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Analysis of pre-ignited improvised incendiary devices using portable Raman

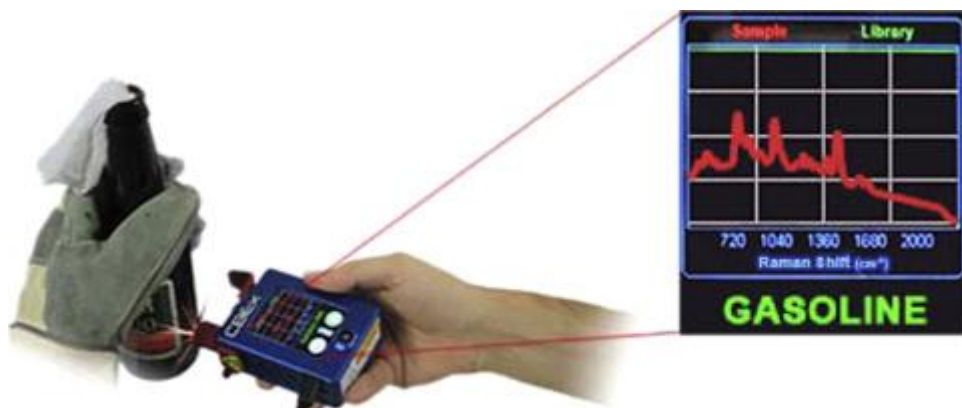
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Abstract: In this work, the use of a portable Raman spectrometer is evaluated for the non-invasive analysis of two types of pre-ignited improvised incendiary devices (IIDs), the classic Molotov cocktails and the chemical ignition Molotov cocktails (CIMCs). The most common ignitable liquids (ILs) used to make classic Molotov cocktails (gasoline, diesel fuel, kerosene and ethanol) were measured in seven different clear and colored glass bottles to evaluate if the container features could hamper the Raman measurements. The results showed that the portable Raman spectrometer can be employed to detect ILs in glass bottles without disturbances. Chemical changes on the ILs are produced when they are mixed with acid; therefore, to evaluate the use of the portable Raman spectrometer for the analysis of CIMCs required an investigation of how time and movement influence the measurements. Thus, two different IL–sulfuric acid mixtures commonly used to make CIMCs (gasoline–sulfuric acid and diesel fuel–sulfuric acid) were measured over time under static and motion conditions. In spite of the intense fluorescence encountered in both CIMCs, it was possible to identify the acid and the gasoline for the first hours of the reaction both in the static and motion experiments. Concerning the diesel fuel present in the CIMC, it underwent instantaneous chemical changes under both measurement conditions, showing high fluorescence that impeded its identification. In view of the results achieved, the portable Raman spectrometer can be a useful instrument for the rapid, non-invasive and safe analysis of pre-ignited IIDs.

Keywords: Molotov cocktail; Containers; Ignitable liquid; Improvised incendiary device; Raman spectroscopy.

Graphical abstract:



1. Introduction

The improvised incendiary devices (IIDs) are a group of homemade devices adapted to cause physical harm to persons, environment, or property by means of fire [1], [2], [3], [4]. These devices are easy to make with readily available and cheap compounds. In most cases, IIDs consist of one or more ignitable liquids (ILs) (i.e., gasoline, diesel fuel, ethanol or kerosene), a container and an ignition source. The most popular IID is the classic Molotov cocktail [5], which consist of a glass bottle filled with IL and a wick that is lighted just before being hurled. An advanced and more dangerous version of this device is the chemical ignition Molotov cocktail (CIMC) [6], [7], [8]. CIMCs are usually closed glass bottles containing gasoline or diesel fuel and concentrated sulfuric acid [5], [7]. Taped to the bottle, a chlorate salt is wrapped in a folded sheet of paper. When the bottle breaks after been thrown at a target, the contact between chlorate salt and sulfuric acid produces a strong exothermic reaction that ignites the IL.

The IIDs samples submitted to the forensic laboratories can be pre-ignited samples (i.e., failed or seized devices) or post-ignited samples (i.e., fire debris or container fragments). Their analysis may provide useful information contributing to the forensic investigation. Nowadays, gas chromatography–mass spectrometry (GC–MS) is the technique commonly used to analyze these samples at the laboratory [9]. Recently, capillary electrophoresis (CE) with a diode array detector was used to detect anions in post-ignited remains of CIMCs [6], [7]. The anions detected provide guidance about the initial composition of the CIMC ignition system. However, there is a lack of specific methods to confirm the presence of ILs and/or strong acids in pre-ignited IIDs, both in the laboratory and on the field, in order to manage the hazards and their associated safety measures. For example, the current methodologies to confirm the presence of sulfuric acid in CIMCs (i.e., litmus paper or a pH-meter) involve the bottle aperture/manipulation exposing the analyst to the acid and hazardous gases (i.e., the reaction between sulfuric acid and some ILs generates hydrogen sulfide) [7], [10]. Therefore, it would be very useful for laboratory technicians and for the first attendees of law enforcement agencies to have fast and non-invasive techniques that can be directly used to identify the above mentioned compounds through transparent containers.

Raman spectroscopy complies with these requirements. Raman spectroscopy was employed to analyze several ILs used in IIDs [11], [12], [13], [14], [15], [16]. Quality indicators as well as the physicochemical properties of gasoline [11], [12], diesel fuel [13] or kerosene [14] were determined using Raman spectroscopy either alone or in

combination with Attenuated Total Reflection Fourier Transform Infrared spectroscopy (ATR-FTIR) or statistical techniques. Other proposed applications of the combined use of Raman spectroscopy with chemometrics are the identification of adulterated gasoline with kerosene [15], methyl tert-butyl ether (MTBE) and benzene [11], or to measure the ethanol proportion in ethanol–gasoline mixtures [16]. However, the use of Raman spectroscopy to analyze pre-ignited IIDs was not evaluated to date.

This article aims to evaluate the use of a portable Raman spectrometer for the non-invasive analysis of pre-ignited classic Molotov cocktails and CIMCs. Field portable Raman spectrometers are rugged, handheld, lightweight tools that allow users without extensive chemistry training to perform rapid raw material verification. In fact, these systems have been used to analyze samples of forensic interest such as gasoline, explosives or abuse drugs [11], [17], [18]. However, various factors may influence the results such as the focalization of the laser beam, the daylight and artificial light sources (i.e., neon light), and the color and thickness of the container [19]. In fact, the color of the glass represents a challenge due to the fluorescence originated from some surface materials [20]. Additionally, it should be considered that chemical modifications are produced over time in the gasoline and diesel fuel due the presence of sulfuric acid [8]. Therefore, in this work, compounds present in IIDs were measured in different glass bottles to assess if the container features hamper the Raman measurements. Additionally, two different types of CIMCs were analyzed over time under static and motion conditions to investigate how time and movement influence the measurements.

2. Materials and methods

2.1. Reagents and containers

Gasoline 98 and 95 Research Octane Number (RON), and diesel fuel were acquired in a local petrol station (Alcalá de Henares, Madrid, Spain). Charcoal starter (trading name: barbecue liquid) made of kerosene 100% (v/v) was obtained in a supermarket (Alcalá de Henares, Madrid, Spain). Ethanol 96% (v/v) was purchased from Panreac (Barcelona, Spain), sulfuric acid of analytical grade 95–98% (m/v) was acquired from Labkem (Mataró, Barcelona, Spain), and potassium chlorate and sodium chlorate were purchased from Sigma-Aldrich (St. Quentin, Fallavier, France).

Seven clear and colored glass bottles were used as containers for Molotov cocktails and CIMCs devices. The type, color and wall thicknesses of the bottles are summarized in Table 1. The wall thickness of the bottle was measured with a hand-held caliper.

Table 1. Types of bottles used.

Bottle type	Glass color	Wall thicknesses (mm)
Tonic water	Clear	20
Mineral water	Clear	30
Sparkling wine	Dark blue	22
Beer	Brown	15
Beer	Dark brown	22
Cough medicine	Amber	28
Beer	Green	15

2.2. Instrumentation

Raman spectra were acquired using a portable CBEX Raman spectrometer (size 9.14x7.11x3.81 cm³ and 0.333 kg weight) from Bonsai Advanced Technologies (Alcobendas, Madrid, Spain) equipped with a 785 nm laser. The laser power was 100 mW (70 mW at sample) and the measurement range was 400–2300 cm⁻¹.

2.3. Sample preparation and data acquisition

The reference spectra of gasoline 98 and 95 RON, diesel fuel, kerosene, ethanol, chlorate salts, and sulfuric acid were collected in quartz cuvettes that were held in close contact against the Raman spectrometer. Then, the ILs and the sulfuric acid were poured in the seven glass bottles and the Raman spectra were measured through the glass, placing the Raman spectrometer as close as possible to the wall bottle. Acquisition times between 0.6 and 3 s and 8 scans were selected. The measurements were taken under illumination (daylight and artificial light) and darkness conditions.

A mixture of 400 mL gasoline 98 RON and 200 mL sulfuric acid and a mixture of 400 mL diesel fuel and 200 mL sulfuric acid were prepared in duplicate in clear glass bottles (mineral water bottles). Clear bottles were selected in order to easily visualize

changes in the physical appearance of the mixture. A total of 5 measurement points at different heights were set (see Fig. 1). The first two points were set on the lower third of the bottle where the sulfuric acid was present. The first point of measurement was taken near the bottom of the bottle and the second one some centimeters above. The other three points of measurement were set on the two-thirds of the upper part of the bottle, where there was IL. The third point of measurement was set near the sulfuric acid, and the fourth and the fifth points of measurement some centimeters above, being the fifth point of measurement the nearest to the bottleneck. For the static experiments, two of the bottles remained motionless until the end of the experiment. They were measured for approximately 10.5 days (each 5 min for the first 8 h and each 8 h for the next 245 h). The second pair of bottles remained under constant motion using an orbital shaker GFL 3005 from GFL Gesellschaft für Labortechnik mbH (Burgwedel, Germany) at 200 rpm. All the bottles remained closed during the measurement period and exposed to daylight and artificial light. The measurements were performed each 5 min for the first 12 h, and after 24 and 48 h at the 5 previously mentioned measurement points. The times for the static and dynamic measurements were different because under the dynamic conditions chemical changes occurred faster. After every measurement, pictures of the bottles were taken.

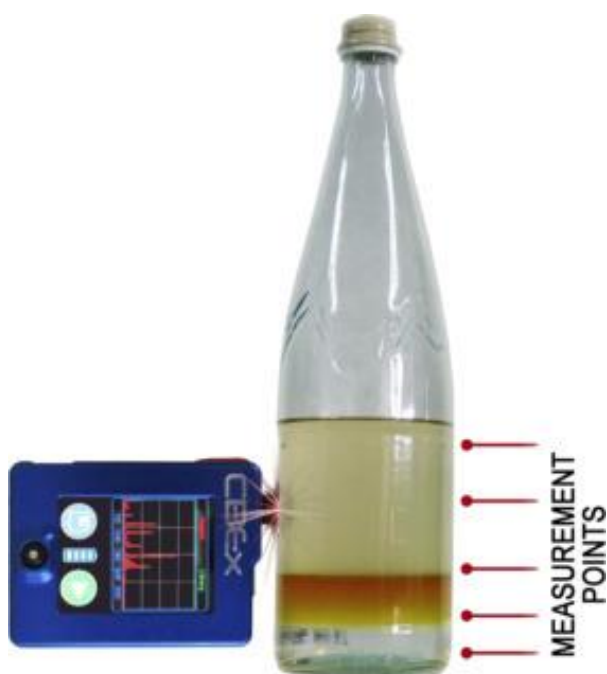


Fig. 1. Scheme of the five points (red arrows) set for the measurement of the CIMCs devices.

2.4. Safety concerns

Under the experimental conditions applied (785 nm laser, 70 mW), sample burning was not observed in any of the samples. Additionally, Harvey et al. analyzed several ILs (gasoline, toluene, hexane, acetone, isooctane, diethyl ether and diesel) with a Raman spectrometer equipped with a 785 nm laser (300 mW) concluding that the safety risks were low [21]. To minimize the risk of laser accidents, especially those involving eye injuries laser safety goggles are recommended to use. Chemical resistance gloves to avoid the skin contact to the acid should be used.

3. Results and discussion

3.1. Analysis of classic Molotov cocktails

Thirty-five classic Molotov cocktails were prepared in seven different glass bottles using gasoline 98 and 95 RON, diesel fuel, kerosene and ethanol. The tip of the Raman spectrometer was initially placed in close contact to the wall bottle. Then, it was moved back several millimeters to evaluate to which extent the distance between the wall bottle and the tip of the Raman spectrometer affected the quality of the spectra obtained. Only the measurements taken in close contact produced good spectra. The measurements performed under illumination (daylight and artificial light) and darkness conditions indicated that both conditions did not affect the spectra obtained. Fig. 2 compares the spectra obtained for neat gasoline 95 RON in several glass bottles (clear, blue, green and brown) and in a quartz cuvette. The Raman bands present in the 1800–600 cm^{-1} region of the gasoline spectrum are predominantly a mixture of C–C skeletal vibrations and C–H deformations [12]. The bands at about 1609, 1380, 1207, 1031, 1004, 788 and 518 cm^{-1} are attributed to the presence of aromatics such as toluene and xylenes [15]. The broad band at about 1450 cm^{-1} can be attributed to a combination of CH₂ scissoring and CH₃ bending [12], [15]. The broad band at about 741 cm^{-1} is a combination of several bands including, very possibly, the band at 724 cm^{-1} assigned to C–C symmetric stretching of the tert-butyl group of the MTBE, which is an oxygenate additive present in gasoline [15]. Although the glass contribute to the spectra with some fluorescence, especially in the case of the green bottle, this effect did not hinder the visualization of the above mentioned bands, allowing the identification of the gasoline. Also the thickness of

the bottles (15–30 mm) did not represent a major stumbling. Fig. 3 shows the spectra of different ILs in some bottles, proving once again that the identification of the ILs can be performed even when they are in colored glass bottles. Ethanol shows bands at 1450 cm^{-1} (CH₃ and CH₂ bending vibrations), 1094 cm^{-1} (CH₃ rock vibrations), 1052 cm^{-1} (C–O stretching vibrations), 883 cm^{-1} (C–C stretching vibrations) and 535 cm^{-1} (bending vibrations of C–O–C) [22]. Gasoline 98 RON, as was expected, shows bands in the same positions as gasoline 95 RON (cf. Fig. 2). The most intense bands of diesel fuel are present at about 1610 , 1450 , 1300 and 1004 cm^{-1} . The band at 1610 cm^{-1} corresponds to the ring stretching of benzene derivatives, the band at 1450 cm^{-1} with C–H deformations of CH₂ and CH₃ groups, the band at 1300 cm^{-1} is related with twist and rock vibration of alkanes and the band at 1004 cm^{-1} arose from the symmetrical (trigonal) ring breathing mode of monocyclic aromatic components in the fuel [13]. Kerosene shows several bands in the $1500\text{--}450\text{ cm}^{-1}$ region, being the band at about 1450 cm^{-1} the most intense, which is attributed to the CH₂ and/or CH₃ deformation in n-alkanes [14].

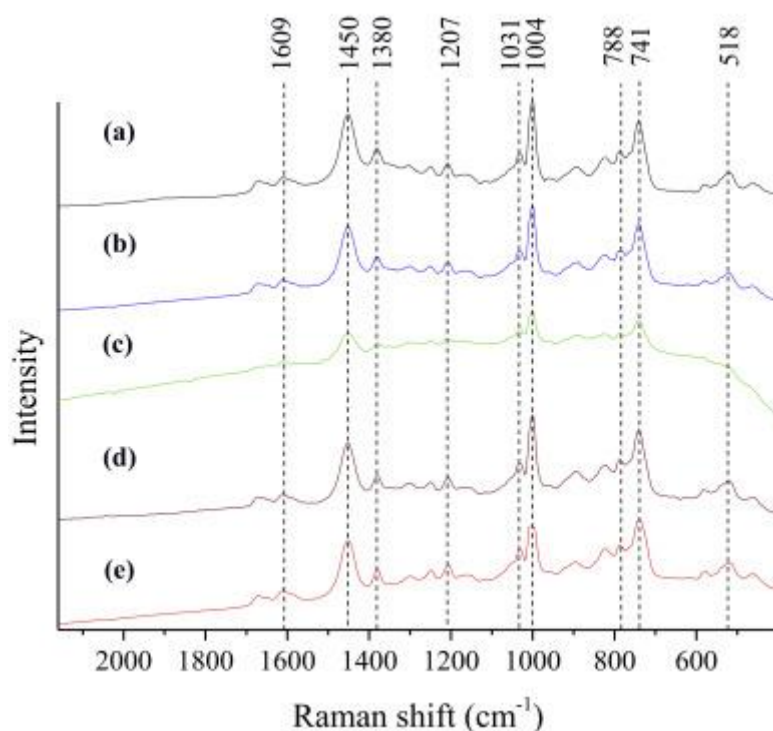


Fig. 2. Raman spectra of gasoline 95 RON in four different glass bottles and in a quartz cuvette. (a) Gasoline 95 RON in clear bottle, (b) gasoline 95 RON in blue bottle, (c) gasoline 95 RON in green bottle, (d) gasoline 95 RON in brown bottle and (e) gasoline 95 RON in a quartz cuvette. Raman conditions: laser at 785 nm, 100 mW, 0.6 s \times 8 acquisitions (clear and blue bottles) and 3 s \times 8 acquisitions (quartz cuvette, and green and brown bottles). Several bands are labeled for clarity.

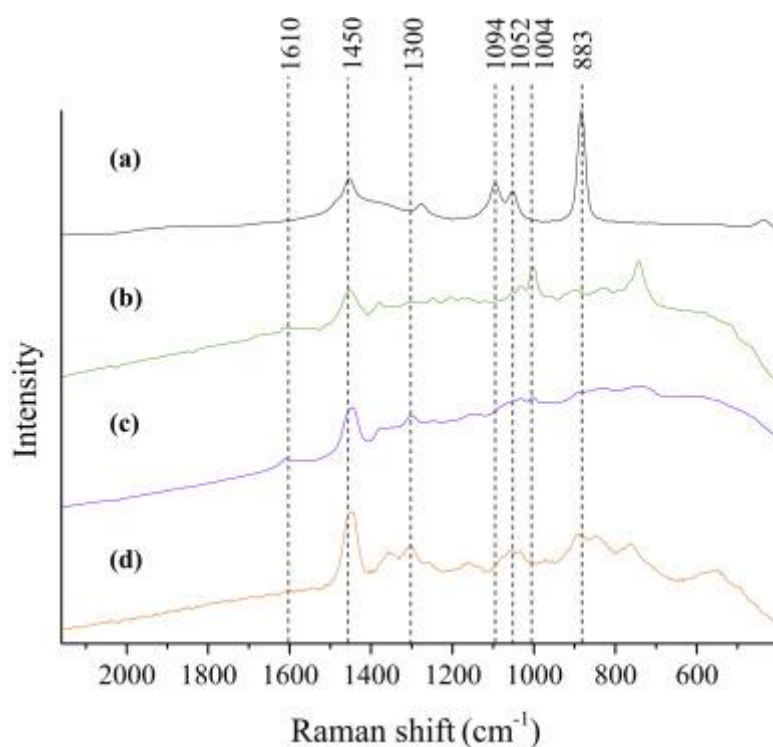


Fig. 3. Raman spectra of (a) ethanol in clear bottle, (b) gasoline 98 RON in green bottle, (c) diesel in blue bottle and (d) kerosene in brown bottle. Raman conditions: laser at 785 nm, 100 mW, 2 s×8 acquisitions (blue bottle), 1 s×8 acquisitions (clear bottle), and 3 s×8 acquisitions (green and brown bottle). Several bands are labeled for clarity.

3.2. Analysis of CIMCs

The mixtures most commonly used to make CIMCs (IL–sulfuric acid) were prepared in clear glass bottles. Clear glass bottles were selected to visualize appearance changes of the mixtures. Two bottles contained gasoline with sulfuric acid while the other two contained diesel fuel with sulfuric acid. Both types of mixtures were measured over time under static and motion conditions in order to evaluate the effect of the time and the bottle movement on the measurements. Pictures were also taken over time to compare the CIMCs appearance with the analytical results.

Fig. 4 depicts some images of the bottles with gasoline–sulfuric acid and diesel fuel–sulfuric acid mixtures under static conditions. The bottle with the gasoline–sulfuric acid mixture showed visual changes in the mixture even at an early stage. As expected, the organic and the inorganic phases formed a two-phase solution. Approximately 15 min after the start of the reaction, a black layer was observed at the top of the inorganic phase. The black layer grew over time and showed great fluorescence hindering the Raman identification of the sulfuric acid. Thus, only the spectra collected at the bottom

of the bottle (first point of measurement) offered good spectra. Fig. 5a depicts several spectra corresponding to the spectrum of the sulfuric acid (spectra taken over time on the first point of measurement). Sulfuric acid shows bands at 1363, 1156 and 561 cm^{-1} which are respectively attributed to asymmetric and symmetric stretching, and bend bending mode of the SO_2 group. The band at 912 cm^{-1} is attributed to symmetric stretching of the $\text{S}[\text{OH}(\text{D})]$ group and the band at 1044 cm^{-1} is attributed to the ion [23]. After 250 h (~10.5 days), only the spectra collected closer to the bottom of the bottle showed weak bands at 1044 and 912 cm^{-1} due to increasing presence of the black layer. The presence of these bands could be a red flag in CIMCs screening, indicating the presence of sulfuric acid. Fig. 4 also depicts how the organic phase (top phase) of the gasoline–sulfuric acid mixture becomes turbid and darker over time. Additionally, blackish-brown droplets gathered on the internal walls of the glass bottle were present at top phase from the start, probably derived from insoluble by-products. These droplets can be clearly observed in the picture taken after 5 h 30 min. When the laser beam was focused on these droplets, fluorescence was observed. Fig. 5b summarizes the gasoline spectral changes observed. The spectra collected in the upper part of the organic phase clearly show the gasoline spectrum during the first 10 min. However, due to the increasing fluorescence, after 40 min only the bands at 1450, 1004 and 741 cm^{-1} were clearly observed. After approximately 2 h, these bands were not visualized anymore due to fluorescence.

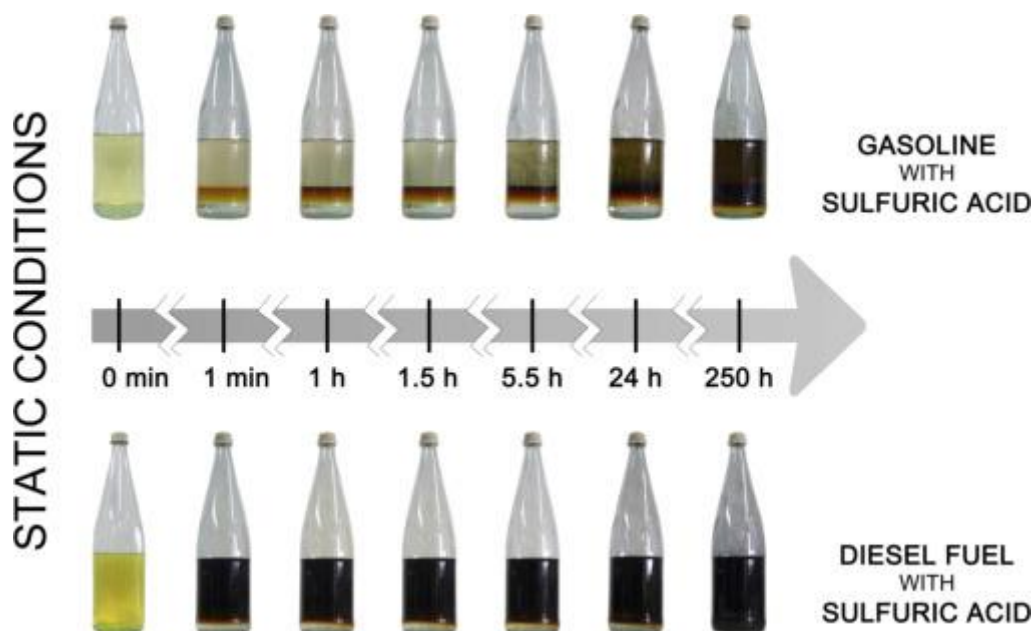


Fig. 4. Pictures over time of ILs–sulfuric acid mixtures under static conditions (gasoline–acid mixture at top and diesel fuel–acid mixture at bottom). The bottles at $t=0$ min only contains gasoline (top) and diesel (bottom).

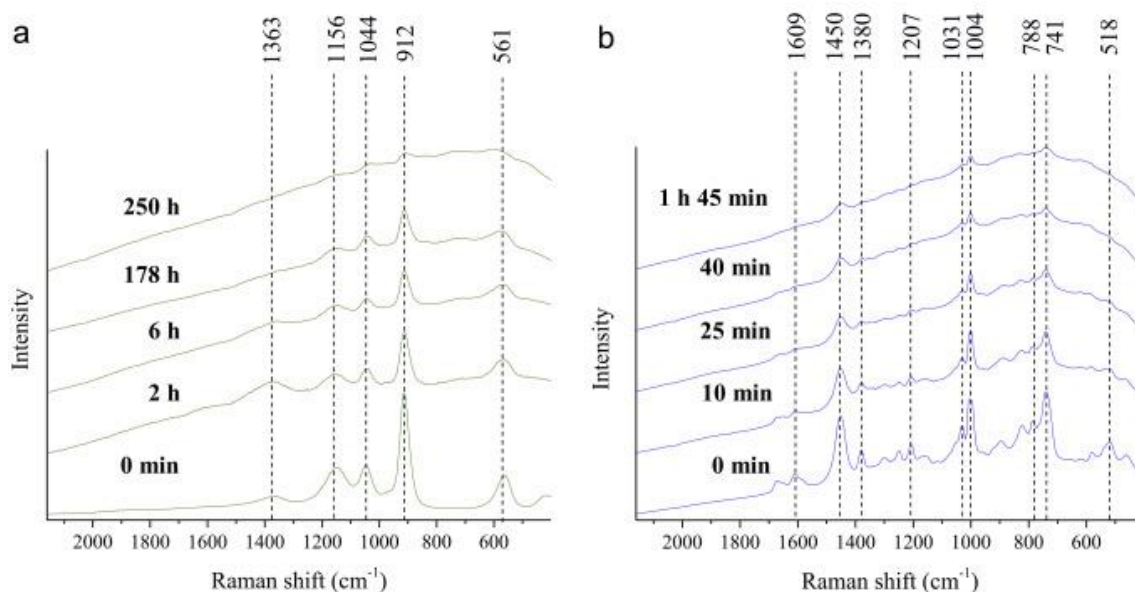


Fig. 5. Raman spectra over time of a gasoline–sulfuric acid mixture measured under static conditions: (a) sulfuric acid and (b) gasoline. Raman conditions: laser at 785 nm, 100 mW, 1 s×8 acquisitions. Several bands are labeled for clarity.

Concerning the bottle with the diesel fuel–sulfuric acid mixture under static measurement conditions, the organic phase became black at the same moment at the diesel fuel was poured to the bottle (Fig. 4). This black layer showed high fluorescence impeding the identification of the diesel fuel from the beginning. On the other hand, as in the case of the gasoline–sulfuric acid mixture, a black layer that grew over time was observed at the top of the inorganic phase. Only the sulfuric acid present at the bottom of the bottle remained transparent. Measurements taken from this clear layer showed the spectrum of the sulfuric acid, even after 29 h. The spectra collected afterwards did not allow the identification of sulfuric acid due to the presence of the above mentioned black layer.

Fig. 6 depicts some images of the bottles with gasoline–sulfuric acid and diesel fuel–sulfuric acid mixtures under motion conditions. As in the above mentioned case (gasoline–sulfuric acid mixture), visual changes can also be observed in the mixture from the start. However, it is possible to observe several differences between both experiments. First, the constant motion of the bottle results in a turbid inorganic phase and a shorter detection time for the sulfuric acid. In fact, the characteristic sulfuric acid bands (1156, 1044, 912 and 561 cm^{-1}) were detected for the first 5 h after the start of the reaction (see Fig. 7a). Secondly, the organic phase became turbid from the beginning and the blackish-brown droplets above mentioned were not observed. The spectra

collected at the organic phase showed the most intense bands of the gasoline spectrum (1450, 1004 and 741 cm^{-1}) and other smaller bands (Fig. 7b) even after 10 h. Then, spectra overwhelmed by fluorescence were obtained. The continuous motion of the mixture could lead to the incorporation of the droplets into the aqueous phase resulting in a longer detection time for the gasoline.

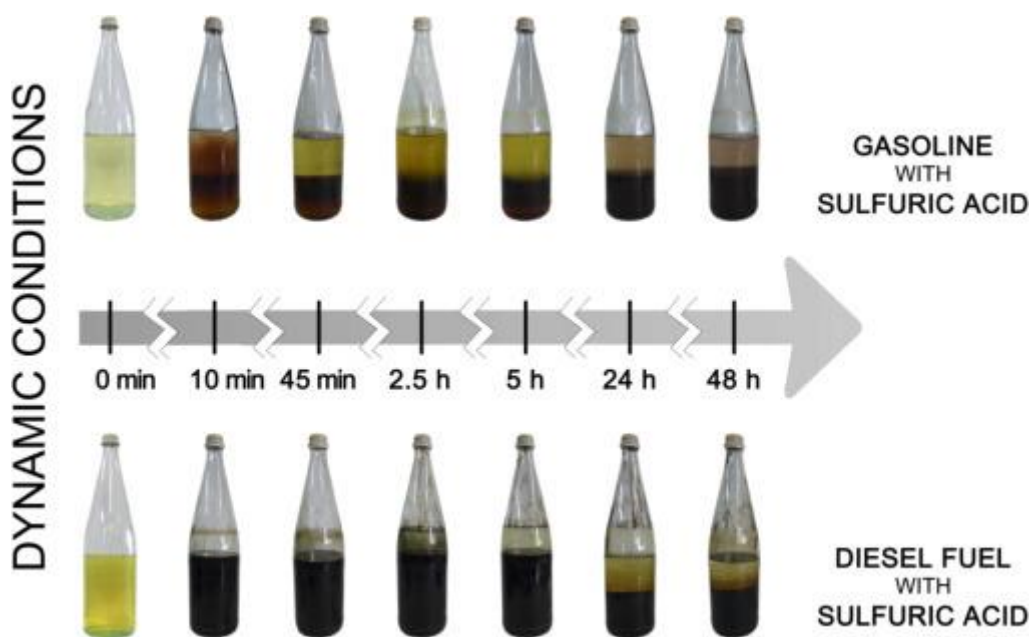


Fig. 6. Pictures over time of ILs–sulfuric acid mixtures under motion (gasoline–acid mixture at top and diesel fuel–acid mixture at bottom). The bottles at $t=0$ min only contains gasoline (top) and diesel (bottom).

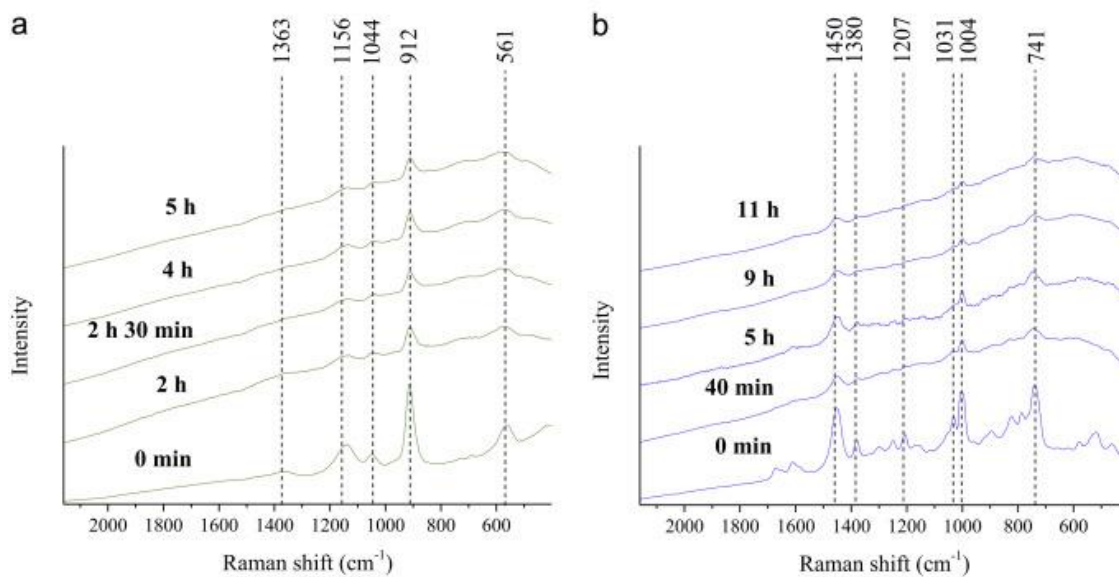


Fig. 7. Raman spectra over time of a gasoline–sulfuric acid mixture under motion conditions: (a) sulfuric acid and (b) gasoline. Raman conditions: laser at 785 nm, 100 mW, 1 s×8 acquisitions. Several bands are labeled for clarity.

In the case of the bottle with the diesel fuel–sulfuric acid mixture under motion, as was expected, the organic phase also became black at the same moment both liquids contacted (see Fig. 6). The main difference between the diesel fuel–sulfuric acid mixture under motion with regard to the same mixture under static conditions was the fact that in the motion experiment both inorganic and organic phases became totally black. Thus, spectra overwhelmed by fluorescence were obtained in both phases. After approximately 19 h, the organic phase became transparent. However, the compounds present could not be identified due to high fluorescence.

Finally, it is important to considerer that, apart from the IL and the sulfuric acid, the presence of chlorate salts is necessary to ignite the CIMCs. Therefore, in real cases it will be necessary to identify these compounds. As an example, Fig. 8 shows the Raman spectra of the two chlorate salts most used for the preparation of CIMCs, potassium chlorate and sodium chlorate. Potassium chlorate shows bands at 978, 936, 615 and 490 cm^{-1} while sodium chlorate was clearly determined by the bands 1028, 987, 938, 624 and 487 cm^{-1} .

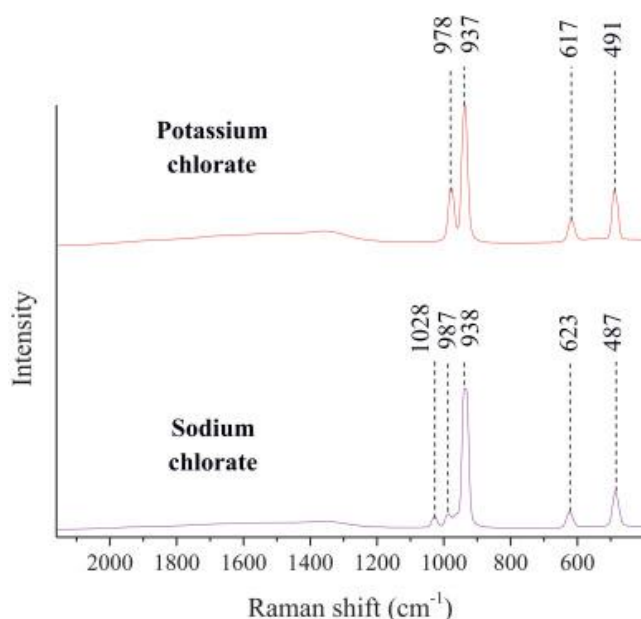


Fig. 8. Potassium and sodium chlorate Raman spectra. Raman conditions: laser at 785 nm, 100 mW, 3 s×8 acquisitions. Several bands are labeled for clarity.

4. Conclusions

The use of a portable Raman spectrometer (785 nm laser wavelength) for a fast and non-invasive analysis of pre-ignited IIDs was evaluated. The measurements taken on ILs in different glass bottles showed that the bottle color or the wall thickness (~15–30 mm) did not impede the identification of the content. Therefore, the portable Raman spectrometer used can be employed to detect ILs commonly used to make classical Molotov cocktails (gasoline, diesel fuel, ethanol and kerosene).

The mixtures of IL–sulfuric acid under static and motion conditions showed several chemical modifications over time. These modifications led to the production of compounds that showed intense fluorescence impeding the identification of the content at certain time. Despite this shortcoming, in the gasoline–sulfuric acid mixtures, it is possible to identify the acid and the gasoline whether the analysis are carried out for the first hours of the reaction and the devices are not exposed to intensive motion. Regarding to the diesel–sulfuric acid mixtures, the sulfuric acid only remained clear under static conditions allowing its identification for the first hours. However, when the diesel fuel was poured in the bottle it became immediately black not allowing its identification even at the beginning.

These findings indicate that portable Raman spectrometers are useful instruments to carry out safe and fast analysis of suspected pre-ignited IIDs both in the laboratory and in the field. The information obtained with these tools could also assist in the decision-making process that first attendees of law enforcement agencies deploy on operational level (intelligence serving security and policing issues). However, in CIMCs the fluorescence is a limiting factor that should be taken into account. Finally, further investigation would be necessary to perform by analyzing other ILs–sulfuric acid mixtures and proportions and its use should be evaluated for the analysis of post-ignited samples.

Acknowledgments

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References

- [1] S.A. Raynis. *Improvised Incendiary Devices: Risk Assessment, Threats, Vulnerabilities and Consequences*. Naval Postgraduate School, USA (2006).
- [2] US-legal definitions: <http://definitions.uslegal.com/i/incendiary-device/> , website visited in June 2015.
- [3] United States Department of State Publication, Bureau of Counter terrorism Office of the Coordinator for Counterterrorism, *Country Reports on Terrorism 2013, Country Reports: Europe Overview*, Published in April 2014, <http://www.state.gov/j/ct/rls/crt/2012/209981.htm> (visited June 2015, Chapter 2).
- [4] A. Sturaro, A. Vianello, P. Denti, R. Rella. Fire debris analysis and scene reconstruction. *Sci. Justice*, 53 (2013), pp. 201-205.
- [5] D. Harber. *The Anarchist Arsenal, Improvised Incendiary and Explosives Techniques* Paladin Press, Boulder, Colorado, USA (1990), pp. 1-10.
- [6] C. Martín-Alberca, J. Sáiz, J.L. Ferrando, C. García-Ruiz. Qualitative determination of inorganic anions in incendiary device residues by capillary electrophoresis. *Anal. Methods*, 4 (2012), pp. 2680-2686.
- [7] C. Martín-Alberca, J.L. Ferrando, C. García-Ruiz. Anionic markers for the forensic identification of chemical ignition Molotov cocktail composition. *Sci. Justice*, 53 (2013), pp. 49-54.
- [8] C. Martín-Alberca, C. García-Ruiz, O. Delemónt. Study of chemical modifications in acidified ignitable liquids analysed by GC–MS. *Sci. Justice* (2015), 10.1016/j.scijus.2015.06.006 (in press).
- [9] E. Stauffer, J.A. Dolan, R. Newman. *Fire Debris Analysis, Chapter 8: Gas Chromatography and Gas Chromatography–Mass Spectrometry*. Elsevier, Academic Press, Amsterdam (2008), pp. 235-291.
- [10] T. Kaneko, H. Yoshida, S. Suzuki. The determination by gas chromatography with atomic emission detection of total sulfur in fuels used as forensic evidence. *Forensic Sci. Int.*, 177 (2008), pp. 112-119.

- [11] X.F. Zhang, X.H. Qi, M.Q. Zou, J.W. Wu. Rapid detection of gasoline by a portable Raman spectrometer and chemometrics. *J. Raman Spectrosc.*, 43 (2012), pp. 1487-1491.
- [12] P.E. Flecher, W.T. Welch, S. Albin, J.B. Cooper. Determination of octane numbers and Reid vapor pressure in commercial gasoline using dispersive fiber-optic Raman spectroscopy. *Spectrochim. Acta Mol. Biomol. Spectrosc.*, 53 (1997), pp. 199-206.
- [13] S. Marinovic, M. Kristovic, B. Spehar, V. Rukavina, A. Jukic. Prediction of diesel fuel properties by vibrational spectroscopy using multivariate analysis. *Anal. Chem.*, 67 (2012), pp. 939-949.
- [14] J.M. Andrade, S. Garrigues, M. de la Guardia, M. Gómez-Carracedo, D. Prada. Non-destructive and clean prediction of aviation fuel characteristics through Fourier transform-Raman spectroscopy and multivariate calibration. *Anal. Chim. Acta*, 482 (2003), pp. 115-128.
- [15] K.M. Tan, I. Barman, N.C. Dingari, G.P. Singh, T.F. Chia, W.L. Tok. Toward the development of Raman spectroscopy as a nonperturbative online monitoring tool for gasoline adulteration. *Anal. Chem.*, 85 (2013), pp. 1846-1851.
- [16] Q. Ye, Q. Xu, Y. Yu, R. Qu, Z. Fang. Rapid and quantitative detection of ethanol proportion in ethanol-gasoline mixtures by Raman spectroscopy. *Opt. Commun.*, 282 (2009), pp. 3785-3788.
- [17] E.L. Izake. Forensic and homeland security applications of modern portable Raman spectroscopy. *Forensic Sci. Int.*, 202 (2010), pp. 1-8.
- [18] P. Vitek, E.M.A. Ali, H.G.M. Edwards, J. Jehlicka, R. Cox, K. Page. Evaluation of portable Raman spectrometer with 1064 nm excitation for geological and forensic applications. *Spectrochim. Acta Mol. Biomol. Spectrosc.*, 86 (2012), pp. 320-327.
- [19] C. Weyermann, Y. Mimoune, F. Anglada, G. Massonnet, P. Esseiva, P. Buzzini. Applications of a transportable Raman spectrometer for the in situ detection of controlled substances at border controls. *Forensic Sci. Int.*, 209 (2011), pp. 21-28.
- [20] C. Eliasson, N.A. Macleod, P. Matousek. Noninvasive detection of concealed liquid explosives using Raman spectroscopy. *Anal. Chem.*, 79 (2007), pp. 8185-8189.
- [21] S.D. Harvey, T.J. Peters, B.W. Wright. Safety considerations for sample analysis using a near-infrared (785 nm) Raman laser source. *Appl. Spectrosc.*, 57 (5) (2003), pp. 580-587.

[22] S. Burikov, T. Dolenko, S. Patsaeva, Y. Starokurov, V. Yuzhakov. Raman and IR spectroscopy research on hydrogen bonding in water–ethanol systems. *Mol. Phys.*, 108 (18) (2010), pp. 2427-2436.

[23] R.J. Gillespie, E.A. Robins. The Raman spectra of sulphuric, deuteriosulphuric, fluorosulphuric, chlorosulphuric, and methanesulphonic acids and their anions. *Can. J. Chem.*, 40 (1963), pp. 644-657.