

Portable Raman Spectroscopy in Forensics: Explosive Residues and Inflammable Liquids

Félix Zapata, Carmen García-Ruiz*, Carlos Martín-Alberca, Gemma Montalvo*

Department of Analytical Chemistry, Physical Chemistry and Chemical Engineering, and University Institute of Research in Police Sciences (IUICP), University of Alcalá, Ctra. Madrid-Barcelona Km.33.6, E-28871 Alcalá de Henares, Madrid, Spain

carmen.gruiz@uah.es; gemma.montalvo@uah.es

Introduction

Forensics and forensic science are highly popular terms nowadays thanks to famous TV series and films. Most people, inspired by these series, normally associate these terms to crime scene investigation (CSI), ocular inspection and evidence recovery. However, forensics involves much more than CSI, including a vast number of sciences, disciplines and studies such as forensic genetics, chemistry, informatics, anthropology, entomology, ballistics, dactylography, questioned documents, acoustics and linguistics. Each forensic discipline deals with perfectly delimited evidence and performs highly particular studies to provide specific information about certain aspects of the crime investigation to such an extent that a certain discipline might be completely decisive in some crimes but totally dispensable in others [1].

One of the disciplines which is present in almost every case, and always with a huge workload, is forensic chemistry. The large number of substances (either illicit, under suspicion, unknown or even usual daily-life products) may provide useful information not only on their own through their identification, but also as linkers between people and the crime scene [2]. Locard's exchange principle which states *'Every contact leaves a trace'* is the basis of any forensic investigation [3]. According to Paul L. Kirk, *'Wherever somebody steps, whatever somebody touches, whatever somebody leaves, even unconsciously, will serve as a silent witness against him. Not only his fingerprints or his footprints, but his hair, the fibers from his clothes, the glass he breaks, the tool mark he leaves, the paint he scratches, the blood or semen he deposits or collects. All of these and more, bear mute witness against him. This is evidence that does not forget. It is not confused by the excitement of the moment. It is not absent because human witnesses are. It is factual evidence. Physical evidence cannot be wrong, it cannot perjure itself, it cannot be wholly absent. Only human failure to find it, study and understand it, can diminish its value'* [4]. Anything might be the trace of a crime perpetration or someone's participation: fingerprints, footprints, tyre marks, hair, skin, bodily fluids, textile fibers, glass fragments, tool marks, paints and dyes, explosives, drugs, gunshot residues, remains of inflammable liquids, inks and documents. Most evidence of this sort is indeed investigated in forensic chemistry laboratories, where every trace is analysed and confirmed using either traditional chemical tests or modern analytical techniques [1, 2].

In fact, the transition from traditional chemical tests to modern analytical techniques is the current state in many forensic laboratories. Particularly, spectroscopic techniques are showing an increase in their potential applications in the forensic field due to the novel instrumentation

which is being developed to be faster, more sensitive, more compact and portable and more flexible to analyse a wider variety of substances. In addition, spectral libraries containing a larger number of spectra for a variety of compounds are being created, facilitating this method of identification of samples under suspicion. Portable Raman spectroscopy is one of these novel spectroscopic techniques. The suitability and potential of Raman spectroscopy in forensics is widely known by forensic specialists who use it in the laboratory to identify a wide variety of compounds including explosives, drugs, paints, textile fibers and inks [5]. However, the use of laboratory-grade Raman outside the laboratory, such as for in-situ analysis at a crime scene, was something thought possible only in forensic-fiction until just a few years ago. Fortunately, modern portable Raman spectrometers are commercially available, and their instrumental features are comparable to Raman lab- spectrometers.

To prove this, some extraordinarily demanding and challenging applications, in which an in-situ standoff identification of samples might be advisable, were tested.

Instrumentation

A i-Raman® Pro Portable Raman system from B&W Tek (Newark, DE, USA) equipped with a 785 nm-wavelength laser was used. One of the most powerful components of this spectrometer is the detector, which is cooled down to -25°C. In addition, two modes of analysis are available, including the direct analysis using the Raman probe and the microscopic analysis using an adapted microscope in which the Raman probe might be easily connected. This enables the detection and Raman analysis of microscopic traces that cannot be directly analysed using the probe. The collection of Raman spectra was performed using the BWSpec® software, which can be controlled from either the inbuilt spectrometer tactile screen or an external laptop. Afterwards, Raman spectra can be exported to more powerful spectroscopy and chemometric software for advanced data analysis.

Results

Identification of pre- and post-blast explosives particles

The rapid identification of compounds suspected to be explosives is crucial and dangerous. After being neutralized, the explosive charge of an explosive or an improvised explosive device (IED) must be analysed in order to confirm the chemical composition and identify the main explosive compound.

In this study, a small amount (around 0.2 mg) of different organic explosives (TNT, TATP, and PETN) and inorganic oxidizing salts (ammonium nitrate, potassium nitrate and sodium chlorate) used for making IEDs were analysed using the probe. The different instrumental parameters (laser power, acquisition time and number of scans) were tested for each explosive and inorganic salt. As an example, Figure 1 shows some of the spectra of TNT at different laser power and acquisition times. To the naked eye, no differences were found between spectra

collected under different instrumental parameters.

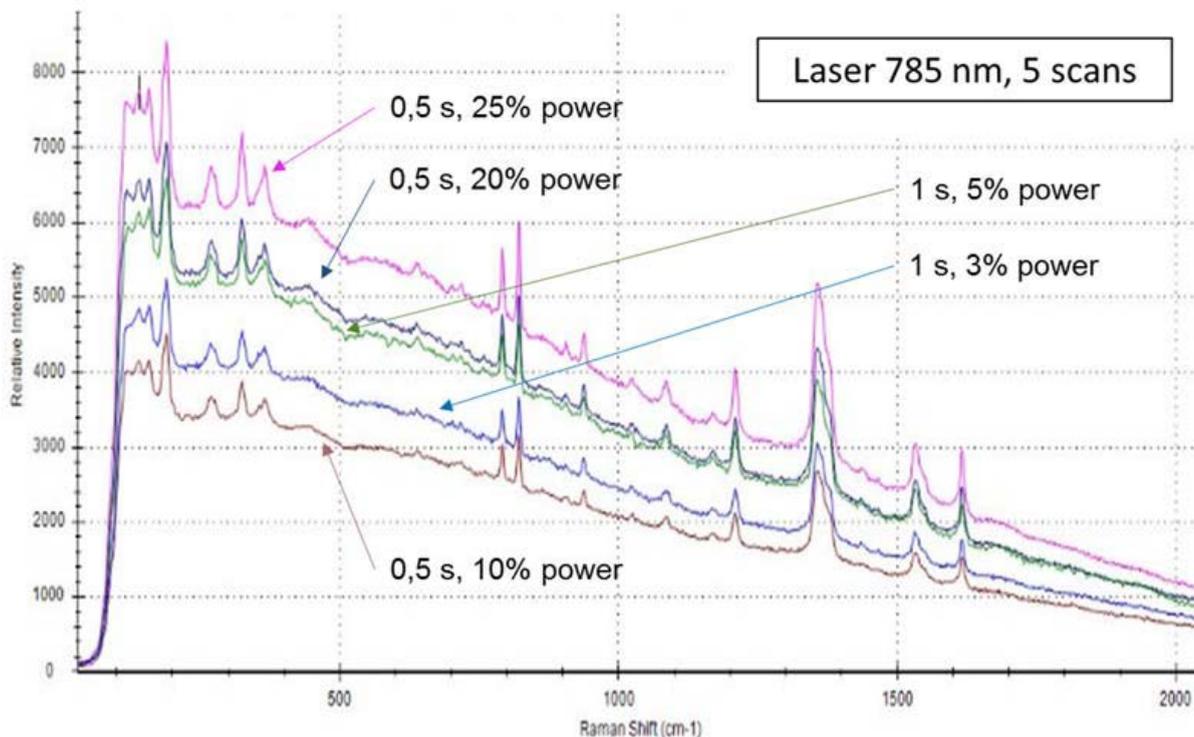
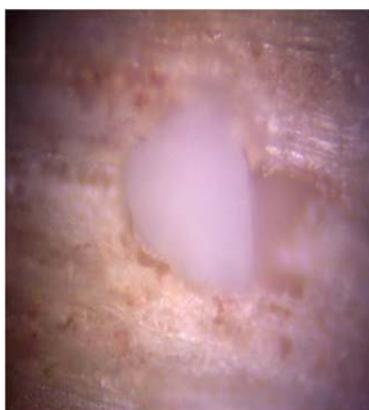
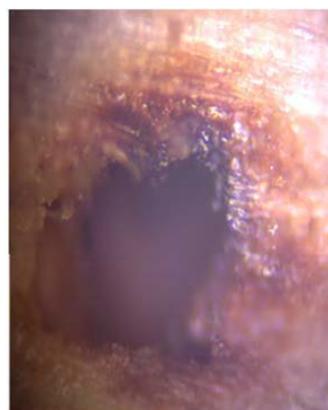


Figure 1. TNT spectra obtained using a 785 nm laser and 5 scans. Different acquisition times and laser power were applied, as shown.

Finally, the parameters selected for spectrum acquisition were 5 scans, 0.5 s and 10% laser power, using a 785 nm laser, since they showed good enough resolution and use a minimum power, which is always recommended when analysing high-energetic materials. As a matter of fact, some of these studied particles were partially burnt or degraded when high power was applied. Figure 2 shows (post-blast) dynamite particles after being analysed. One of them combusted after using 30% laser power.



10% power



30% power

Figure 2. Post-blast dynamite particle after being irradiated with a laser power of 10% (left) and 30% (right).

After optimizing these parameters, the spectrum of each explosive and inorganic salt was collected. Some of them were subjected to baseline correction to make their visual comparison easier. These spectra are displayed in Figure 3.

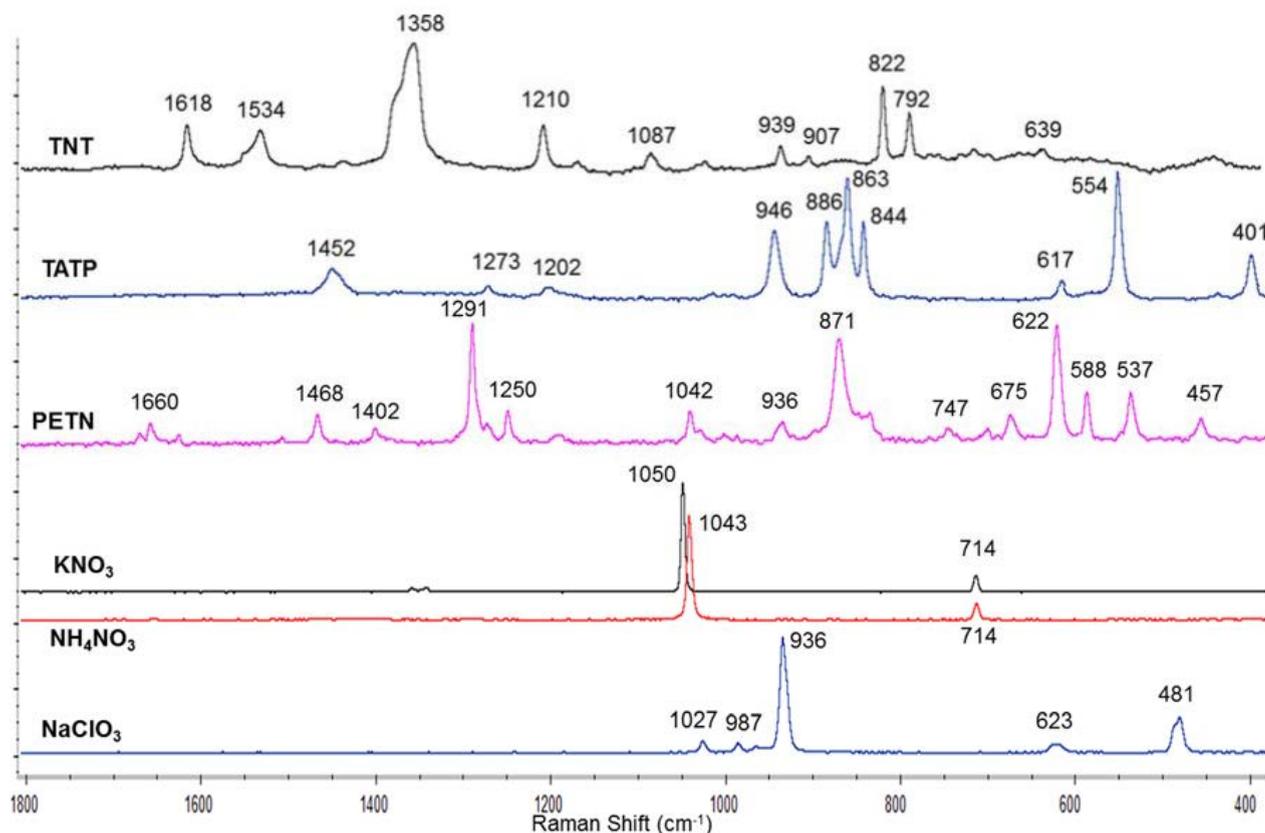


Figure 3. Raman spectra of several explosives and inorganic salts obtained using a 785 nm laser, 5 scans, 0.5 s acquisition time and 10% laser power. Baselines were corrected by software.

These spectra were satisfactorily compared to those collected in literature and spectral libraries for these explosives and salts, enabling this way the confirmation of each substance. Interestingly, ammonium nitrate was discriminated from potassium nitrate. The Raman spectra of these two nitrate salts only differ 7 cm^{-1} in their nitrate stretching vibration [6]. Other handheld and portable Raman spectrometers had been previously tested in our research group, failing in discriminating these two nitrate salts because of their limited spectral resolution. However, that limitation shared by most portable Raman spectrometers has been overcome in the B&W Tek portable Raman by using a cooled spectrograph at -25°C .

In order to prove statistically the discrimination of explosives and main inorganic salts used in IEDs besides their visual comparison, a principal component analysis (PCA) using Raman spectra from each explosive was performed. Results are displayed in Figure 4. TNT (black) and PETN (orange) were completely separated from the rest of the explosives. TATP (brown), potassium nitrate (blue), ammonium nitrate (green) and sodium chlorate (red), though closer, were also separated enough, so as not to be misleading.

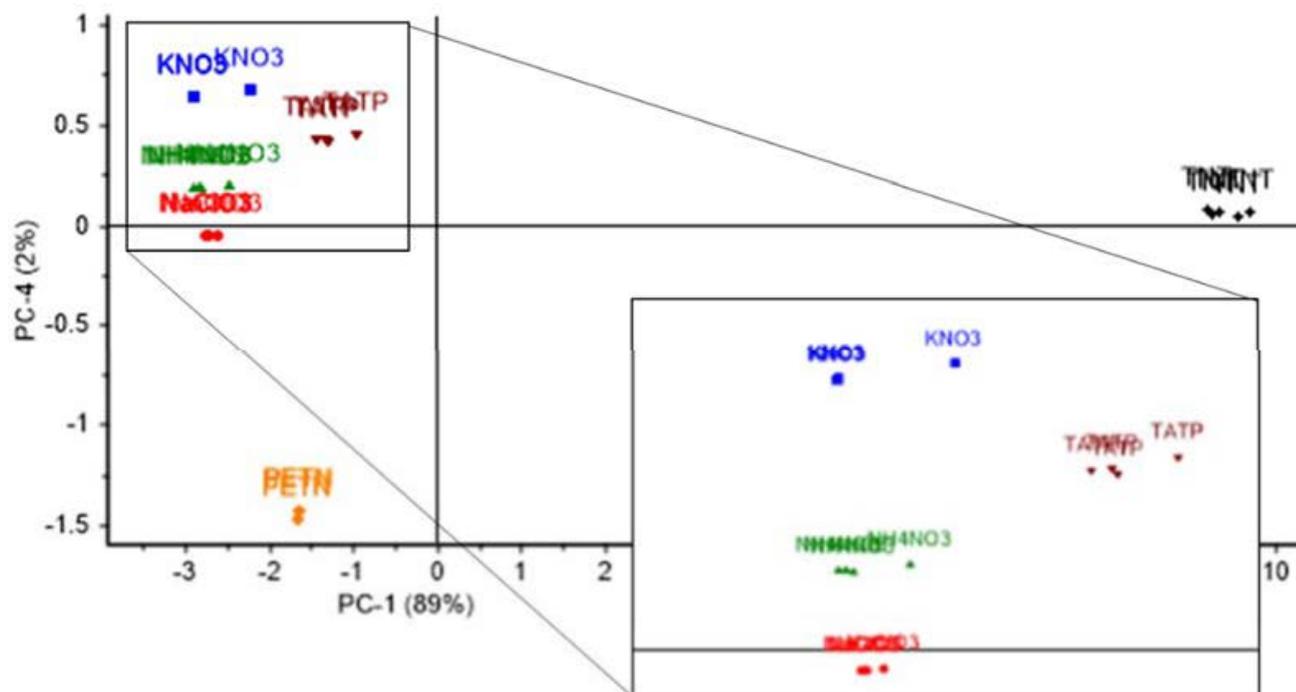


Figure 4. PCA analysis; Scores plot of Principal Component (PC) 1 and 4, showing a variability with a 91% confidence level among all studied intact explosives and inorganic salts: TATP, PETN, KNO₃, NH₄NO₃ and NaClO₃.

In the same way, in cases where the explosive material actually explodes, post-blast residues must be analysed in order to find out the explosive composition used. As evidenced in previous studies [6], a small amount of unburnt particles from the explosive usually remains spread out all around the crater. In this study, post blast residues from real explosions using dynamite, ANFO and chloratite were detected and analysed thanks to the portable microscope coupled to the Raman instrument. This way, even microscopic particles which are undetectable using the probe might be identified using the portable coupled microscope, which is a portable approach of a confocal Raman lab-instrument. As an example, Figure 5 shows the Raman spectrum of three post-blast particles. Particles of dynamite and ANFO displayed the Raman spectrum of ammonium nitrate (the major component in those explosive compositions) whereas the particle of chloratite displayed the Raman spectrum of sodium chlorate (which is the major component in chloratite composition).

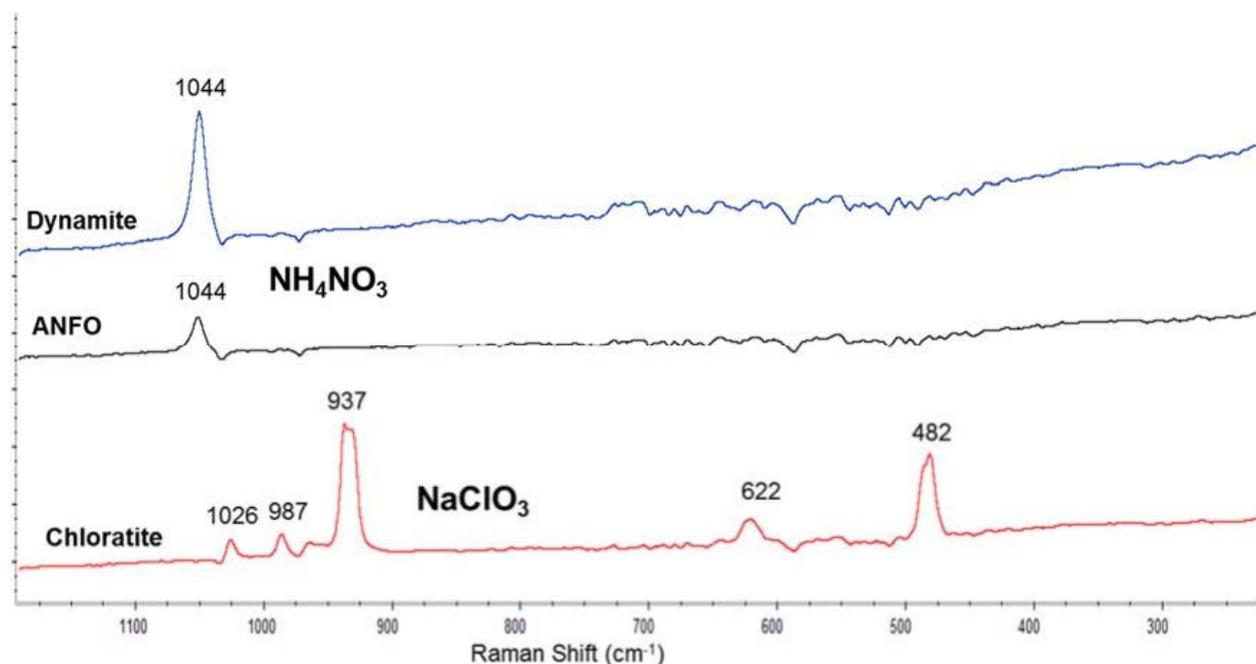


Figure 5. Raman spectra of post-blast particles produced from several explosive compositions. Spectra collected using a 785 nm laser, 5 scans, 0.5 s acquisition time and 10% laser power. Baselines were corrected by software.

Identification of inflammable liquids inside glass bottles

There exists another category of homemade device, the improvised incendiary device (IID). IIDs could be really dangerous, since they are designed to rapidly spread fire, and are adapted to cause physical harm to persons, environment, or property by means of fire [7]. They are constructed with readily available and cheap components, mainly inflammable liquids, a container and an ignition source. In addition, they can contain additional hazardous chemicals such as strong acids. The most popular IID is the Molotov cocktail. Another dangerous IID is its advanced version, the chemical ignition Molotov cocktail (CIMC), which is made in a closed glass bottle.

The rapid and non-invasive identification of compounds suspected to be inflammable liquids contained inside closed bottles could be of interest for first responders at crime scenes (analysis of intact devices, seized or non-activated) or for safety officers of security checks at airports or governmental entities. In addition, forensic experts at official laboratories could take advantage of a potential non-invasive analysis, avoiding the manipulation and exposure of devices such as the CIMC, which may contain hazardous components and by-products (e.g., hydrogen sulphide or sulphuric acid). The standoff identification of liquids inside bottles without opening the bottle is a high challenge. Fortunately, the Raman laser penetration is sufficient to reach the liquid in a non-invasive way and obtain the liquid's Raman spectrum with little contribution from the bottle [7]. In the case of glass bottles, the glass contribution is almost negligible contrary to plastic bottles whose Raman spectra is quite more overlapping. In this study, four different flammable liquids including gasoline 98 octane rating, diesel fuel,

ethanol and acetone inside glass bottles were analysed using the probe of the Raman instrument. In order to analyse the largest amount of liquid (i.e. analysing deeper in the glass bottle) and minimize the contribution from the bottle, the distance regulator at the end of the probe was removed to perform these measurements. The spectra collected for each liquid are displayed in Figure 6. These spectra are in accordance with those in literature and spectral libraries for these inflammable liquids.

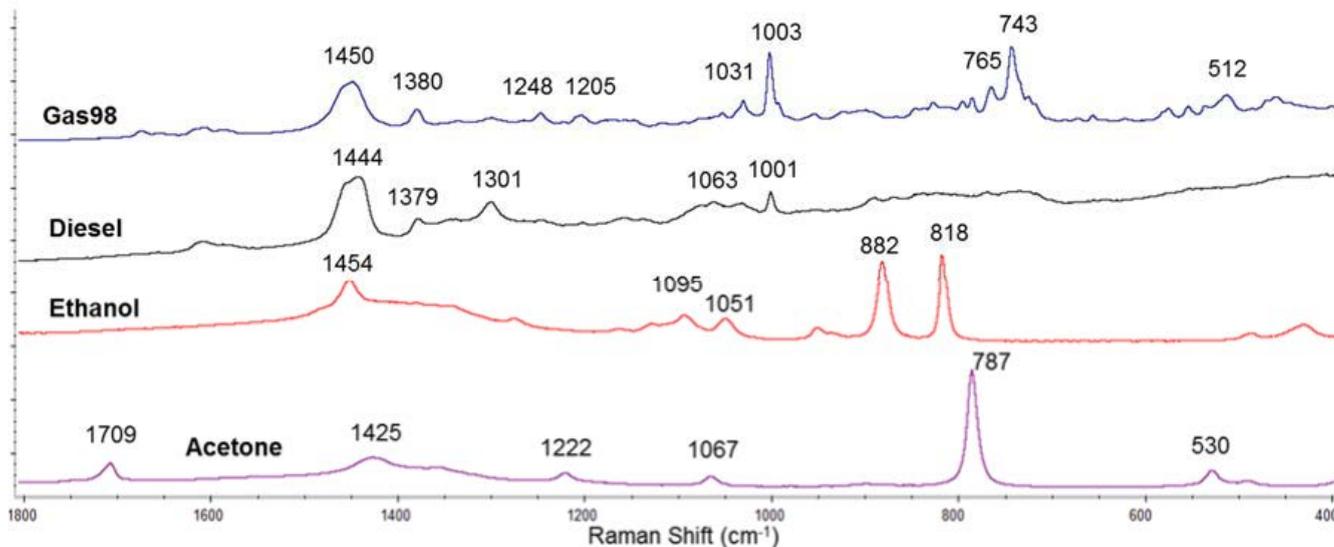


Figure 6. Raman spectra of several inflammable liquids: gasoline 98 octane rating (Gas98), diesel fuel, ethanol and acetone.

A PCA using Raman spectra from each inflammable liquid can be performed to statistically verify their description (Figure 7). As can be seen, those liquids can be clearly discriminated.

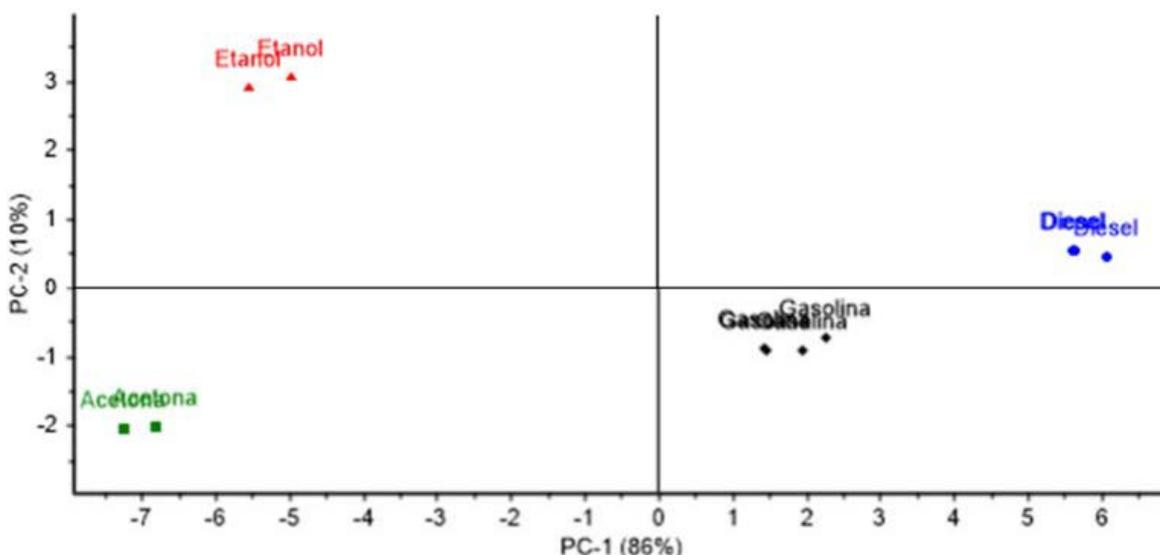


Figure 7. PCA analysis; Scores plot of PC 1 and 2, showing a variability with a 96% confidence level among all studied inflammable liquids: Gasoline 98 octane rating (black diamond marker), diesel fuel (blue circle marker), ethanol (red triangle marker) and acetone (green square marker).

Conclusion

The portable i-Raman Pro has provided satisfactory results in the different challenges tested. The advantages of having a cooled detector, which greatly improves signal-to-noise ratio and spectral resolution, has enabled the discrimination of highly similar explosives such as ammonium and potassium nitrate. The possibility of using a microscope enhances the potential of portable Raman spectrometers in such a way that microscopic traces as post-blast explosive particles can be analysed and identified *in-situ*. Furthermore, the use of the probe through glass bottles can give a rapid and non-invasive *in-situ* identification of compounds of suspected IIDs. This can improve the safety and decision-making of analyst experts, security forces and first responders.

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