Explosives identification by infrared spectrometry

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Abstract. In order to identify various explosives and their precursors, technicians worldwide rely on chemical analysis instruments for rapid specific identification results to help ensure a safe remediation. This is one of the central tasks for homeland security and public safety personnel, especially since the recent proliferation of improvised explosive devices (IEDs). These instruments that are being used in the field, are extremely important for first responders. For this paper and the experiments made, a FTIR spectrometer (Fourier-transform infrared spectroscopy) was used. This is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. A FTIR spectrometer simultaneously collects high-resolution spectral data over a wide spectral range. They are essentially in identifying unknown chemicals on a wide range of colors. Given the fact that this spectrometer does not generate energy during the sampling process, makes it ideal for verifying substances such as: Semtex, smokeless powders, dynamite, TNT and hundreds of other colored materials. Since contact is required between the sample and the instrument, we took extreme caution measures while analyzing these pressure sensitive substances. In this paper, determinations were made for the identification of functional groups from a series of explosives for civil use, in order to establish the necessary steps in developing an ideal method of identification.

1 Introduction

An explosive is a substance or a device that rapidly releases a significant quantity of energy when it is exposed to heat, collision, friction, or detonation. All of the materials in the area are transformed into hot compressed gases as a result of the energy's abrupt release, which also results in incredible temperature and pressure rises. Due to the extremely high temperature and pressure of these gases, they quickly expand and it causes what is known as a "shock wave" in the surrounding medium. Numerous categories could be used to group the numerous varieties of explosives. Two possible classes are outlined in Figure 1, along with some significant instances for each class [1].

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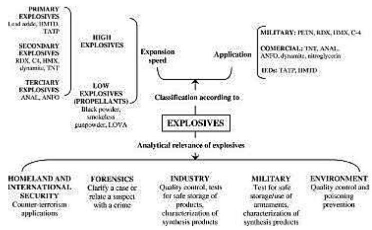


Fig. 1. Classification of explosives and industries that place a high value on analytical analysis of explosives.

Explosives are divided into high-energy and low-energy categories depending on how quickly they spread [2]. High explosives explode, and they are typically split into primary or initiatory explosives, secondary explosives, and tertiary explosives, with the first being the most sensitive and the third being the least sensitive, depending on their sensitivity. A propellant can only be detonated under extremely adverse circumstances since low explosives burn or detonate [3].

2 IR spectroscopy supplemented by Raman spectroscopy

In a variety of fields, the detection of explosives and associated substances is a critical concern. Identification of explosives and associated devices in security has received more attention recently for applications in homeland security and counterterrorism. To combat the issues of concealed explosives at public locations, such as airports and train or bus stations, law enforcement agencies must support research and development for effective detection technologies. If, unfortunately, the terrorist attack or the crime was successful, the development of analytical technologies that can identify explosive residues is of utmost relevance in the forensic sector for crime-scene reconstruction. However, because explosives are also utilized in several non-criminal applications, interest in explosives is tied to more than just a prior crime or attempt at a crime. This indicates that explosives are analyzed both during and after production to assure quality control and proper product storage. Military research facilities also carry out this final examination to make sure their weapons are in good working order and to create rules for handling and using explosives safely. Monitoring environmental regions can benefit from the study of explosives [4, 5].

2.1 Open Road Fourier transform infrared (FTIR) spectroscopy technique

Chemical in the gas phase can be found and identified using the analytical tool of infrared transmission spectroscopy. Open road Fourier transform infrared (FTIR) spectroscopy is a well-established technique for detecting chemical warfare agents (CWA) as well as harmful gas emissions from industrial plants and aircraft exhaust gases. So open path FTIR is another potential way for finding explosives. Due to the low power of the thermal radiation sources often used, open path FTIR suffers from the lengthy integration time required to capture a spectrum. This is particularly true if it is necessary to identify trace substances, which only exhibit minute spectral features in the spectra. The trustworthy gas phase spectra of the chemicals serve as the foundation for detection, sensitivity, and selectivity by infrared transmission. Figure 2 shows the mid-infrared infrared spectra of TATP and TNT [6, 7].

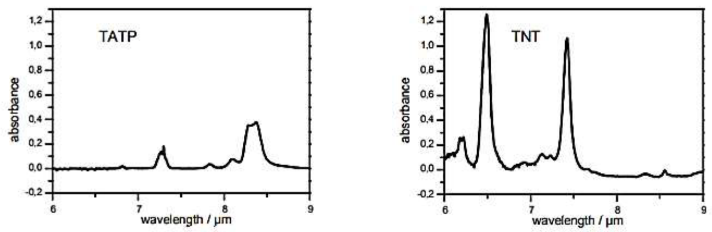


Fig. 2. Infrared spectra in the gas phase of TATP (left) and TNT (right).

The FTIR spectrum of 150 mg/l TATP at 70°C shows a characteristic absorption at 8,35µm with a maximum absorbance of 0.38 (left). Infrared spectrum of 90 mg/l TNT at 200°C (right).

The identification of a wide variety of explosives and related substances is best accomplished using Fourier transform infrared (FTIR) and Raman spectroscopy techniques, which have significant benefits over conventional analytical methods. Some of these benefits include the ability to analyze samples with various physical states (solids, liquids, or gases) or compositions (organic and inorganic), the ability to use both techniques with little to no sample preparation, the ability to analyze minute explosive particulates with spectrometers that include microscope-based systems, the ability to build stand-off systems or portable spectrometers, and the ability to complete sample analysis in a matter of minutes or seconds It should be emphasized that both methods have low consumable and instrument maintenance requirements and are highly reproducible, dependable, and durable. These characteristics have led to the publication of numerous intriguing studies over the past ten years that deal with the identification of explosives using both spectroscopic approaches [7].

2.2. Raman spectroscopy technique (inelastic light scattering)

In order to learn more about the vibrations of different chemical species, IR spectroscopy is supplemented by Raman spectroscopy (inelastic light scattering). Raman spectroscopy transfers this data from the infrared to the visible or near-infrared regions of the spectrum, which have stronger sources and more effective detectors. Although most explosive compounds of relevance have Raman spectra accessible (Table 1), this technique has only lately emerged as a promising option for trace level identification. The Raman scattering technique' inherent weakness and the complicated gear needed until recently for Raman spectroscopy are the two main drawbacks of Raman spectroscopy.

Table 1. Raman spectroscopic data for explosives and related molecules.

Technique	Species	Information or data
Raman	RDX	632.8 nm excitation
Raman	NG, PETN RDX, TNT	20–40 ng detected on activated charcoal
FT-Raman	RDX, PETN	Component identification Semtex
FT-Raman	32 materials	10 µm sample size

FT-Raman	RDX	Vibrational frequencies used to estimate impact sensitivity
Raman microscopy	RDX, PETN	$1(\mu m)^3$ sample size
Raman	PETN	Fiber-optic probe
FT-Raman	HMX, RDX, PETN nitroguanidine nitrocellulose	Low-frequency modes
SERS	TNT	1 pg TNT detected
Raman microprobe	RDX	
Raman imaging	RDX, PETN	
Single Pulse	TNB, MATB	
Raman	DATB, TATB	

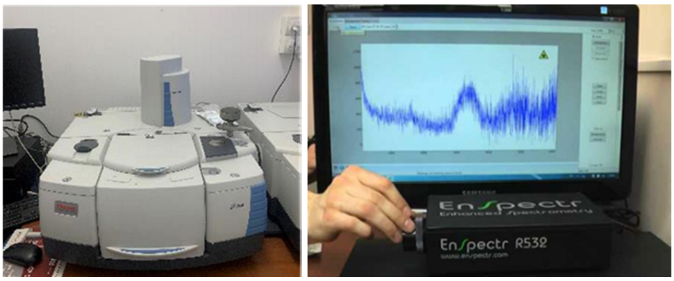
In this article were performed experiments in order to detect explosives and explosive precursors with FTIR and Raman techniques.

3 Materials and methods

The equipment used for the FTIR determinations was Nicolet IS 50 Thermo Scientific spectrometer (Figure 3.a.) with the range 4000 – 400 cm^{-1}, and accuracy of 4 cm^{-1}.

ATR analysis method is a very useful method, which does not actually require a sample preparation, whether we are talking about a powder, film or even a smooth surface of the finished object. The analysis is no longer done by passing the IR beam through the sample, but by its reflection on the surface of the sample, the beam penetrating inside the sample approximately 1µm. The beam is directed to the window by means of an optical mirror system.

The equipment used for the RAMAN determinations was Enspectr. EnSpectr R532 utilizes a 20 (30 optional) µm entrance slit, 1200 g/mm holographic grating, cutting-edge low pass filter, as well as a 30mW single mode laser emitting at 532 nm to provide high accuracy Raman and luminescent measurements in a broad spectral range from 140 to 6030 cm-1 (Figure 3.b.).



a. **b.**

Fig. 3.a. FTIR equipment type Nicolet IS 50; **b.** Enspectr Raman equipment.

4 Results and discussion

In this work, there were tested in order to identify two explosives samples and 1 sample of explosive precursors, as follows:

In the figure below (Figure 4) there is presented the obtained spectrum for a sample that after performing the analysis the database showed a very high match (over 90 %) with plastic explosive C3.

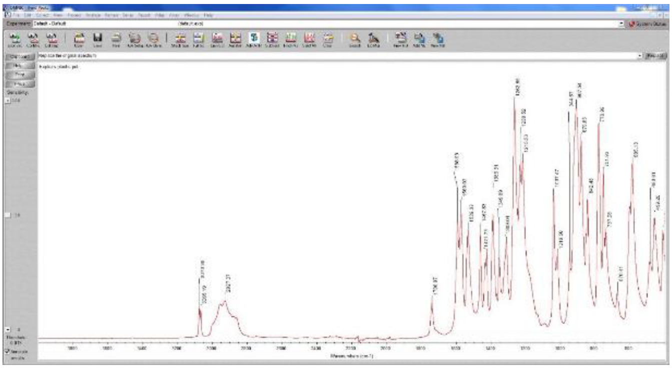


Fig. 4. FTIR Spectrum of a plastic explosive.

The characteristic peaks are similar with those obtained in the literature [8] as can be seen in the Figure 5:

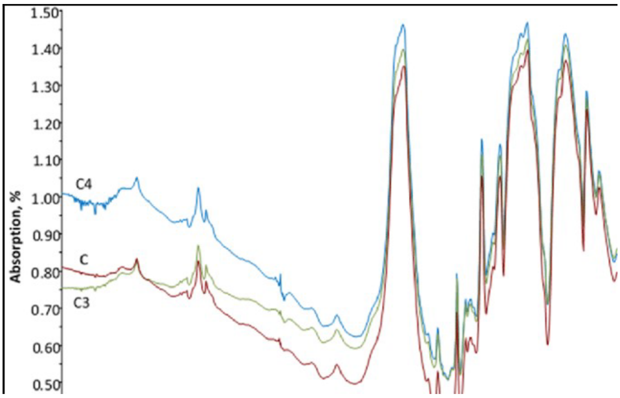


Fig. 5. The characteristic peaks.

In the figure below (Figure 6) there is presented the obtained spectrum for a sample that after performing the analysis the database showed a very high match (over 90 %) with TNT (trinitrotoluene).

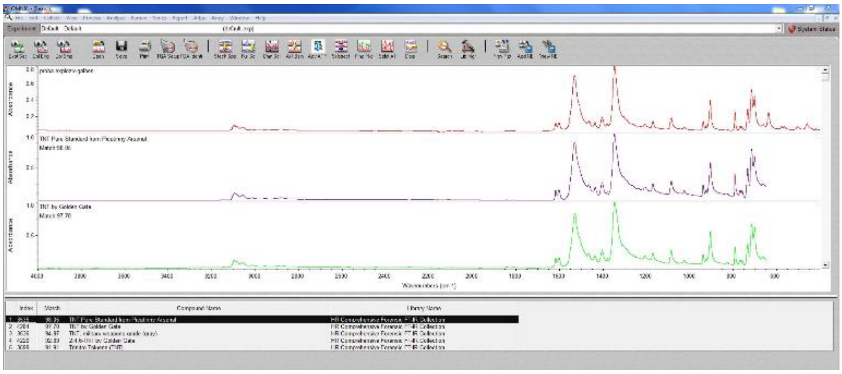


Fig. 6. FTIR Spectrum of TNT explosive.

The characteristic peaks are similar with those obtained in the literature [9] as can be seen in the Figure 7:

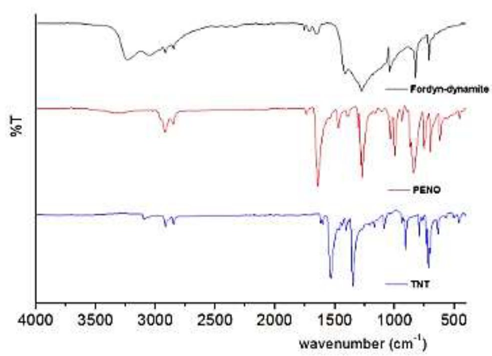


Fig. 7. Pure explosive FTIR Spectrum [9].

The next test with FTIR method was to identify an explosive precursor, namely Hexamine. Hexamine is flammable and can be easily ignited by brief exposure to a source of ignition and continues to burn after removal from the source. The finer the hexamine is distributed, the greater the risk of ignition. It can cause dust explosions. Hexamine easily dissolves in water, is hygroscopic and sensitive to moisture. An explosion or violent reaction can occur when hexamine comes into contact with acids (e.g., nitric acid), peroxides or oxidizers. Suitable extinguishing agents are water (spray jet), dry extinguishing powder, foam and carbon dioxide. Hexamine is moderately dangerous for water supplies [10]. The match for this sample after performing the ATR FTIR was almost 100 %. The characteristic peaks can be seen in Figure 8.

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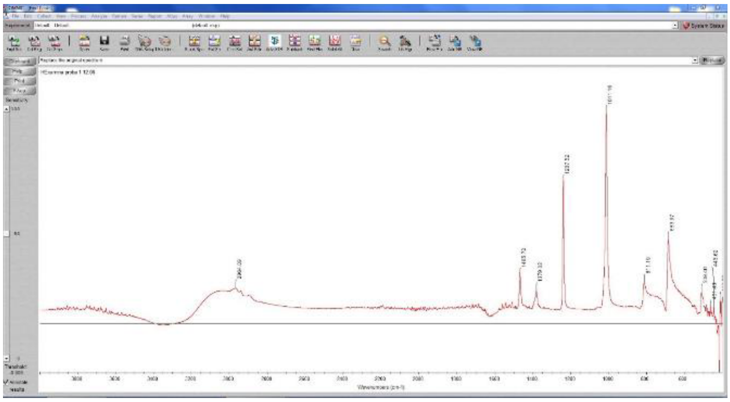

Fig. 8. Hexamine FTIR Spectrum.

Another explosive precursor, namely Sodium Chlorate. Sodium chlorate can be mixed with sucrose sugar to make a highly explosive fuel, similar to that of gunpowder, that burns in airtight spaces. The match for this sample after performing the ATR FTIR was almost 100 %. The characteristic peaks and match can be seen in Figure 9.

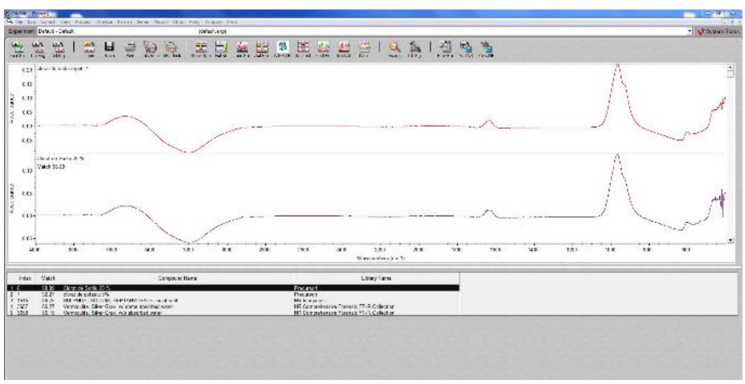

Fig. 9. Sodium Chlorate FTIR Spectrum.

A Raman spectrum was obtained for a sample of TNT, with a match of 0.972 (Figure 10), the method for identify being more rapid and safer, given the fact that the sample is placed into a small vial that comes in front of the spectrometer laser beam.

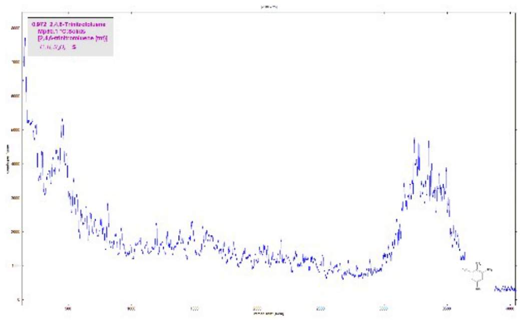

Fig. 10. RAMAN shift for TNT.

5 Conclusions

In a variety of fields, the detection of explosives and associated substances is a critical concern. Identification of explosives and associated devices in security has received more attention recently for applications in homeland security and counterterrorism.

For the identification of a wide variety of explosives and related substances, Fourier transform infrared (FTIR) and Raman spectroscopy techniques are superior to other analytical techniques due to their many benefits. Some of these benefits include the ability to analyze samples with various physical states (solids, liquids, or gases) or compositions (organic and inorganic), the ability to use both techniques with little to no sample preparation, the ability to analyze minute explosive particulates with spectrometers that include microscope-based systems, the ability to build stand-off systems or portable spectrometers, and the ability to complete sample analysis in a matter of minutes (or even seconds). It should be highlighted that both methods have low consumable and instrument maintenance requirements, and they are exceedingly dependable, reproducible, and durable.

Two explosives were detected using FTIR an RAMAN technique, showing that the methods are suitable for the determinations.

References

1. M. López-López, C. García-Ruiz, TrAC **54,** 36-44 (2014)
2. J.P. Agrawal, *High energy Materials: Propellants, explosives and pyrotechnics* (Wiley, Hoboken, Weinheim, 2010)
3. Explosives detection technologies to protect passenger rail **GAO-10-898**, United States Government Accountability Office, Washington D.C. (2010)
4. S. Wallin, A. Petterson, H. Öst, *Forensic and Environmental Detection of Explosives* (John Wiley & Sons, West Sussex, 1999)
5. J. Hildenbrand, J. Herbst, J. Wöllenstein, A. Lambrecht, SPIE **7222 72220B-2** (2018)
6. M.B. Pushkarsky, M.E. Webber, T. Macdonald, C.Kumar M. Patel, Appl. Phys. Lett. **88**, 044103 (2006)
7. J. I. Steinfeld, Annu. Rev. Phys. Chem. **32**, 49-203 (1998)
8. A. Sankauskaitė, V. Rubeziene, D. Kubilienė, A. Abraitienė, Polymers **12** (6),1319s (2020)
9. J. Kuula, Heikki J. Rinta, I. Pölönen, H. Puupponen, M. Haukkamäki, T. Teräväinen, CBREN, **9073** (2014)
10. Basic chemistry of explosives and hazards of home-made explosives and chemical precursors handbook. Available on: https://www.gichd.org/fileadmin/GICHD-resources/rec-documents/IEDD_Handbook_Chapter_5.pdf