B124 Raman Microscopy of Low Explosives Obtained From Sparkler Material

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The goal of this presentation is to present results of a study on the Raman microspectrophotometry of common ingredients in sparklers and their combustion products. This paper is the sequel to an earlier paper presented in this Meeting, titled "Raman microscopy of low explosives and their combustion products."

This presentation will impact the forensic community and/or humanity by illustrataing that sparklers are a convenient source of low explosives and that burnt and unburnt sparkler materials can be easily identified using Raman microscopy.

Background: Low explosives are often used in homemade bombs and improvised explosive devices (IEDs). Although low explosives normally deflagrate burning very rapidly at a subsonic propagation velocity, they can generate the gas pressure necessary for an explosion if confined within an appropriate container. Inorganic low explosives usually consist of oxidizer-fuel mixtures. They can be made using ordinary laboratory chemicals, ammonium nitrate fertilizer, black powder, and pyrotechnic materials from sparklers, flash powders, and fireworks.

Sparklers are a convenient source of low explosives for small homemade devices. Two main types of sparklers are widely available: wire sparklers and tube sparklers. Wire sparklers are more common and consist of pyrotechnic mixture coated on a length of fairly rigid metal wire. Variants of wire sparklers include dipped sticks where the pyrotechnic mixture is coated on a stick, whistling sparklers that emit a shrill whistle, and crackling sparklers that produce a series of sharp popping or crackling sounds as they burn. Tubed sparklers (or cylindrical fountains) contain the pyrotechnic mixture in loosely-filled cylindrical tubes that resemble pencils in size and shape. A priming mixture is often painted on the tip of sparklers to make ignition easier. Sparklers are stable at room temperature and normally safe to be hand-held for ignition. Lighting the ignition tip results in a flame that propagates down the wire or tube, producing a flame envelope surrounded by shower of colored sparks.

Pyrotechnic materials can be easily scraped off wire sparklers or emptied out of a large number of tubed sparklers. Alternatively, wire sparklers can be bundled together using tape to increase explosive effects. The typical pyrotechnic composition of sparklers is a mixture of oxidiser, fuel, combustible binder (eg, sugar, starch, gum arabic and shellac) and a color agent. Fuels include fine metal powder (glazed iron, aluminium, zinc, magnesium, titanium), meal gunpowder, sulfur and charcoal. Oxidisers are usually nitrates, chlorates or perchlorates. In wire sparklers, the iron or mild steel support wires also serve as a heat conductor, promoting the smooth propagation of the pyrotechnic reaction along the sparkler. Combustion produces a slight pressure, which ejects glowing metal particles, forming sparks that cool quickly.

Nature of Study: In the earlier paper titled "Raman microscopy of low explosives and their combustion products," Raman microscopy was shown to be a rapid, non-destructive and highly specific technique for identifying inorganic low explosives and their combustion products at low detection limits. Raman microscopy identifies both the cationic and anionic moieties of these substances with minimal sample preparation. This second paper illustrates the application of dispersive Raman microscopy to the identification of sparkler materials and their combustion products. Scanning electron microscopy with energy dispersive x-ray analysis (SEM/EDX) is a powerful screening technique to determine elemental composition, particle morphology and the presence of organic constituents, but cannot identify molecular and ionic species and therefore needs to be complemented by a spectroscopic technique such as Raman microscopy. Raman analysis does not give signals for metals, chlorides and some oxides but these elements are readily detected in SEM/EDX analysis. Water extraction allows separation of water-soluble components and oxidisers from the matrix, simplifying subsequent identifications. A twoprong approach combining SEM/EDX and Raman microscopy is recommended for the conclusive identification of inorganic explosive ingredients.

Materials and Methods: Analyses were performed on a Renishaw RM1000 dispersive Raman spectrometer. The spectrometer was calibrated using a silicon standard. Materials studied were several commercially available wire sparklers. Sparkler materials were analysed before and after combustion, in solid form and aqueous extracts.

Sampling method for Raman analysis: Small amounts of the unburnt, burnt or recrystallised solids were placed on ordinary glass slides. Samples mounted on graphite stubs for SEM/EDX analysis were also directly analysed in the Raman microscope. Aqueous solutions were taken up into glass capillary tubes for direct analysis in the Raman microscope.

Analysis of unburnt sparkler tip and body: Materials were carefully scraped and removed from the different layers of pyrotechnic coating for SEM/EDX and Raman analyses. These materials were also extracted with DI water, and the extracts analysed in aqueous solution and as dried recrystallised form.

Analysis of combustion products: A sparkler was burnt and materials were carefully sampled from different parts (tip, middle, bottom, exterior, core) of it for SEM/EDX and Raman analyses. DI water was also used to extract post-combustion debris for any residual water-soluble products.

Results and Discussion: The results for a 12-inch whistling sparkler are presented in this abstract. Additional results for other sparklers will be presented and discussed further during the oral presentation. The whistling sparklers came in a box of 100, priced at about $4-5 USD a box. Each sparkler was 29.5 cm long and had a pyrotechnic coating measuring 13.7 cm in length. The average weight of a sparkler was 6.05 g. The average amount of pyrotechnic coating on each sparkler was 3.55 g. Each sparkler had a greenish ignition tip, a grey exterior and a white core. The white whistling core was present only in the upper part.

Analysis of unburnt whistling sparkler materials: Raman analysis indicated that the unburnt sparkler tip contained mostly barium nitrate (oxidiser) and antimony sulfide (fuel and enhancer of sound effects). The white core of the unburnt sparkler contained mainly potassium perchlorate (oxidiser) and a small amount of organic ingredients. T he exterior contained mainly barium nitrate, carbon and silicon nitride (a refractory material that raises the flame temperature and prevents caking). SEM/EDX indicated the presence of aluminium powder (fuel).

Analysis of solids recrystallised from water extracts of unburnt sparkler: Recrystallised materials from water extracts of a mixture of exterior and core materials contained barium nitrate and potassium perchlorate, indicating that no ion exchange occurred during recrystallisation.

Analysis of combustion products: The whistling sparkler burned with golden sparks for 45 s and emitted a shrill whistling sound for the initial 5 seconds. The ignition tip and the white whistling core were consumed, leaving a hollow shell in the upper part of the wire and a reduced diameter in the rest of the wire. The average weight of solid residues left was 1.8 g and the loss on ignition was 1.74 g (49% loss). The upper part of the burnt body yielded materials with no significant peaks in Raman analysis, but SEM/EDX analysis indicated barium, aluminium, oxygen potassium and chlorine peaks, consistent with barium oxide, aluminium oxide, and potassium chloride. The lower burnt body also contained carbon with trace amounts of silicon nitride. Material from the burnt body gave little solid residue when extracted with water.

Conclusion: Sparklers are a convenient and readily available source of premixed low explosives for making small IEDs. The inorganic ingredients used in sparkler compositions and their corresponding combustion products can be conclusively identified using SEM/EDX and Raman microscopy. Raman microscopy provided rapid, sensitive and unequivocal information on molecular and ionic structures. Metal particles, and some metal oxides and chlorides were not detected by Raman analysis but were easily detected by SEM/EDX analysis. A two-prong approach combining the strengths of Raman microscopy and SEM/EDX offers clear advantages over traditional techniques such as polarised light microscopy and microchemical (spot) tests.

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Raman Microscopy, Sparklers, Low Explosives

