# Crystals Under the Lens: A Microscopical and Micro-Raman Analysis of Inorganic Oxidizers in Pyrotechnic-Based IEDs

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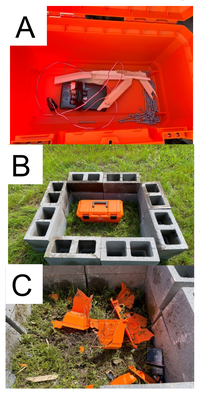
## INTRODUCTION

The threat, manufacture, and use of improvised explosive devices (IEDs) became the focus of U.S. intelligence and law enforcement communities primarily in the late 1990s and early 2000s due to multiple attacks taking place domestically and abroad. In the last decade, chlorate and perchlorate-based mixtures have become increasingly popular in criminal acts and terrorism.

Pyrotechnics and their compositions have been previously studied in a forensic setting due to their identification as contraband in several countries and other uses in IEDs. Using alternative techniques to chromatography is important in forensic casework, as the non-destructive nature of certain techniques is strongly desired, along with the necessity of analysis to be rapid and reliable. Light microscopy and micro-Raman spectroscopy fulfill these needs while requiring little sample preparation. Given their accessibility and growing use in IEDs, the characterization of inorganic oxidizing salts in consumer pyrotechnics before and after an explosion is essential. This study, therefore, aimed to demonstrate the efficiency of an analytical scheme combining polarized light microscopy (PLM) and micro-Raman spectroscopy that trace evidence analysts can utilize to identify and differentiate inorganic oxidizing salts in a post-blast scenario

## MATERIALS & METHODS

**Sample Preparation –** Inorganic salt standards were recrystallized using the method outlined by Hopen and Kilbourn, as well as Organization of Scientific Area Committee (OSAC) guidelines for recrystallization [(1,2)]. The intact pyrotechnic mixture was recrystallized on glass slides using the decantation method described by Chamot and Mason [(3)].




**Construction, Explosion, and Collection of Post-Blast Debris –** Two polyvinyl chloride (PVC) pipe bombs were constructed. They were loaded with a 2.0 oz pyrotechnic mixture prepared by opening commercial fireworks, isolating the powders, and weighing them to maintain consistent composition across the two devices. The IED was constructed by placing the pipe bomb inside an orange polypropylene toolbox containing various witness materials (**Figure 1A**). The IED was then placed into a 4 × 4 × 2-foot square of cinderblocks (**Figure 1B**) to facilitate collection and limit the spread of debris post-blast (**Figure 1C**).

**Figure 1.** Materials used in the construction of IED (pipe bomb not pictured) (**A**), device surrounded by cinder block setup (**B**) and post-blast debris collected within cinder block setup (**C**)

**Figure 2.** Area on PVC pipe swabbed with wet and dry swabs after explosion

**Comparison of swabbing techniques –** Post-blast fragments (**Figure 2**) were swabbed in similar locations with a dry cotton swab and one wetted with DI water. The swabs were then placed into a microcentrifuge tube with 1 mL of deionized water and extracted for 3 minutes. After extraction, 10 µL of each extract were pipetted onto glass slides, recrystallized using OSAC guidelines [(2)], and compared.

**Light Microscopy –** Polarized light microscopy (PLM) examination was conducted using a Leica DM 2700 P microscope. Photomicrographs were taken using an AmScope WF200 camera and AmScope camera software v4.11.

**Micro-Raman Spectroscopy –** Raman data were collected on glass slide using the High Confocality (HC) mode of a Renishaw in-Via™ InSpect confocal Raman microscope using a 532 nm laser, a laser power ranging from 2.5 mW to 5 mW at the source, 100× objective, 3 accumulations, and a 100-2,000 $cm^{-1}$ scan range.

## RESULTS & DISCUSSION

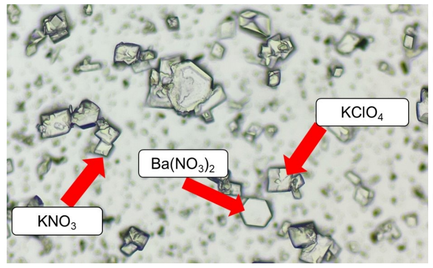



**Figure 3:** Photomicrograph of resulting crystals after decantation recrystallization. $KNO_3$ is shown here as a subhedral rhombohedrum.

- $KNO_3$, $KClO_4$, and $Ba(NO_3)_2$ crystals were observed for the intact fireworks mixture recrystallized on glass slide (**Figure 3**).
- $KNO_3$ crystal is shown in **Figure 3** as a subhedral rhombohedrum, $Ba(NO_3)_2$ exhibited a cubic octahedron form, and $KClO_4$ displayed an orthorhombic form.
- Microscopical identifications of the crystals in the mixtures were confirmed using the Raman data by comparing their spectra to those of the inorganic oxidizer standards.
- Spectrum 1 in **Figure 5** shows characteristic bands of $KClO_4$ (464 $cm^{-1}$: Cl-O deformation band, theoretically inactive; ~629-641 $cm^{-1}$: Raman active Cl-O deformation bands; and 942 $cm^{-1}$: symmetrical Cl-O stretch).
- Spectrum 2 in **Figure 5** shows characteristic bands of $KNO_3$ (1050 $cm^{-1}$: N-O symmetric stretch, 716 $cm^{-1}$: N-O plane deformation).

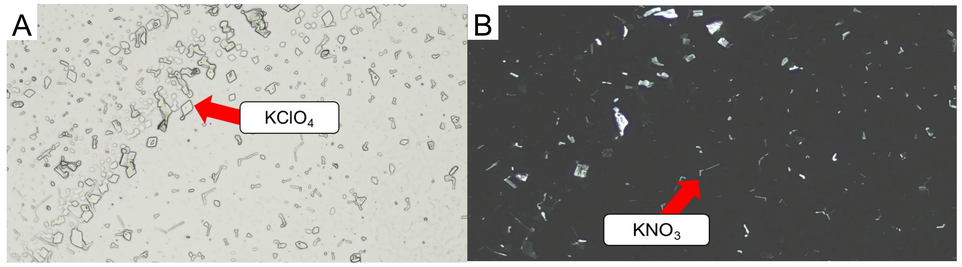



**Figure 4:** Photomicrographs of swab recrystallization taken from the post blast switch substrate in (**A**) transmitted light and (**B**) under slightly uncrossed polars.

- Transmitted light and PLM allowed identification of crystals in most post-blast samples, with some limitations (**Figure 4**).
- The formation of fully formed crystals for all inorganics was difficult due to their low abundance post blast.
- Certain crystals were only observed in beginning stages of growth and never grew into euhedral forms.
- Limited crystal growth unintentionally improved micro-Raman analysis.
- The isolated crystal shown as inset in **Figure 6** was identified as $KClO_4$ by PLM examination, and angle measurements; however, when the spectrum was collected using micro-Raman, a band was observed at 1053 $cm^{-1}$, which corresponds to the major peak of $KNO_3$ (green spectrum), attributed to the symmetric stretching of the N–O group. This indicates the presence of a mix-crystal.

**Table 1.** Inorganic oxidizers identified in swab extracts by light microscopy and micro-Raman spectroscopy per explosion

| Replicate | $KClO_4$ | | $KNO_3$ | | $Ba(NO_3)_4$ | |
|---|---|---|---|---|---|---|
| | Microscopy | Raman | Microscopy | Raman | Microscopy | Raman |
| Explosion 1 | 26 | 27 | 3 | 21 | 0 | 1 |
| Explosion 2 | 28 | 28 | 6 | 28 | 0 | 0 |

- Micro-Raman spectroscopy showed higher sensitivity than polarized light microscopy for detecting low-abundance oxidizers, particularly $KNO_3$ (**Table 1**).
- $KNO_3$ often recrystallized only after samples were near dryness, enabling its detection by micro-Raman but not during earlier microscopical analysis.
- $Ba(NO_3)_2$ (~5% of the mixture) was identified in only one swab; its late crystal formation limited detection by microscopy alone.
- Combining polarized light microscopy and micro-Raman enhanced detection of post blast oxidizers.

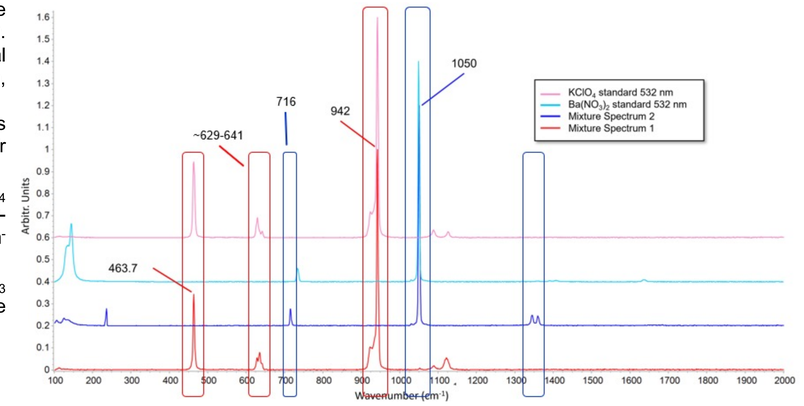



**Figure 5:** Raman spectrum of $KClO_4$ standard (pink), $Ba(NO_3)_2$ standard (light blue), fireworks mixture 2 (dark blue), fireworks mixture 1 (red).

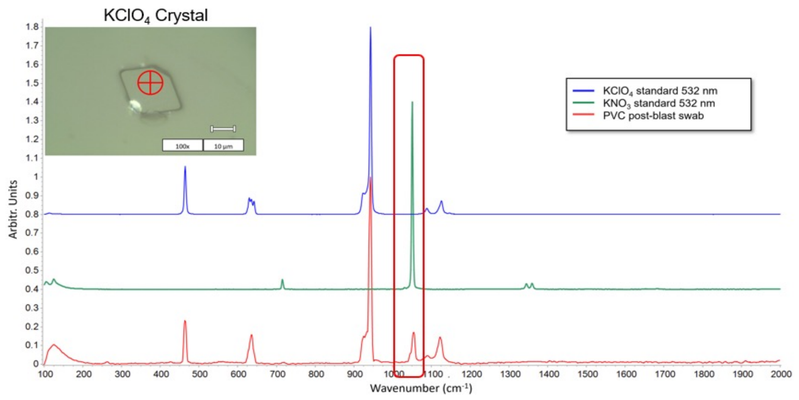



**Figure 6:** Raman spectrum of $KClO_4$ standard (blue), $KNO_3$ standard (green), and recrystallized explosive residue swabbed from the post-blast debris (red). Inset photomicrograph shows measurement location in transmitted light with a slight chromatic aberration.

## CONCLUSIONS

- The detection of inorganic oxidizing salts post blast was successful using the application of polarized light microscopy and micro-Raman spectroscopy.
- Recrystallization of inorganic salts from water was shown to affect the Raman spectrum for certain salts.
- Changes to the lattice vibrations after recrystallization were observed for $KNO_3$, namely the abundance of the rotational and translational lattice modes.
- Raman analysis was essential to identify minor constituents.

## REFERENCES

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