <sub>3</sub> (DNT)	1424	2 <sup>nd</sup> comb CH/CH <sub>2</sub>
<b>Powder 3</b> <b>(double base)</b>	3 ArCH (DNT)		
	1n CH <sub>2</sub> (NC)	2350, 2303, 2251	$\nu\text{CH}+\delta\text{CH}_2 / \nu\text{CH}_2+\delta\text{CH}_2 / 3\delta\text{CH} / 3\delta\text{CH}_2$ (1 <sup>st</sup> comb CH/CH <sub>2</sub> )
	5n CH (NC)	2153, 2034, 1898	$\nu\text{OH}+\delta\text{OH} / \nu\text{OH}+\nu\text{CO} / \nu\text{OH}+\delta\text{CO} / \delta\text{OH}+\nu\text{CO} / 3\delta\text{OH}$ (1 <sup>st</sup> comb OH)
<b>Powder 4</b> <b>(single base)</b>	0.5n OH (NC)	1710, 1667	$2\nu\text{CH} / 2\nu_a\text{CH}_2 / 2\nu_s\text{CH}_2$
	2 CH <sub>2</sub> (NG)	1419	2 <sup>nd</sup> comb CH/CH <sub>2</sub>
	1 CH (NG)		
	1n CH <sub>2</sub> (NC)	2351, 2303, 2250	$\nu\text{CH}+\delta\text{CH}_2 / \nu\text{CH}_2+\delta\text{CH}_2 / 3\delta\text{CH} / 3\delta\text{CH}_2$ (1 <sup>st</sup> comb CH/CH <sub>2</sub> )
<b>(single base)</b>	5n CH (NC)	2151, 2030, 1899	$\nu\text{OH}+\delta\text{OH} / \nu\text{OH}+\nu\text{CO} / \nu\text{OH}+\delta\text{CO} / \delta\text{OH}+\nu\text{CO} / 3\delta\text{OH}$ (1 <sup>st</sup> comb OH)
	0.5n OH (NC)	1710, 1666	$2\nu\text{CH} / 2\nu_a\text{CH}_2 / 2\nu_s\text{CH}_2$
		1415	2 <sup>nd</sup> comb CH/CH <sub>2</sub>

**Abbreviations:** n (per monomer of glucose), comb (combination region), 2v (first overtone of stretching fundamental vibration), 3δ (second overtone of bending fundamental vibration), v<sub>a</sub> (antisymmetric stretching), v<sub>s</sub> (symmetric stretching), ν (stretching), δ (bending).

Particularly, these bands are due to the combination of O-H stretching with O-H bending ( $\nu\text{OH} + \delta\text{OH}$ ) and/or the combination of O-H stretching/bending with C-O stretching/bending ( $\nu\text{OH} + \nu\text{CO} / \nu\text{OH} + \delta\text{CO} / \delta\text{OH} + \nu\text{CO}$ ) and/or the second overtone of O-H bending ( $3\delta\text{OH}$ ), though the specific assignment for each band was unclear.

From the identification point of view, most organic explosives provided selective NIR spectral profiles that enabled their discrimination and unequivocal identification. Particularly, the most discriminative regions were those corresponding to C–H first overtone (1600–1750 nm) and C–H/N–H combination region (1900–2500 nm). Almost all organic explosives under study (TNT, PETN, RDX, TATP, HMTD and triple-base smokeless powder) were unequivocally identified based on their different NIR spectra. On the contrary, the NIR spectra provided by single-hand double-base smokeless



**Fig. 3.** Near infrared spectra (1100–2500 nm) of dynamite, ANFO, ammonium nitrate, sodium nitrate, potassium nitrate, sodium chlorate, potassium chlorate, sodium perchlorate and potassium perchlorate. Each spectrum is the average of three replicates.

powders were extremely similar. The NIR bands from NC dominated their spectra while no characteristic bands from the second component in double-base smokeless powders (NG or DNT) were observed. This result seems to evidence that only major components (whose mass percentage is over 30% in the mixture) are detectable by NIR spectroscopy. Thus, those explosives mainly composed of the same major component will not be discriminated by NIR spectroscopy, as occurred for single-base (94% NC) and double-base (85% or 71% NC) smokeless powders. Nevertheless, it should be noted that this result will also depend on how NIR active the minor components are.

Regarding inorganic salts, only ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), which contains NH bonds, was noticeably active in NIR spectroscopy, as displayed in Fig. 3. Particularly, NIR spectrum of ammonium nitrate displayed a doublet located at 1569 and 1642 nm due to the first overtone of symmetric and antisymmetric  $\text{NH}_4$  stretching vibrations ( $2\nu_{\text{symNH}_4}$ ,  $2\nu_{\text{asymNH}_4}$ ), and a wide doublet located at 2031 and 2133 nm due to the first combination region (i.e. the combination of  $\text{NH}_4$  stretching and  $\text{NH}_4$  bending modes ( $\nu_{\text{NH}_4} + \delta_{\text{NH}_4}$ )). Table 4 summarizes the assignment of the NIR bands displayed by inorganic salts and AN-based explosives. An additional band located at 1270 nm, whose vibrational assignment is unclear, was observed in the NIR spectrum of AN. Likewise, dynamite and ANFO also displayed these NIR bands since ammonium nitrate is the major component of ANFO (~90%) and dynamite (~66%). Regarding the ANFO composition studied in this work, 10% of ANFO was diesel fuel (a mixture mainly composed by aliphatic and aromatic hydrocarbons). Nevertheless, no bands from the overtones of CH vibrations are observed in the NIR spectrum of ANFO. This is likely due to the low proportion of diesel compared to  $\text{NH}_4\text{NO}_3$  in ANFO mixture. Unlike ANFO, the NIR spectrum of dynamite displayed an extra band located at 1698 nm (besides the bands of  $\text{NH}_4\text{NO}_3$ ). This band seems to correspond to ethylene glycol dinitrate (EGDN), particularly to the first overtone ( $2\nu$ ) of stretching modes of the two  $\text{CH}_2$  groups in this molecule ( $\text{O}_2\text{NO}-\text{CH}_2-\text{CH}_2-\text{ONO}_2$ ). The reason why EGDN bands were observed could be explained by the fact that 29% of dynamite is EGDN, which is almost half of  $\text{NH}_4\text{NO}_3$  (66%), which is much more than the 10% of diesel fuel mixed with 90% of  $\text{NH}_4\text{NO}_3$  in ANFO.

The other inorganic salts have few or no bands in their NIR spectra because of the absence of CH, NH or OH bonds in their structure. Actually, they are ionic compounds whose

unique covalent bonds are those from the anion (N-O in nitrates or Cl-O in chlorates/perchlorates). The first overtones and combination bands of the fundamental modes of these covalent bonds do not appear in the NIR region. In fact, no bands were observed in the spectrum of KClO<sub>4</sub> and the weak bands observed in the spectra of NaClO<sub>3</sub>, KClO<sub>3</sub> and NaClO<sub>4</sub> were assigned to water (humidity). These weak bands were located at 1920–1930 nm (combination of antisymmetric H<sub>2</sub>O stretching with H<sub>2</sub>O bending ( $\nu_a\text{H}_2\text{O} + \delta\text{H}_2\text{O}$ )) and 1435 nm (combination of symmetric and antisymmetric H<sub>2</sub>O stretching ( $\nu_a\text{H}_2\text{O} + \nu_s\text{H}_2\text{O}$ )), as previously reported in literature for water [2]. Even though every salt was purchased anhydrous, some water molecules (from humidity) likely attached to these hygroscopic salts. However, nitrate salts (NaNO<sub>3</sub> and KNO<sub>3</sub>) displayed some additional medium-intense bands that did not correspond to water, particularly within the region 1900–2500 nm. To this respect, it should be noted that the spectral signature and specific wavelengths of these bands was different for sodium and potassium nitrates. This fact necessarily means that neither water nor the nitrate anion are the unique components providing these NIR bands, but the interaction cation-nitrate (sodium-nitrate or potassium-nitrate). Despite being ionic bonds, some kinds of NIR-active vibrations are presumed to be occurring between these alkaline cations and nitrate. Actually, it is noticeable the fact that wavelength values of NIR bands of potassium nitrate are shifted to higher values in comparison to those of sodium nitrate. According to Hook's Law, this means that weaker interactions (i.e. the frequency of the strength of the interaction is lower – and consequently, the wavelength is higher) occur between potassium and nitrate than between sodium and nitrate. This is in accordance with the respective size of sodium and potassium atoms (potassium > sodium). Nevertheless, further studies are necessary to comprehend in detail the assignment of every particular band for these ionic compounds.

#### 4. Conclusions

NIR spectroscopy has been demonstrated to be a suitable technique to identify explosives containing C-H and N-H bonds because the combination bands and overtones of the fundamental C-H/N-H/ O-H vibrations are located within the NIR range 1000–2500 nm. Particularly, NIR spectra of organic explosives (TNT, PETN, RDX, TATP, HMTD, single-, double and triple-smokeless powders) were dominated by multiple bands within the range 2100–2500 (due to the CH/CH<sub>2</sub>/CH<sub>3</sub> first combination region) and 1650–1750 nm (due to the CH/CH<sub>2</sub>/CH<sub>3</sub> first overtone). In addition, those explosive containing N-H bonds such as NQ and AN-based explosives (NH<sub>4</sub>NO<sub>3</sub>, ANFO and dynamite) also displayed multiple bands due to the NH/NH<sub>2</sub>/NH<sub>4</sub> first combination region (1900–2200 nm) and first overtone (1450–1650 nm). NaNO<sub>3</sub> and KNO<sub>3</sub> provided few medium-intense NIR bands, which were not clearly assigned, while chlorate and perchlorate salts were not NIR active, since the unique NIR bands that were observed were those corresponding to water.

Table 4. Summary of X-H NIR active groups contained in AN-based explosives (ANFO and dynamite) and inorganic salts included in this study; the experimental bands obtained for each explosive/ salt; and their assignment (when possible) to the specific vibration (overtone or combination region) according to the literature [2].

Explosive	X-H NIR active groups	Experimental NIR bands (nm)	NIR bands assignment
NH <sub>4</sub> NO <sub>3</sub>	1 NH <sub>4</sub> <sup>+</sup>	2133, 2031 1642, 1569 1270	$\nu\text{NH}_4 + \delta\text{NH}_4$ (1 <sup>st</sup> comb NH <sub>4</sub> <sup>+</sup> ) $2\nu_3\text{NH}_4 / 2\nu_3\text{NH}_4$ -
ANFO	1 NH <sub>4</sub> <sup>+</sup> (AN) n CH (Diesel)	2133, 2032 1642, 1569	$\nu\text{NH}_4 + \delta\text{NH}_4$ (1 <sup>st</sup> comb NH <sub>4</sub> <sup>+</sup> ) $2\nu_3\text{NH}_4 / 2\nu_3\text{NH}_4$
Dynamite	1 NH <sub>4</sub> <sup>+</sup> (AN) 2 CH <sub>2</sub> (EGDN)	2129, 2030 1698 1644, 1570 1269	$\nu\text{NH}_4 + \delta\text{NH}_4$ (1 <sup>st</sup> comb NH <sub>4</sub> <sup>+</sup> ) $2\nu\text{CH}_2$ $2\nu_3\text{NH}_4 / 2\nu_3\text{NH}_4$ -
NaNO <sub>3</sub>	-	2429, 2219, 2064, 1943	-
KNO <sub>3</sub>	-	2469-2431, 2252, 2098, 1972-1938	-
NaClO <sub>3</sub>	-	1922	$\nu_a\text{H}_2\text{O} + \delta\text{H}_2\text{O}$
KClO <sub>3</sub>	-	1924	$\nu_a\text{H}_2\text{O} + \delta\text{H}_2\text{O}$
NaClO <sub>4</sub>	-	1922 1435	$\nu_a\text{H}_2\text{O} + \delta\text{H}_2\text{O}$ $\nu_a\text{H}_2\text{O} + \nu_s\text{H}_2\text{O}$
KClO <sub>4</sub>	-	-	-

**Abbreviations:** n (depending on Diesel composition), comb (combination region), 2ν (first overtone of stretching fundamental vibration), ν<sub>a</sub> (antisymmetric stretching), ν<sub>s</sub> (symmetric stretching), ν (stretching), δ (bending).

Regarding the discrimination of single and double-base smokeless powders, whose major component is NC (N70%), undistinguishable NIR spectra were obtained, which was entirely attributed to NC. This outcome evidenced the limitation of NIR spectroscopy of only detecting the major components in explosive mixtures. In fact, no noticeable NIR signal from the minor components whose mass percentage was below 30% was observed when the mass percentage of the major component was over 70%. On the contrary, when the mass percentage of the major component was below 70%, the NIR characteristic bands of other components started to be perceptible, as occurred for dynamite in which low intense but perceptible bands of EGDN (29%) were detected over the bands of ammonium nitrate (66%).

## Conflicts of Interests

Authors have declared no conflicts of interest.

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