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Review

Infrared and Raman spectroscopy techniques applied to identification of explosives

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A B S T R A C T

This review summarizes the recent trends and developments of infrared and Raman spectroscopy applied to the identification of explosives that have been published over the past decade, focusing on the different fields where explosives were studied: homeland and international security, forensics, environmental, characterization of explosives, trace detection and fluorescence-free Raman analysis of explosives.
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Contents

Abbreviations: AN, Ammonium nitrate; ATR, Attenuated total reflectance; CARS, Coherent anti-Stokes Raman spectroscopy; CCD, Charge-coupled device; DNT, Dinitrotoluene; FT, Fourier transform; FTIR, Fourier transform infrared; GC, Gas chromatography; HMTD, Hexamethylene triperoxide diamine; HMX, High melting explosive; HPLC, High-performance liquid chromatography; ICCD, Intensified charge-coupled device; IED, Improvised explosive device; LIBS, Laser-induced breakdown spectroscopy; LOD, Limit of detection; PCA, Principal-component analysis; PETN, Pentaerythritol tetranitrate; RDX, Cyclotrimethylenetrinitramine; RRS, Resonance Raman spectroscopy; SEM–EDS, Scanning electron microscopy–energy dispersive spectroscopy; SERS, Surface-enhanced Raman spectroscopy; SORS, Spatially-offset Raman spectroscopy; TATP, Triacetone triperoxide; TNT, Trinitrotoluene; TRRS, Time-resolved Raman spectroscopy.

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1. Introduction

An explosive is a substance or a device that, when subjected to heat, impact, friction, or detonation, releases a large amount of energy extremely fast. The sudden liberation of energy causes incredible increases of temperature and pressure, so that all the materials present are converted into hot compressed gases. Since these gases are at very high temperature and pressure, they expand rapidly and thus initiate a pressure wave, called "shock wave" in the surrounding medium. The many different types of explosives could be categorized in several ways. Fig. 1 summarizes two possible classifications and includes some important examples of each class.

If the speed at which explosives expand is first considered, they are categorized as high-energy and low-energy explosives [1]. High explosives detonate and are usually subdivided according to their sensitivity into primary or initiatory explosives, secondary explosives, and tertiary explosives, the first being the most sensitive and the third the least. However, low explosives undergo burning or deflagration, meaning that a propellant can only be detonated under extreme conditions [2].

Although explosives are of immense value in many peaceful applications, the best-known use of explosives has been in warfare or terrorist attacks, so Fig. 1 also depicts a second division of high explosives into three classes [military, commercial, and improvised explosive devices (IEDs)] based on their use. Military explosives and commercial explosives can only be purchased by legitimate buyers through explosives distributors and typically terrorists obtain such explosives by trafficking or stealing them [3]. However, IEDs are destructive devices to destroy, incapacitate, harass, or distract that can be made from wide range of non-military components, chemicals, and compounds that are commercially available to civilians in most countries [4].

The detection of explosives and related compounds is an issue of major importance in very different fields. In security, identification of explosives and related devices has become a heightened priority in recent years for homeland security and counter-terrorism applications. Law-enforcement forces throughout the world have to promote research and development for efficient detection systems to face the problems of hidden explosives at public places, such as airports, and railway or coach stations. Also, the development of analytical tools that can identify explosive remains is of tremendous importance in the forensic field for crime-scene reconstruction, if, unfortunately, the terrorist attack or the crime was successful.

But, interest in explosives is related to not only a previous crime or attempt at crime but also because explosives are also used in many peaceful applications. This means that the analysis of explosives is also performed during the explosives manufacture for quality control and afterwards to ensure good product storage. This last analysis is also performed by military laboratories to ensure the good condition of their armaments and to establish safety regulations related to use and manipulation of explosives. The analysis of explosives can also be relevant in environmental areas to monitor the quality of soil, water, and groundwater suspected of being contaminated by explosives and their degradation products, in order to prevent poisoning of populations of humans and animals [5].

Independently of the areas where analysis of explosives is required, analysts have to deal with several drawbacks, such as the explosive nature of the analyte, the identification of very small amounts of sample, and the complexity of the samples. To overcome these disadvantages, a wide variety of analytical techniques is required to provide national security tools, information, justice, and safety, or to prevent environmental damage.

Fourier transform infrared (FTIR) and Raman spectroscopic techniques have several advantages over other analytical techniques that make them optimal for the identification of a large range of explosives and related compounds. Some of these advantages are the possibility to analyze samples with different physical states (solids, liquids or gases) or composition (organic and inorganic), both techniques can be utilized with no or minimal sample preparation, minute explosive particulates can be readily analyzed if spectrometers include microscope-based systems, stand-off systems or portable spectrometers can be built, and sample analysis can be achieved in a few minutes (or even seconds). Also, it should be noted that both techniques are robust, reproducible, and very reliable, with minimal instrumental maintenance and requirements for consumables. Due to these features, many interesting studies have been published over the past decade dealing with

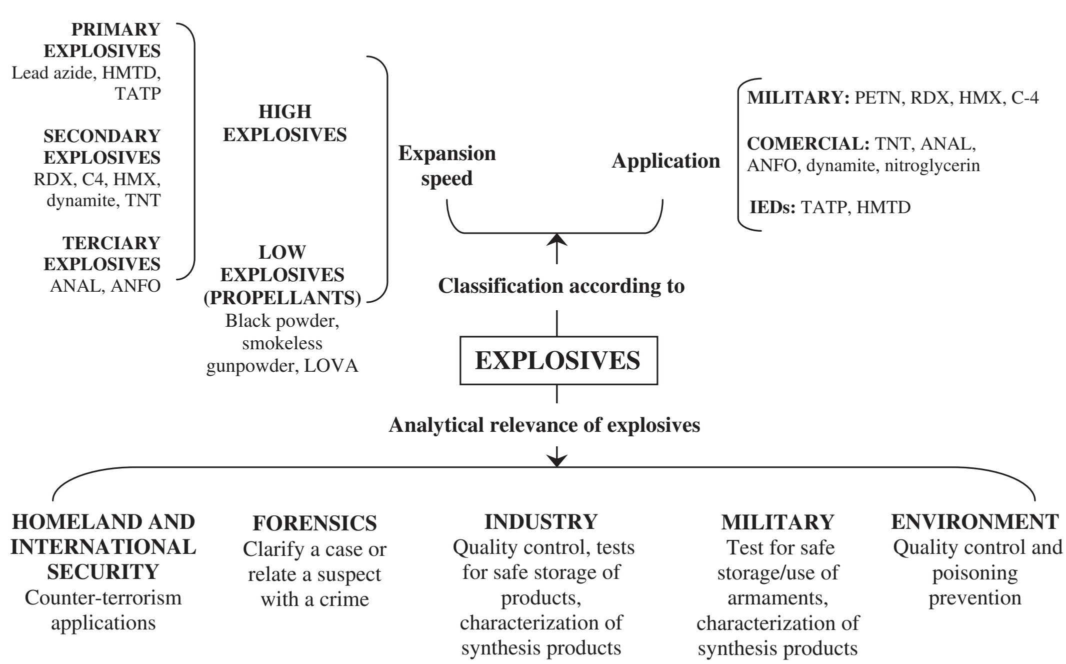

Fig. 1. Classification of explosives and fields where the analytical analysis of explosives has great importance.

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