Spectroscopic Study of Some IED's Precursors by Means of Laser Photoacoustic Spectroscopy Combined with Multivariate Analysis

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Keywords: Photoacoustic Spectroscopy, Improvised Explosive Device, Principal Component Analysis.

Abstract: The Improvised Explosive Device (IED) is the most prevalent form of explosive device utilized by terrorists today being easy to realize and difficult to detect. These explosive devices are made by mixing different precursor substances that are generally cheap and commercially available. Thus, attention should be focused on developing fast and reliable methods able to identify such substances. In this paper we applied laser photoacoustic spectroscopy method for the spectral characterization and identification of a number of common chemicals used as precursors of IEDs: potassium sulfate, potassium nitrate, magnesium sulfate, ammonium perchlorate, ammonium nitrate, and acetone. The analyzed chemical species were classified by Principal Component Analysis applied to the collected spectral data. As conclusion of the study, the laser photoacoustic spectroscopy combined with chemometrics has confirmed to be a useful tool that could support the fight against the increased realization of modern bombs for criminal use.

1 INTRODUCTION

The use of explosives and Improvised Explosive Devices (IEDs) by terrorists continue to pose a significant threat for civilians. The most prevalent form of explosive device utilized in the attacks are the IEDs. These mixtures are homemade, non-conventional explosives, fabricated by combining common chemicals to manufacture a rudimental but efficient bomb. As traditional explosives are difficult to obtain, bomb makers search for chemicals commercially available in hardware stores, pharmacies and cosmetics stores to use them as explosives precursors. A list of some chemicals used as precursors of IEDs is reported in Table 1. The number of explosives which can be home-manufactured is limited by the imagination and knowledge as well as by the cost and availability of these chemicals on the market. Improvised explosives are typically mixtures of an oxidizer and a fuel. The first substance must be rich in Oxygen and the second one must be able to react very fast so that it changes and multiplies its volume (Australian Explosives Manufacturers Safety Committee Report, 1999). Nowadays, there is a need to develop new efficient methods able of sensitive and selective detection of such chemicals during transportation or storing by terrorists. The fight against the increased realization of modern bombs for criminal use is approached by developing fast real-time easy-to-use methods for the detection of IED precursors such as Infrared Laser Photo-acoustic Spectroscopy (IR-LPAS). IR-LPAS already demonstrated to be promising in the design of an integrated optical system for the real time detection and identification of explosive species in traces to support homeland security (Chaudhary at al. 2006, Giubileo et al. 2010, Giubileo et al 2012, Puiu at al. 2012).

Table 1: Chemicals used as precursors of IEDs. (Rostberg, 2005, Singapore Police Force 2007).

Acetone	Hydrogen peroxide	Potassium sulfate
Ammonium nitrate	Hexamine	Potassium perchlorate
Ammonium perchlorate	Magnesium sulfate	Sodium chlorate
Barium nitrate	Nitric acid	Sodium nitrate
Citric acid	Nitromethane	Sulphuric acid
Guanidine nitrate	Potassium chlorate	Hydrochloric acid
Urea	Potassium nitrate	

In this paper we report the LPAS analysis of a number of common chemicals used as IED precursors: potassium sulfate, potassium nitrate,

Puiu A., Giubileo G. and Palucci A..
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DOI: 10.5220/0005335500260030
In *Proceedings of the 3rd International Conference on Photonics, Optics and Laser Technology* (PHOTOPTICS-2015), pages 26-30
ISBN: 978-989-758-092-5

magnesium sulfate, ammonium perchlorate, ammonium nitrate, and acetone. The analyzed chemical species were classified by Principal Component Analysis (PCA) applied to the collected IR spectral data, which facilitate the recognition capability of the adopted method.

2 MATERIALS AND METHODS

The experimental work was performed by using a home-made LPAS apparatus equipped with a line tuneable 10 Watts Continuous Wave stabilized CO_2 laser source and with a home-made 3cc photoacoustic (PA) cell. System control and Data acquisition are achieved through a specialized card, IEEE488.2 - GPIB National Instruments, with signal processed by a lock-in amplifier, SR830 Stanford Research Systems, in a LabView environment. A schematic of the LPAS apparatus is shown in Figure1. More details on the Photoacoustic facility were reported in a previous paper (Giubileo et al. 2010). The PA signal produced by a few hundreds of μg/cm^2 of each chemical was filtered by a low pass pre-amplifier and selectively amplified by a lock-in amplifier. The background signal was negligible when compared to the sample signal.

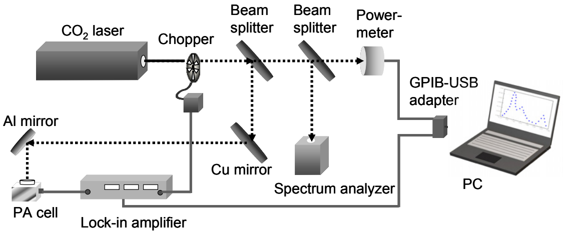

Figure1: Schematic of the LPAS set-up.

The list of chemical substances considered in the present experimental work is reported in Table 2.

Table 2: List of LPAS analyzed IED precursors.

Precursor	Chemical formula	m.p. (°C)
Acetone	CH_3-CO-CH_3	-95
Ammonium nitrate	NH_4NO_3	169
Ammonium perchlorate	NH_4ClO_4	200
Magnesium sulfate	$MgSO_4$	1124
Potassium sulfate	K_2SO_4	1069
Potassium nitrate	KNO_3	334

All the pure solid substances purchased from Carlo Erba were analyzed without any pretreatment in weighted amounts of 100 - 300 μg. The samples were directly warmed by the incident laser beam so that the PA signal was generated without previously warm the sample to bring out vapours. Before each measurement, the PA cell was shortly cleaned by vacuum pumping.

3 RESULTS

The concept of LPAS recognition of IED precursors has been demonstrated by performing measurements on the selected set of chemicals reported in Table 2. Examples of some IEDs PA spectra are shown in Figures 2 to 5. The spectra were collected in the 9.2-10.8 μm spectral range covered by the adopted laser source. All the considered chemicals underwent the same analytical procedure.

As it can be observed, characteristic absorption peaks distribution was found in the investigated spectral range for each analyzed sample. The error bars in the graphs represent the standard deviation of ten different PA signal acquisitions on the given laser emission line.

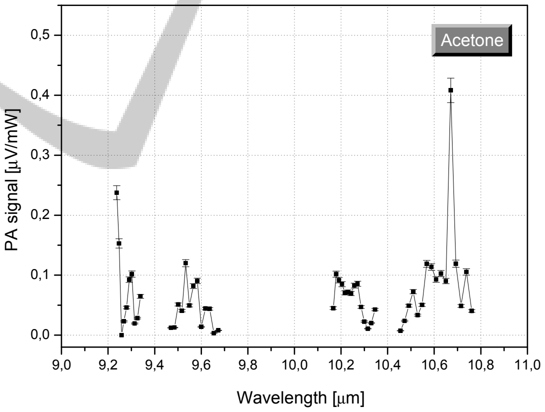

Figure 2: Photoacoustic spectrum of acetone.

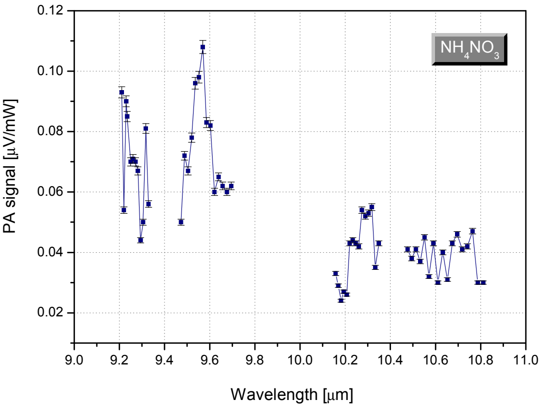

Figure 3: Photoacoustic spectrum of ammonium nitrate.

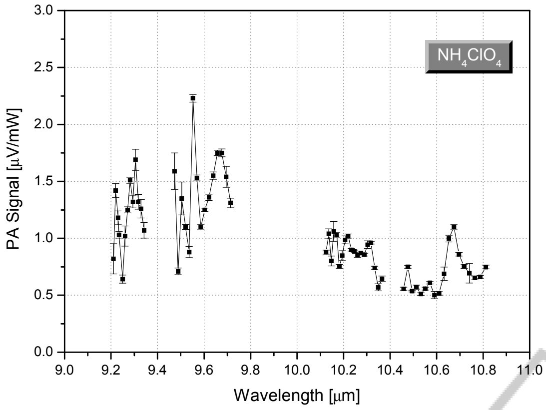

Figure 4: Photoacoustic spectrum of ammonium perchlorate.

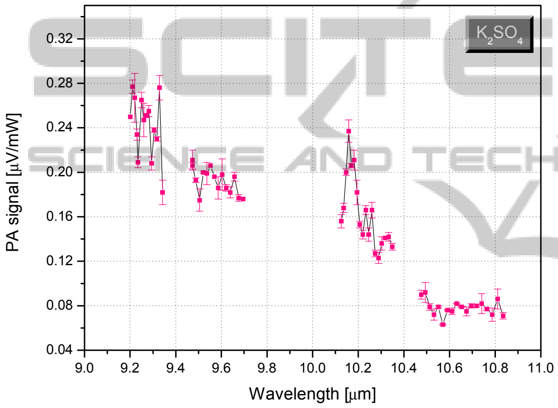

Figure 5: Photoacoustic spectrum of potassium sulfate.

The strong absorption band presented by NH_4ClO_4 (ammonium perchlorate) at 9 -10 µm determines the relatively higher LPAS signals recorded for this chemical in the mentioned interval. For NH_4NO_3 and K_2SO_4 species, an increasing LPAS signal going from 11µm toward 9µm was recorded, as confirmed also by FTIR data in the literature (Miller et al. 1952).

Despite the analyzed samples are inorganic substances that do not possess the rich band structure generally found for the organic species in the fingerprint region (6-20µm), the high resolution PA spectroscopy put in evidence different spectral patterns characteristic for each substance in the spectral interval covered by the CO_2 laser (9-11 µm), even in the absence of specific absorption bands ascribable to some roto-vibrational motions within the molecule.

4 PRINCIPAL COMPONENT ANALYSIS

From a first graphs examination it appears that the spectral features of the analyzed substances are sufficiently different from each other. Nevertheless, a direct comparison of the collected spectra is quite difficult in practice.

In order to achieve the unambiguous and rapid recognition of trace explosive compounds, a chemometric approach based on Principal Component Analysis (PCA) was applied to the set of experimental data. PCA gives valuable information about the factors which mainly affect the spectral variations among different analyzed samples.

The result of PCA treatment on the investigated precursors is shown in Figure 6. Looking at the graph it appears evident the discrimination capability of the LPAS analysis coupled to the PCA chemometric algorithm.

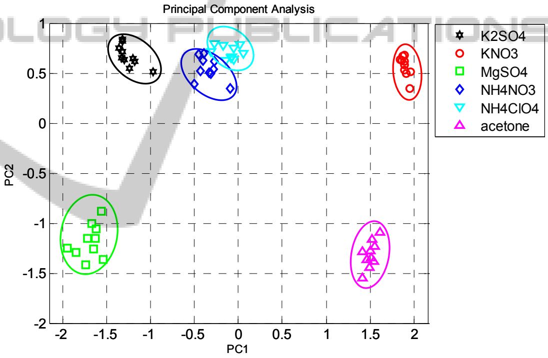

Figure 6: Graphical presentation of PC1 versus PC2 applied to photoacoustic spectra of different IED precursors.

The infrared photoacoustic spectra were previously normalized to the laser power, and then to their maximum peak value. We recorded the PA signal from 55 emission wavelengths of the CO_2 laser. Thus, by using a software developed in MatLab environment, the PCA was applied to a data matrix of 55 datapoints and 60 samples. On a data matrix containing elements x_{ik}, where index k is used for the experimental measurements and index i for the samples under study, the PCA model is described by the equation (1):

$$x_{ij} - \bar{x}_k = e_{ik} + \sum_{j=1}^{N} t_{jk} p_{jk} \qquad (1)$$

where the loadings p_{jk} depend only on the experimentally measured variables and the scores t_{ij} only depend on the sample constituents; N is the number of significant components (Giubileo et al. 2012).

After performing the PCA resulted that the first three principal components are explaining 78.3% of the overall spectral variation. The corresponding loading plots, which indicate the specific contribution of each absorption line in the total variance of the spectral data, are reported in the Figure 7. The first principal component, PC1, which accounts for the 42.8 % of spectral variance, has one isolated peak around 9.5 µm that correspond to some vibrations in the two nitro-compounds (NH_4NO_3 and KNO_3). Generally, the fingerprints of inorganic compounds fall in the region 25 µm – 1 mm (400 – 10 cm^{-1}) due to the presence of the lattice modes of vibration which are characteristic of a specific crystal geometry (Nyquist et al. 1997). These modes result from the motion of one polyatomic group relative to another within the unit cell. Thus, there are no absorption peaks in the interval 9-11 µm which can be ascribed to a specific mode of vibration of some functional groups inside the sample.

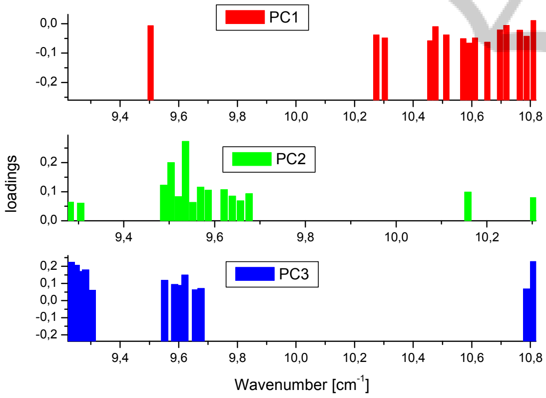

Figure 7: Loadings plots for the first three components.

In the second component, PC2, with an explained spectral variance of 19.8 %, there is a wider band centered around one isolated peak around 9.5 µm that correspond to some vibrations in the NH_4NO_3, NH_4ClO_4 and KNO_3.

The loading plot for PC3, which explains the 15.7 % of spectral variance, shows, besides the peaks in position equivalent to those in the PC1 or PC2, a strong band in the 9P branch of the CO_2 laser emission wavelengths.

In general, a low number of PC able to explain more than 60% of the spectral variances is correlated with a large spectral difference among the samples. Thus, in our case only two components can be sufficient to describe the data set, as evidenced in Figure 6, which shows the PCA plot for the PC1 and PC2, the two largest principal components of the dataset, which explain 62.6 % of the spectral variance between the samples. In this plot each sample is represented by a point, and the six groups, each corresponding to a precursor substance, are clearly separated.

In Figure 8 we report the 3D plot of PC1, PC2 and PC3 (78.3 % explained variance), which clearly shows that each compound can be correctly grouped with no misassignment. Therefore, the application of PCA to the LPAS spectra expressed by 55 different wavelengths allowed to reduce the output to only three components. The score plots indicate that the proposed model is able to correctly group the IED's precursors in spite of the oversimplification of LPAS spectra.

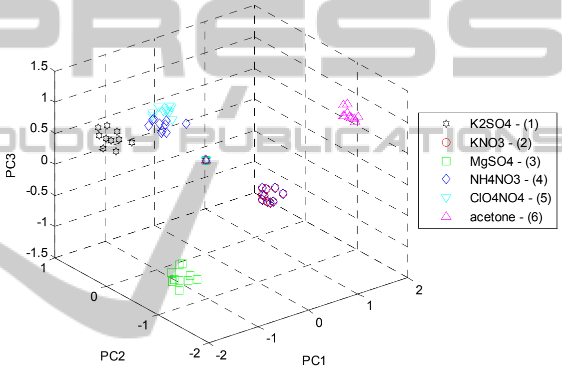

Figure 8: PCA results in the 3D space generated by the first three components (PC1, PC2, and PC3).

5 CONCLUSIONS

The concept of LPAS recognition of IED precursors has been demonstrated by performing measurements on the selected set of chemicals reported in Table 2. PA spectroscopy put in evidence different spectral patterns characteristic for each substance in the spectral interval covered by the CO_2 laser. Nevertheless, in order to simplify the daunting task of substance identification, a multivariate statistical analysis tool based on PCA was developed in MatLab. In spite of the fact that inorganic compounds identification by infrared spectroscopy is considered somewhat less successful in the middle infrared (MIR) region, the recognition ability of MIR-LPAS technique coupled with a PCA data treatment was demonstrated by the reported results. Applying PCA to the LPAS spectra, it was found that 78.3 % of the spectral variation was accounted for by the first three principal components. This percentage obtained with only a few number of components indicates a large spectral difference among the samples. Even if no spectral features attributable to specific vibrational modes of a certain functional group are present in the LPAS spectra, analysis of the score and loadings plot for these components showed that the samples can be well identified due to the presence of lattice modes of vibration.

In conclusion, LPAS coupled with PCA could provide an useful detection method to support the fight to the increased realization of modern bombs for criminal use. Moreover, an integration with complementary methods such as Raman spectroscopy may further increase the specificity of detection, especially for the chemicals exhibiting poor infrared absorption profiles.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support of the EU projects ISOTREX, BONAS and EDEN.

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