

Engineering Laser Systems for Defence Applications

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Abstract: - Over time, the growing danger posed by improvised explosive devices (IEDs) has prompted endeavors to create sensitive detection techniques capable of foreseeing, detecting, and safeguarding against such makeshift assaults. Laser technologies have advanced significantly in defense strategies. Laser-based spectroscopic techniques offer swift and precise detection of chemicals in improvised explosives; however, no singular method can detect every component of all explosives. This study employs two spectroscopic methods to sensitively identify eight explosive chemical substances in both powder and vapor forms. The absorption spectra of benzene, toluene, acetone, and ethylene glycol were analyzed using CO₂ laser photoacoustic spectroscopy. The photoacoustic signals of the samples were captured within the CO₂ laser emission spectrum spanning from 9.2 to 10.8 μm, revealing distinct spectral behaviors for each substance under analysis. Time-domain spectroscopy employing THz radiation was utilized to examine transmission spectra of ammonium nitrate, potassium chlorate, dinitrobenzene, and hexamethylene teramine within the 0.1-3 THz range, revealing characteristic THz fingerprint spectra for each compound. Both CO₂ laser photoacoustic spectroscopy and THz time-domain spectroscopy have demonstrated their effectiveness in identifying explosive constituents. The integration of these spectroscopic techniques represents an innovative and promising approach for detecting a wide array of IED components.

Key-Words: - laser, infrared, terahertz, spectroscopy, chemical identification, explosive agents, security

Received: July 17, 2023. Revised: February 2, 2024. Accepted: March 7, 2024. Published: April 2, 2024.

1 Introduction

Recent events worldwide have underscored the ongoing threat posed by energy attacks, particularly those stemming from improvised explosive devices (IEDs) and homemade explosives (HMEs). These incidents continue to endanger both military and civilian personnel [1]. Consequently, there is a pressing need for methods that enable the swift identification of explosives before they are detonated. Laser-based spectroscopy methods, renowned for their high sensitivity, selectivity, and ability to detect multiple components, have introduced innovative solutions for identifying and characterizing explosive materials [2].

Various spectroscopic techniques such as Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), laser-induced breakdown

spectroscopy (LIBS), terahertz spectroscopy, gas chromatography-mass spectrometry (GC-MS), and ion mobility spectrometry (IMS) are commonly employed for explosives identification and detection [3-8].

Two sensitive laser-based methods, CO₂ laser photoacoustic spectroscopy (CO₂LPAS - CO₂ laser photoacoustic spectroscopy) and THz radiation time domain spectroscopy (THz-TDS - terahertz time domain spectroscopy), have attracted attention for the identification of chemical agents both in gaseous form as well as powders covering the spectral region from mid-infrared (MIR - mid infrared) and far infrared (FIR - far infrared -THz) [9,10].

Chemical characterization of explosive vapors and mixtures can lead to a better understanding of the signature of explosive agents, providing improved chemical and biological detection of explosive

threats, as well as extending existing laboratory-based models for continued sensor development.

2 Problem Formulation

The identification and detection of explosives and related substances remain a work in progress due to the complexity of the physical-chemistry involved in this challenging field.

Chemical substances used in the production of explosives are not individually categorized as explosive materials but are governed by legal frameworks regarding their acquisition, use, and storage. These substances are commonly available in retail stores and are frequently utilized for domestic purposes. Ammonium nitrate, a fertilizer widely manufactured globally, exemplifies this criteria and is recognized as one of the most commonly used explosive materials [11].

The increasing sophistication of IEDs has prompted the Commission of the European Communities to prioritize research on the identification of explosives and precursors [12]. Detecting IEDs during the initial stages of preparation offers higher accuracy and less time constraints compared to later stages. In addition to audio and video monitoring, an intriguing approach involves detecting precursors released around the site as they are handled and transformed into the final IEDs.

Laser-based spectroscopy methods, renowned for their high sensitivity, selectivity, and ability to detect multiple components, have introduced innovative solutions for identifying and characterizing explosive materials. CO₂LPAS and THz-TDS methods can be used to identify explosive chemical agents in both gaseous and powder form.

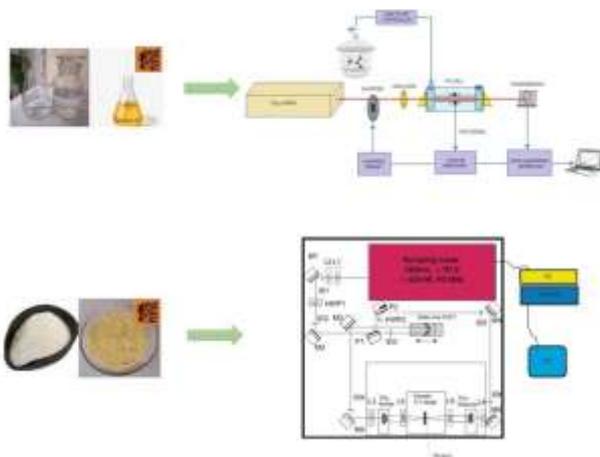


Fig.1 CO₂LPAS and THz-TDS methods used to identify explosive chemical agents in gaseous and powder form

CO₂LPAS is a method that can simultaneously provide high sensitivity of parts-per-billion-volume (ppbv) detection, selectivity, multi-gas measurement with a wide dynamic range [13]. The main components of the system are a frequency-stabilized line-tunable CO₂ laser and a resonant photoacoustic cell where the gas concentration is detected and analyzed in combination with a flow-through system. In order for gas traces to be detected, it is necessary that the target molecules possess a so-called molecular fingerprint in the emission spectral range of the CO₂ laser, in the spectral region 9.2 - 10.8 μm , a region in which a wide range of gaseous compounds. The resonant photoacoustic has a resonance frequency of 564 Hz and is characterized by the quality factor of 16.1. For a system cell constant of 4375 Pa $\cdot\text{cm}/\text{W}$, the responsivity is 350 cm V/W (Figure 1). Although CO₂LPAS has proven to be a very powerful trace gas investigation technique, it has been very little used as an integrated system for the on-line detection of trace explosives in the vapor state.

The THz-TDS system has been continuously improved over the past 10 years. THz-TDS, is a spectroscopic technique for determining the properties of a sample probed by short pulses of THz radiation. Collecting data in this frequency range has many advantages; biological samples do not ionize from THz radiation and many compounds, such as explosives, have unique fingerprints in this region making this method particularly valuable for security [14].

The substances ammonium nitrate, potassium chlorate, dinitrobenzene, hexamethylenetetramine were analyzed with a THz-TDS kit from Ekspla. The system uses a Toptica Photonics FFS Erbium-YAG laser in ultrashort pulses, emitting at 780 nm, with pulse duration <70 fs and power >60 mW, having a 30-mW input pulse on the 10 μW transmitting antenna.

In the 0.1-3 THz range, the transmission spectra were obtained for ammonium nitrate, potassium chlorate, dinitrobenzene, hexamethylenetetramine, taking as a reference the transmission spectrum of the polyethylene container in which they were measured (Figure 1).

The objective of this study was to detect explosive chemical agents in both gaseous and powder forms utilizing two sensitive techniques: CO₂LPAS and THz-TDS. These methods offer insights into the presence of explosive chemical agents within specific IED processing environments or on particular surfaces. Building a database containing spectra in the infrared and terahertz range enables the identification of increasingly complex

substances, thereby mitigating potential hazards associated with processing energetic materials.

3 Problem Solution

Our study was centred on four gaseous compounds (benzene, toluene, acetone, ethylene glycol), which were analyzed using CO₂LPAS, and four powders (ammonium nitrate, potassium chlorate, dinitrobenzene, hexamethylenetetramine), which were examined using THz-TDS. The samples of explosive chemical agents were procured from the chemistry laboratory of the National Institute of Lasers, Plasma and Radiation, Romania.

Determination of absorption spectra of the explosive chemicals benzene, toluene, acetone and ethylene glycol were performed by LPAS. The absorption spectra of each gaseous sample was obtained by completely evaporating 0.1 mL of the standard solution at 25°C inside the 1.5 L volume glass enclosure together with room air and introduced into the PA cell. The CO₂ laser was tuned and directed onto the sample and the PA signal of the sample was recorded for each laser emission. The same procedure was adopted for each compound and absorption spectra were investigated for each specific chemical signature.

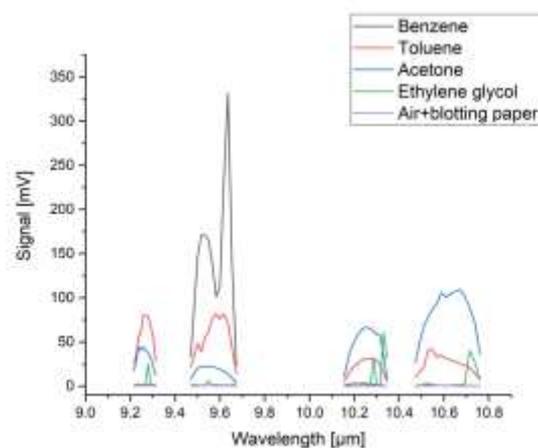


Figure 1. Absorption spectra of benzene, toluene, acetone, ethylene glycol.

The maximum value of the benzene signal was observed at the 9,636 μm wavelength of the CO₂ laser, corresponding to the 9P(30) laser line. Toluene shows 4 maxima on the 9P(24), 9P(28), 9R(22), 9R(20) lines at wavelengths 9.583 μm, 9.618 μm, with 9.258 μm, 9.268 μm. Acetone presents high absorption on the 10P(28) and 10P(20) lines corresponding to wavelengths 10.671 μm and 10.588 μm. Ethylene glycol has a maximum signal value on the 10R(8) line at 10.330 μm and

two smaller values on the 10R(6) lines at 10.346 μm and 10R(14) at 10.286 μm. By determining the absorption spectra of these substances, their maximum absorption was observed in the range 9.2-10.8 μm. Knowing these absorption lines, target compounds can be easily detected quantitatively using CO₂LPAS from possible IED fabrication sites. Ammonium nitrate, potassium chlorate, dinitrobenzene, hexamethylenetetramine powders were investigated with THz-TDS method.

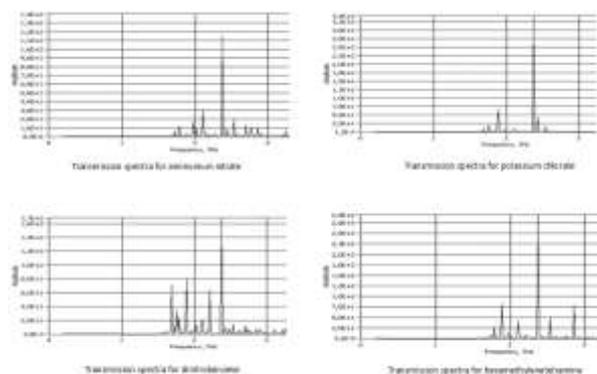


Figure 6. Transmission spectra for ammonium nitrate, potassium chlorate, dinitrobenzene, hexamethylenetetramine.

In the case of the ammonium nitrate chemical compound, its transmission presented two significant peaks at 2.4THz and 3.5THz, which constitute the unique spectral signature of the compound. The two maxima correspond to laser wavelengths of 0.1873 μm and 85.6 μm, respectively. The spectral signatures in this region of the spectrum are low-frequency motions, recognized to be intermolecular vibrations, intramolecular torsions, and lattice vibrations. Potassium chlorate has a transmission maximum at 2.5 THz, corresponding to the laser wavelength of 119.91 μm. Dinitrobenzene emits a maximum at 2.4 THz, i.e. at 124.91 μm. Hexamethylenetetramine has a THz maximum emission at the frequency of 2.3 THz, corresponding to the laser wavelength of 130.34 μm.

The obtained results show that they have characteristic THz fingerprint spectra that can be used to identify threats in THz security application.

4 Conclusion

Identification of explosive chemical agents in gaseous and powder form was achieved by determining absorption and transmission spectra using two sensitive techniques such as CO₂LPAS and THz-TDS.

The maximum values of the signals were observed on the 9P(30) line for benzene, on the 9P(24), 9P(28), 9R(22), 9R(20) lines for toluene, 10P(28) and 10P(20) for acetone and 10R(6) for ethylene glycol. It was observed that the PA signals obtained for each analyzed sample present a different distribution of absorption peaks.

Transmission spectra were obtained in the range 0.1 - 3 THz with maximum values at 2.4 THz and 3.5 THz for ammonium nitrate, at 2.5 THz for potassium chlorate, at 2.4 THz for dinitrobenzene and at 2.3 THz for hexamethylenetetramine. Knowing the spectral signatures of these substances, THz-TDS can be used for their detection in packaging and containers.

The use of these two techniques to identify as many dangerous substances as possible, represents a novelty in the field of security, both nationally and internationally, being able to identify in real time, dangerous substances for the security of people, defence, anti-terrorism and smuggling by recognizing the spectral signature of the hazardous material.

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Contribution of Individual Authors to the Creation of a Scientific Article (Ghostwriting Policy)

Ana-Maria Bratu, Cristina Popa, Mioara Bercu designed the study and organized and executed the experiments with LPAS method.

Mihaela Bojan organized and executed the experiments with THz-TDS method.

Sources of Funding for Research Presented in a Scientific Article or Scientific Article Itself

This research was funded by Program LAPLAS VII – contract no. 30N/2023, and project number PN-III-P1-1.1-TE-2021-0717.

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