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Technical Note

Analysis of different materials subjected to open-air explosions in search of explosive traces by Raman microscopy

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ABSTRACT

Post-explosion scenes offer such chaos and destruction that evidence recovery and detection of post-blast residues from the explosive in the surrounding materials is highly challenging and difficult. The suitability of materials to retain explosives residues and their subsequent analysis has been scarcely investigated. Particularly, the use of explosive mixtures containing inorganic oxidizing salts to make improvised explosive devices (IEDs) is a current security concern due to their wide availability and lax control. In this work, a wide variety of materials such as glass, steel, plywood, plastic bag, brick, cardboard or cotton subjected to open-air explosions were examined using confocal Raman microscopy, aiming to detect the inorganic oxidizing salts contained in explosives as black powder, chloratite, dynamite, ammonium nitrate fuel oil and ammonal. Post-blast residues were detected through microscopic examination of materials surfaces. In general, the more homogeneous and smoother the surface was, the less difficulties and better results in terms of identification were obtained. However, those highly irregular surfaces were the most unsuitable collectors for the posterior identification of explosive traces by Raman microscopy. The findings, difficulties and some recommendations related to the identification of post-blast particles in the different materials studied are thoroughly discussed.

1. Introduction

Amongst the large variety of explosive compositions, explosive mixtures based on oxidizing energetic salts are certainly the explosives most frequently used by civilians (non-militaries) to carry out, not only legitimate commercial purposes such as demolitions and pyrotechnics, but also to commit criminal actions [1–5]. As a result of the wide availability, easy acquisition and lax control of these explosives precursors, oxidizing energetic salts are usually employed by dissidents, extremists and terrorists in the elaboration of improvised explosive devices (IEDs). The mixture of oxidizing energetic salts with fuels produces explosive compositions that can be used as explosive charge in IEDs such as black powder, dynamite or ammonium nitrate fuel oil (ANFO) [1,3]. Oxidizing salts commonly used in these explosive mixtures are nitrate and chlorate salts [1,3], which may be combined (in different proportions) with a large variety of fuels such as charcoal, fuel oil or sugar. However, it is important to highlight that whatever the composition is, the oxidizing salt is usually the main and major component in the mixture to ensure the consumption of the fuel and cause the consequent explosion. As a result, post-blast residues from these explosives mostly consist of non-reacted remains of the oxidizing salt [6–12]. Due to their ionic nature, forensic laboratories routinely analyse them by either capillary electrophoresis or ion chromatography, and a wide research involving these two techniques for the analysis of inorganic oxidizing salts from explosives have been published [11–20]. Nevertheless, both techniques are destructive, time-consuming, require a sample treatment and dissociate the salt into its ions. On the contrary, spectroscopic techniques such as Raman spectroscopy has shown an interesting potential for the identification of salts in explosives [10,12,21–24]. However, the material in which post-blast particles of these oxidizing salts are adsorbed during an explosion, may play an important (and scarcely studied) role in both evidence recovery and spectroscopic measurements [25]. Different materials are expected to offer a different adsorption in relation to the capture of those post-blast particles and, thus, some materials are expected to be more efficient than others. The investigation of this aspect is crucially important for providing forensic investigators know how on the different materials they

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should preferentially collect during evidence recovery. In addition, each material has a characteristic spectral signature according to its composition, which may occasionally overlap the characteristic bands of the studied salts. This fact may hinder the spectroscopic detection and identification of post-blast particles, especially when no focusing system is used to exclusively analyse a selected post-blast particle. In this respect, microscopy coupled to Raman spectroscopy has demonstrated to be a useful methodology for the microscopic detection and spectroscopic identification of post-blast microscopic particles of explosives on smooth and homogeneous surfaces [10,12]. Particularly, in this previous study accomplished by our group [10], IEDs based on oxidizing-fuel explosive compositions as well as IEDs based on high organic explosives were exploded and their post-blast residues were subsequently analysed over a smooth homogeneous surface. Results revealed that only those IEDs based on oxidizing-fuel explosive compositions left, after their explosion, microscopic non-reacted particles large enough to be detected by confocal Raman microscopy. Nonetheless, there is a large variety of different materials that may be found in post-explosion scenes that makes evidence recovery an extremely complicate process [2]. The knowledge about the suitability of either homogeneous or heterogeneous materials to catch and retain post-blast residues that are microscopically perceptible by microscopy is a current forensic need. To this end, in this work, a large variety of materials was subjected to different explosions and the appropriateness of each material for post-blast residues detection using confocal Raman microscopy has been deeply examined.

2. Materials and experiments

2.1. Materials, standards and explosives

Eleven different materials (3 replicates per material except for tyre with only 1 replicate) were placed as explosive trace collectors surrounding each explosion at a distance of 1.5–2 m in order to study the detection of post blast residues on them. These materials included glass, steel, plastic bag, plywood, chipboard, cardboard, tyre, brick, plaster board, cotton fabric and pig meat, besides the ground from crater. These materials were chosen because they are likely to be found in real terrorist attacks either in the street or within a building. Table 1 collects the size of the pieces of each material.

Standards of potassium nitrate and ammonium nitrate (determined at the end of Section 3.1 for proving their identification profile) were obtained from Sigma-Aldrich in ACS reagent grade (>99.0%).

Five explosions were performed by Spanish EOD specialists using improvised explosive devices (IEDs) made of five different inorganic explosives as those reported in a previous work [10], which contained inorganic oxidizing salts including black powder (75% potassium nitrate), chloratite (80% sodium chlorate), dynamite (66% ammonium nitrate), ANFO (90% ammonium nitrate) and ammonal (85% ammonium nitrate).

After each explosion, collectors were recovered and sealed by EOD specialists and were carried out to the laboratory where they were analyzed by confocal Raman microscopy.

Table 1
Size of collectors in cm. R refers to the spoke of the tyre (wheel).

Material	Size (cm)
Glass	18 × 13
Metal (steel)	20 × 6
Plastic bag	30 × 20
Plywood	20 × 15
Chipboard	20 × 15
Cardboard	30 × 20
Tyre	R 30
Brick	25 × 15 × 12
Plasterboard	20 × 20
Cotton fabric	30 × 20
Pig meat	~15 × 10

2.2. Instrumentation and analysis

A Thermo Scientific DXR Raman microscope (Waltham, MA, USA) using the Thermo Scientific Omnic for dispersive Raman 8 software (Waltham, MA, USA) was used to analyze the surfaces of materials. First, each material (collector) was analyzed to establish the representative Raman spectrum of each material and be used as blank. In addition, to set up the characteristic Raman spectrum of each explosive, small samples from the five explosives were analyzed by Raman spectroscopy. Afterwards, the surface of all post-blast samples was observed with both the naked eye and microscopically, as explained in previous work [10]. Briefly, after visualizing potential post blast residues, that region was microscopically examined through 10× and 50× magnification objectives. Afterwards, the alleged post-blast particles were analyzed by Raman spectroscopy in order to confirm or dismiss, based on their Raman spectra, whether they were remains from the explosive. Raman spectra were collected from 2500 to 200 cm^{-1}, accumulating 5 scans of 6 s per scan and using a 780 nm excitation wavelength of 10 mW power. Each Raman spectrum was visually and statistically compared (Pearson correlation) with a spectra database previously registered for the explosives.

3. Results and discussion

3.1. Materials and explosives Raman spectra

The knowledge of these spectra was necessary to later identify residues from the explosives on these materials. As shown in Fig. 1(a), given the Raman conditions, the materials studied mostly provided no relevant Raman signals except brick. In summary, neither steel, plastic bag, chipboard, cardboard nor tyre provided characteristic Raman bands, except for some fluorescence in chipboard. Plywood displayed a weak band (almost worthless) at 1596 cm^{-1}. Plasterboard, besides providing a bit fluorescence, was dominated by a unique prominent band located at 1006 cm^{-1}. Though cotton and pig meat displayed some characteristic bands along their spectra, they were little intense. Glass was dominated by two highly distinctive wide prominent bands at 1958 and 1455 cm^{-1}. Finally, brick displayed, unlike previous materials, a large number of bands, some of them, noticeably intense such as those at 1668 and 1460 cm^{-1}.

On the contrary, explosives were clearly characterized by the Raman spectra of their respective oxidizing salts, as shown in Fig. 1(b). This result was not unexpected since oxidizing salts are the major component in these explosives mixtures. What was an unexpected result was the low Raman signals provided by most materials because of the fact that Raman spectroscopy is being proved as a suitable technique to characterize a wide variety of materials. At the selected Raman conditions only those highly Raman active compounds and Raman active vibrations such as those in nitrates and chlorates were properly determined. This result was highly favorable because it meant that most materials would not overlap the Raman spectra from explosives.

As shown in Fig. 1(b), the different oxidizing salts from explosives (potassium nitrate, sodium chlorate and ammonium nitrate) are easily identified by Raman spectroscopy according to their different Raman spectra. Thus, as reported in our previous