Forensic Analysis of Recrystallized Inorganic Oxidizing Salts Used in Pyrotechnic-Based Improvised Explosive Devices Using Light Microscopy and Micro-Raman Spectroscopy

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Improvised explosive devices (IEDs) Background

- Threat, manufacture and use of IEDs became focus of U.S. intelligence and law enforcement communities in late 1990s and early 2000s
- Due to multiple attacks occurring domestically and abroad
  - Oklahoma City Bombing, 1995

https://www.fbi.gov/history/famous-cases/oklahoma-city-bombing

Current Prominence of Pyrotechnics in Explosive Incidents

- Pyrotechnic mixtures identified as the main charge in 36% of explosive incidents in 2022 [1]
- ATF does not regulate importation, distribution, or storage of consumer fireworks
- Regulated by federal, state and local agencies to certain extent
- Easily accessible and widely available
  - Street vendor or local shop

[1] United States Bomb Data Center, United States Bomb Data Center (USBDC) Explosives Incident report (EIR) 2022, Bureau of Alcohol, Tobacco, Firearms and Explosives, Redstone Arsenal, AL, 2022. https://www.atf.gov/resource-center/docs/report/2022-explosives-incident-report-eir/download (accessed January 25, 2024).

Pyrotechnics Composition

- Similar to composition of propellants and explosives
  - Fuel: Metals (aluminum, magnesium and iron) and nonmetals (silicon, carbon, sulfur and some organic compounds)
  - Oxidizer: Potassium chlorate, potassium perchlorate, and potassium nitrate
  - Binders and additives
  - Compounds to produce color, sound or smoke

Previous Work

- Pyrotechnics and composition previously studied in forensic setting
- SEM-EDS has been most commonly used technique for identification of pyrotechnics compositions [2,3]
- Vibrational spectroscopy also used in analyzing intact pyrotechnic compositions using both Raman and Fourier-transform infrared (FTIR) spectroscopy [2,4]

[2] Castro, K.; De Vallejuelo, S.F.; Astondoa, I.; Goñi, F.M.; and Madariaga, J.M. "Analysis of Confiscated Fireworks Using Raman Spectroscopy Assisted with SEM-EDS and FTIR," Journal of Raman Spectroscopy, 42:11, pp 2000–2005, 2011; https://doi.org/10.1002/.
[3] Trimpe, M. "Analysis of Fireworks for Particles of the Type Found in Primer Residue (GSR)," Midwestern Association of Forensic Scientists Newsletter, 32, pp 68–76, Winter 2003.
[4] López-López, M. and García-Ruiz, C. "Infrared and Raman Spectroscopy Techniques Applied to Identification of Explosives," TrAC Trends in Analytical Chemistry, 54, pp 36–44, 2014; https://doi.org/10.1016/j.trac.2013.10.011.

Gaps in Research

- Limited literature discussing detection of inorganic oxidizing salts from pyrotechnics after deflagration or possible detonation
- Alternative techniques to SEM-EDS and IC are important for forensic casework
  - Non-destructive
  - Rapid
  - Reliable

ASTM 3329−21 [5]

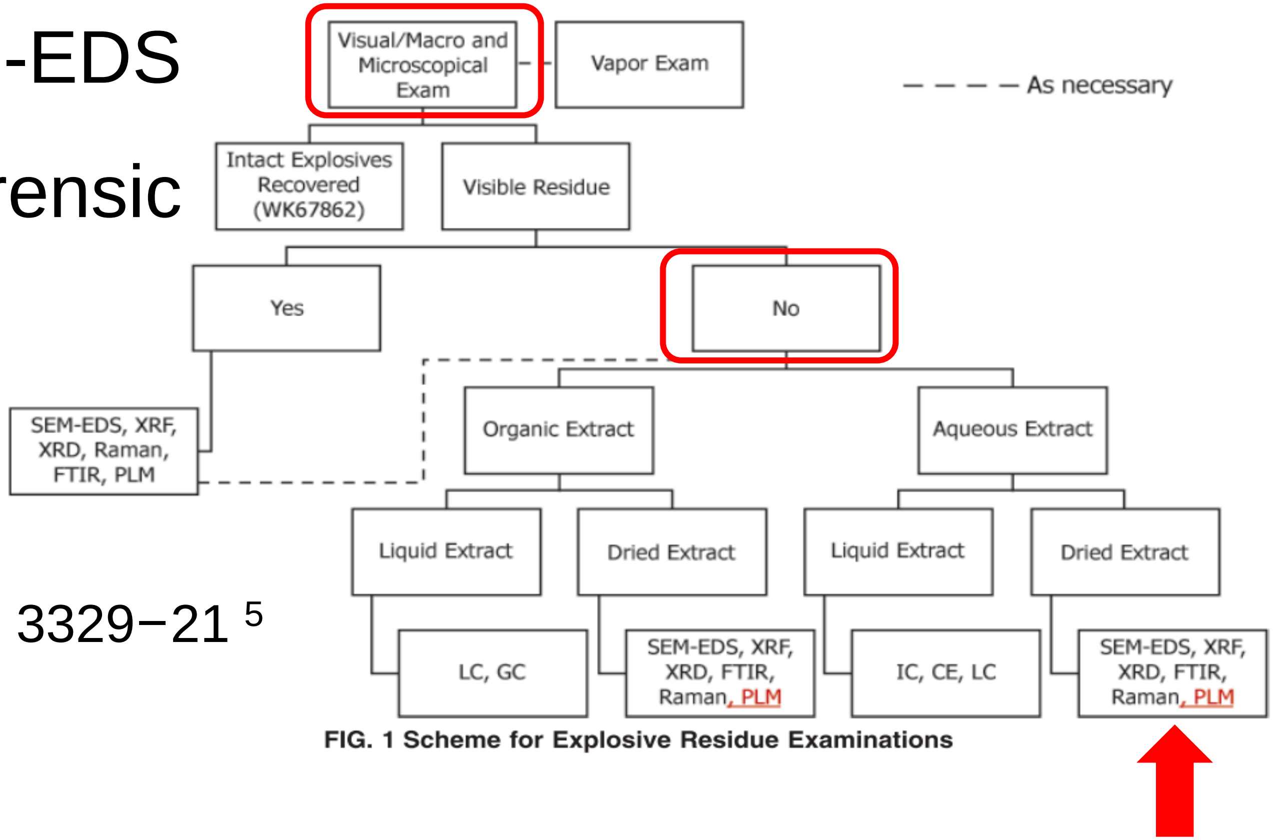


FIG. 1 Scheme for Explosive Residue Examinations

[5] ASTM International. "Standard Practice for Establishing an Examination Scheme for Explosive Residues," 2022; https://doi.org/10.1520/E3329-21E0

Research Goal and Objectives

- Evaluate the advantages and challenges of analyzing post-blast pyrotechnics using a combination of light microscopy and micro-Raman spectroscopy
    - Qualitatively evaluate two swabbing methods (wet vs dry swabs) to determine most optimal for subsequent recrystallization of exploded samples
    - Recrystallize and identify the inorganic oxidizing salts present in the intact pyrotechnic and post blast debris
    - Compare results obtained with microscopy and micro-Raman spectroscopy

Construction of IEDs

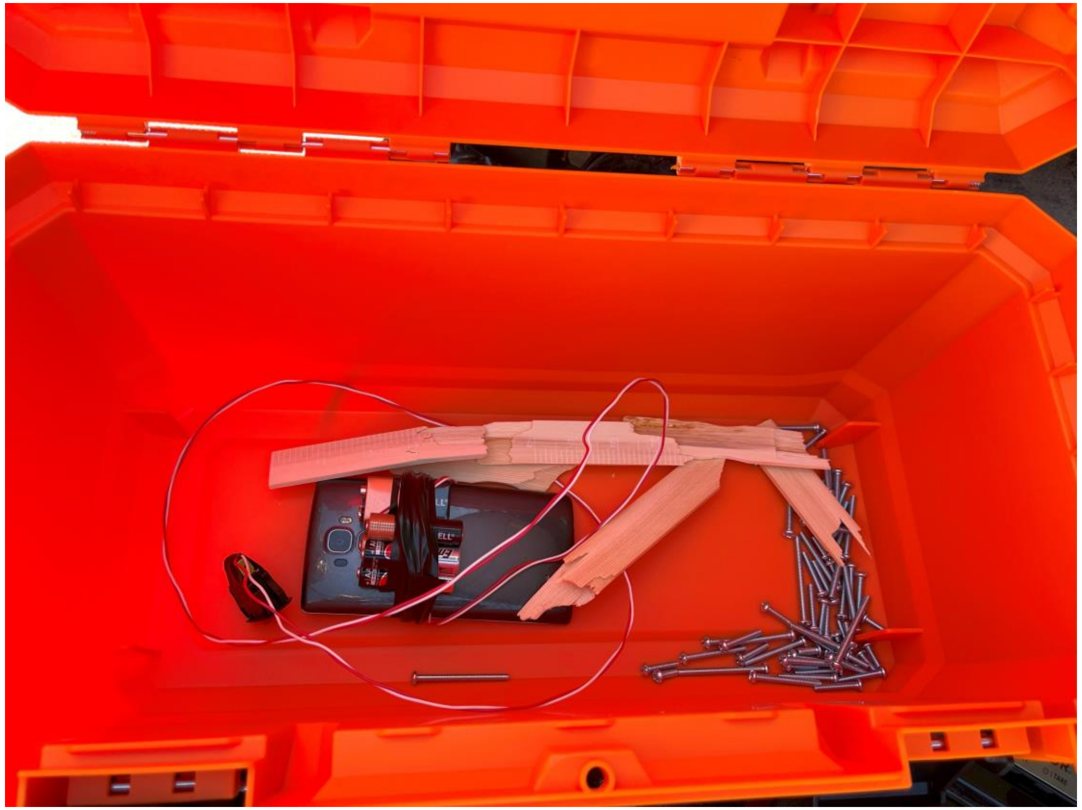
- Collaboration with MCFMO
  - Set-up of explosive charge
  - IED initiation and debris collection
- Both IEDs constructed using same components
  - Toolbox (polypropylene) filled with 10 substrates made of various materials

Construction of IEDs and Collection of Post-Blast Debris

- Each IED made of one PVC pipe filled with pyrotechnics
  - 2.0 oz pyrotechnic mixture obtained by cutting fireworks open and collecting powder
  - Powder weighed to ensure similar weight and composition between two devices
  - Mixture contained 1.4 oz of Mighty Cracker, 0.3 oz of Roman Candle 10 ball and 0.3 oz of two-color Spaceship



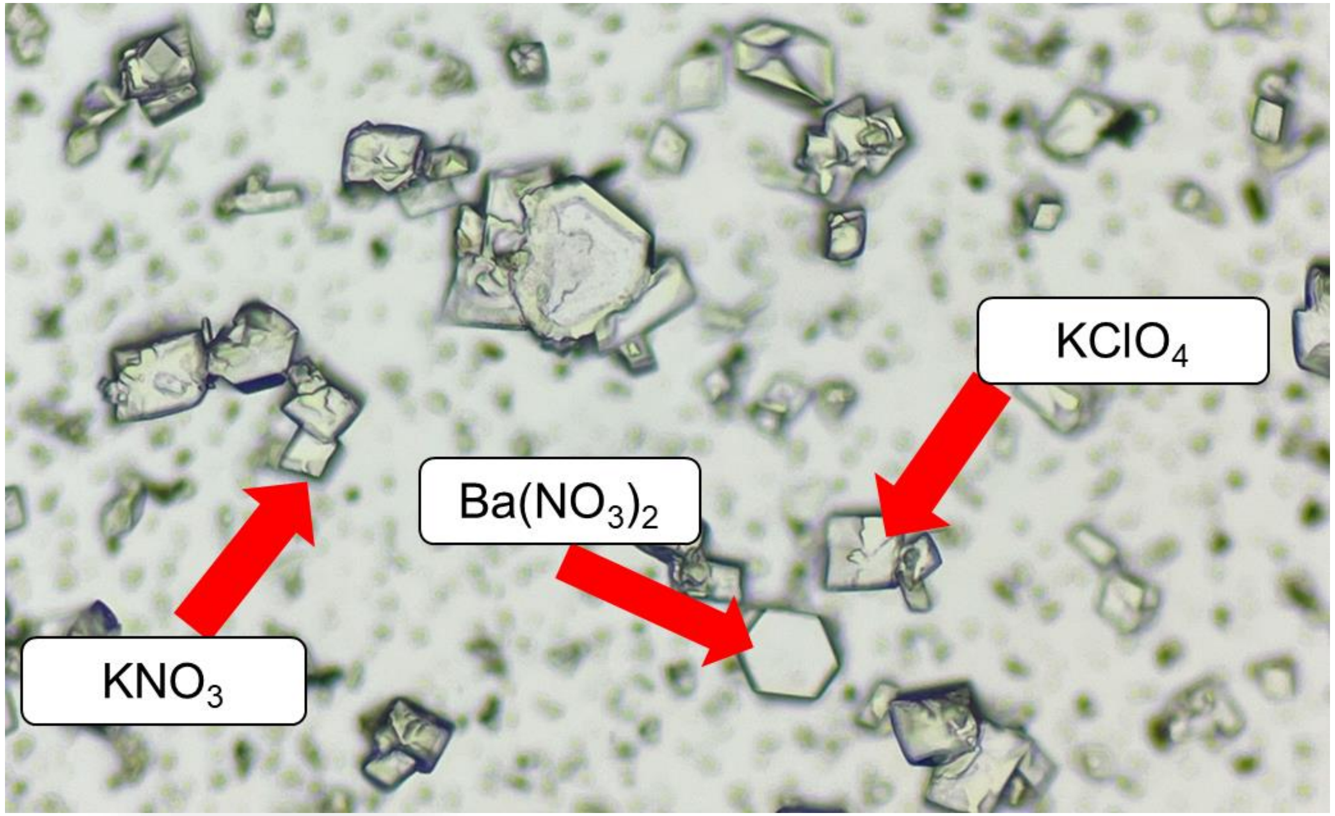
Field Experiments: Intact



- Pipe bomb containing mixture of pyrotechnics not pictured

Field Experiments: Post-Blast

Analysis of Intact Mixture: Brightfield microscopy and PLM



- Mixture recrystallized on glass slides using decantation method by Chamot and Mason [5]
- Presence of KNO_3, $KClO_4$, and $Ba(NO_3)_2$ crystals

- Brightfield & PLM enabled selection of euhedral and subhedral crystals as targets for Raman measurement

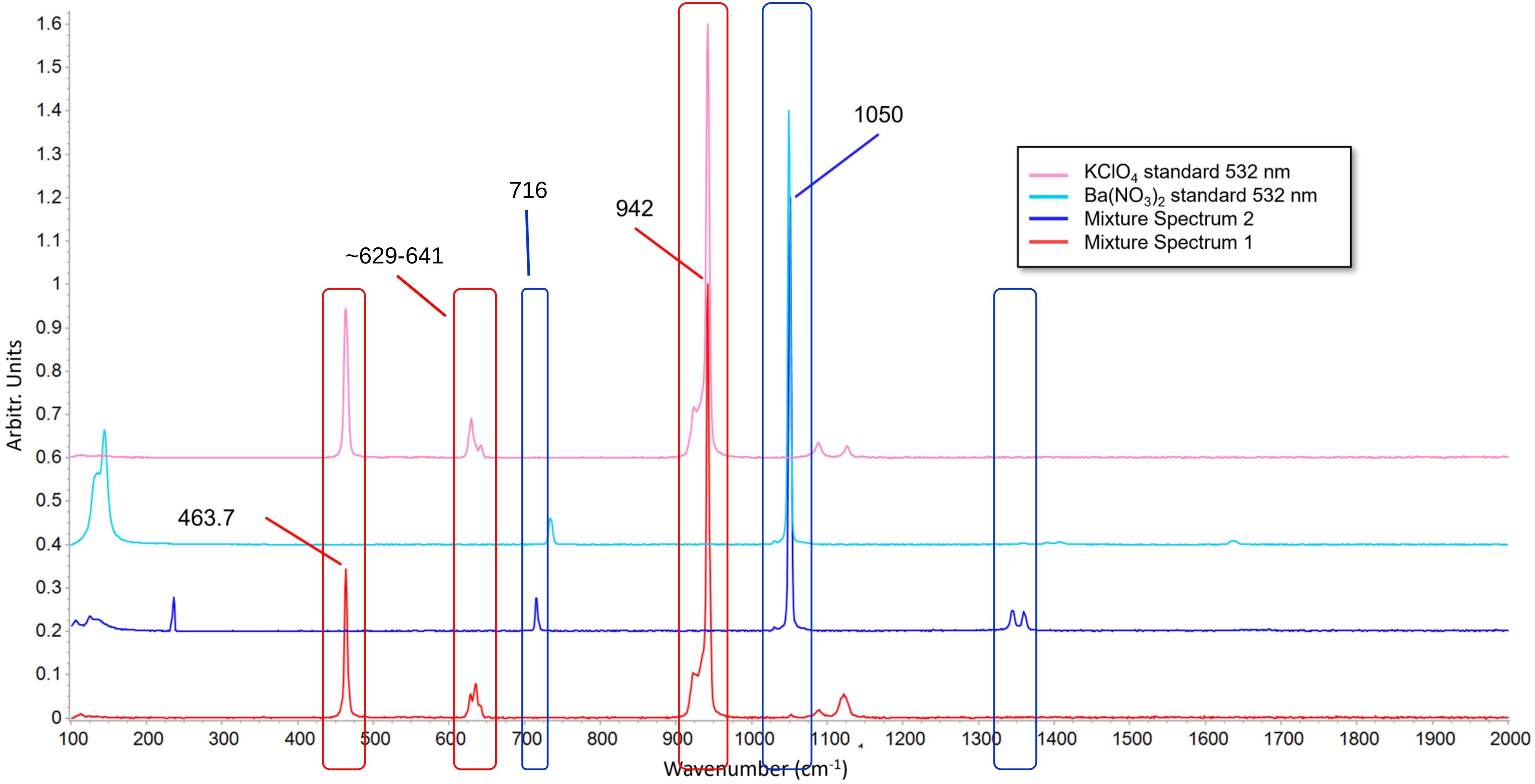
[5] Chamot, É.M. and Mason, C.W. Handbook of Chemical Microscopy, Volume II, 2nd Ed; John Wiley & Sons, Inc.: New York, 1940.

Instrumentation: Confocal Raman Microscopy

- Renishaw InVia™ InSpect Raman microscope
- Parameters
  - 532 nm laser
  - 2.5 mW to 5mW at the source
  - 100× objective
  - 3 accumulations
  - Scan range of 100 to 2,000 cm^{-1}
  - 3 spectra collected per crystal to confirm the identity of the salt

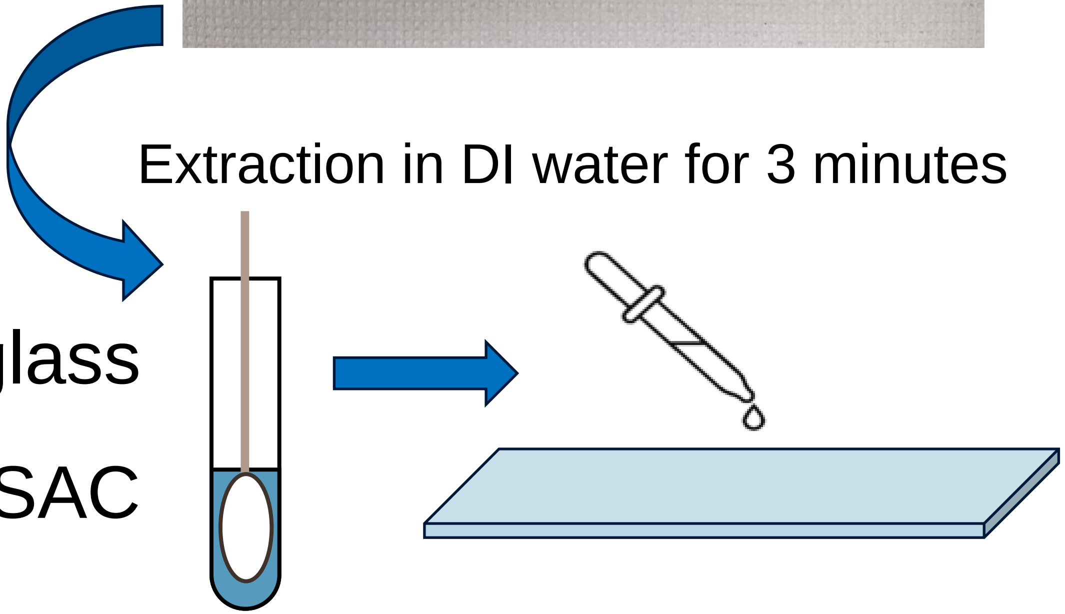
- Raman spectra collected on fully dried samples directly off glass slides
  - High confocality

Raman Analysis of Intact Mixture

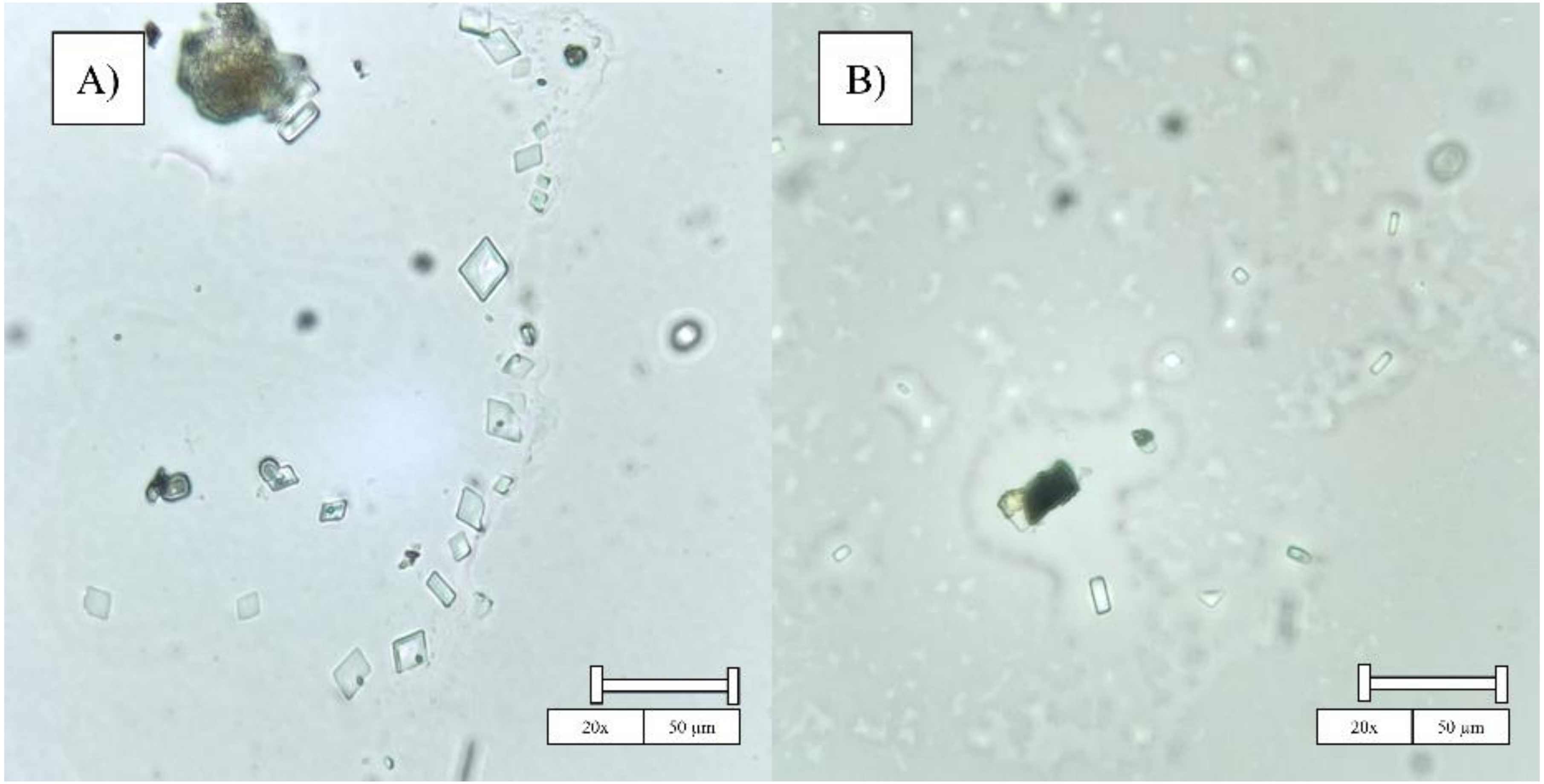


Swabbing Method Comparison

- Wet vs. Dry swabs
- Debris swabbed in similar locations
  - Ensured comparative results
- Swabs placed in microtube
- 1 mL of DI water added
- Left to extract for 3 minutes
- 10 µL of extract pipetted onto glass slides, then recrystallized using OSAC 2022-S-0023 guidelines



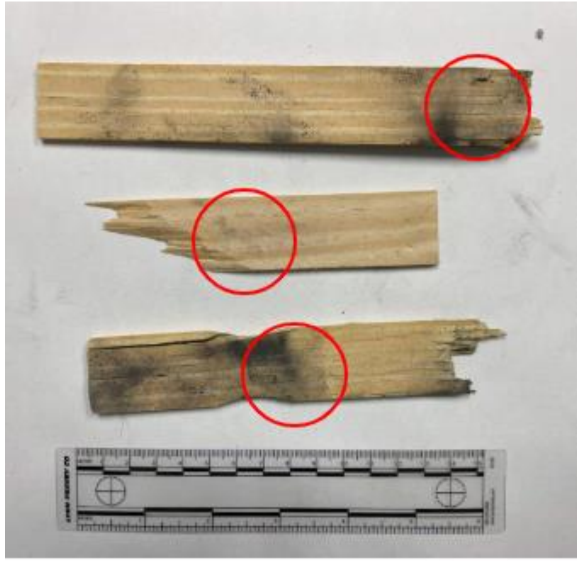
Swab method comparison

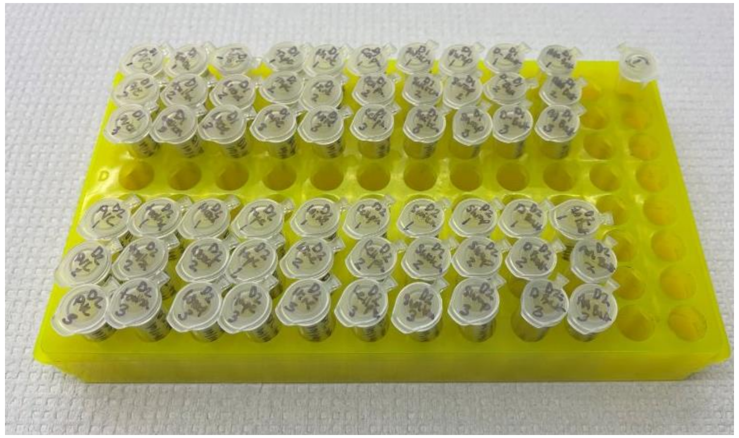


Exemplar photomicrographs of A) wet swab recrystallization and B) dry swab recrystallization

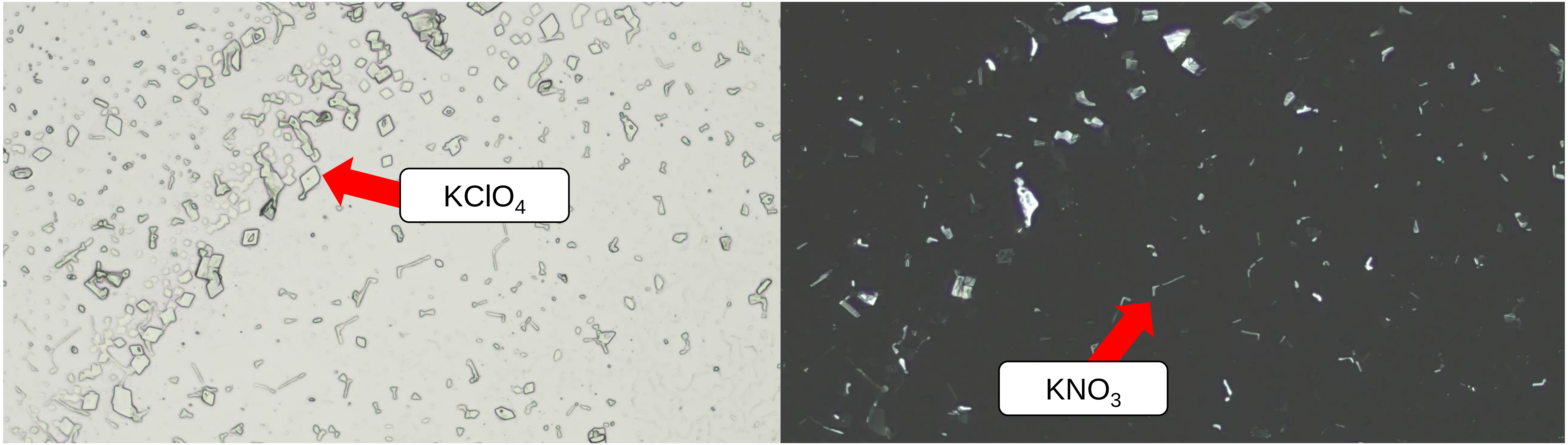
Swabbing Process for Post-Blast Debris

1. Prewet cotton swab with DI water
2. Swab substrate with cotton swab
3. Place into 1 mL of DI water in microtube for 3 minutes
4. Squeeze out water from swab
5. Discard swab
6. Recrystallize from extract





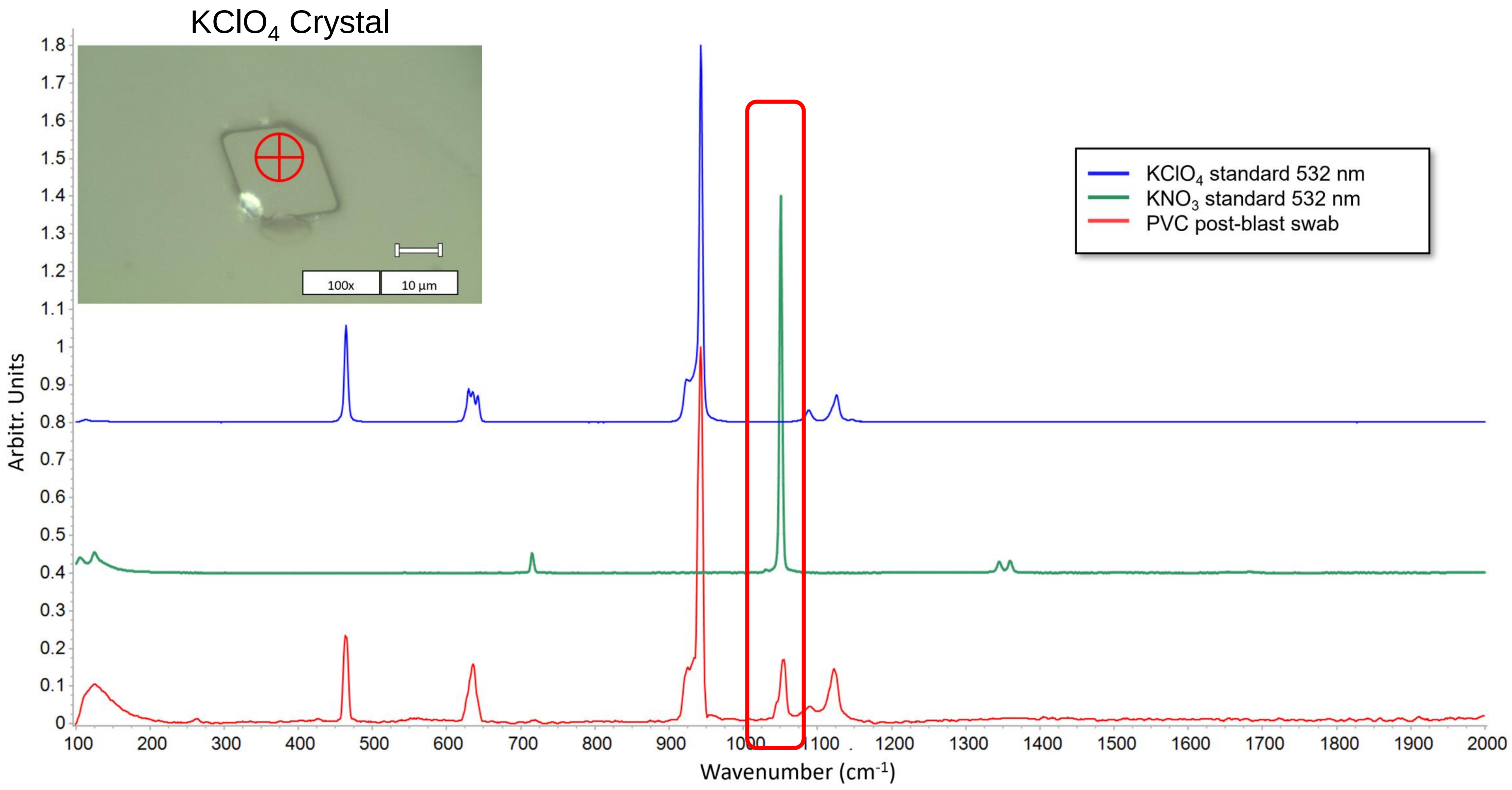
Microscopy of Recrystallized Post-Blast Extracts



*Brightened for clarity

- BF and PLM allowed identification of crystals in most post-blast samples – with some limitations
  - Formation of fully formed crystals for all inorganics was difficult due to low abundance
  - Crystals observed only in beginning stages of growth and never grew into euhedral forms
    - Unintended consequence of preventing unconstrained crystal growth
  - Aided micro-Raman analysis by providing measurement locations on individual crystals

Mixture of Inorganics in Single Crystals



Summary of Post-Blast Extracts Results

- Microscopy was able to confirm $KClO_4$ in most samples
  - KNO_3 was more challenging – lower abundance relative to $KClO_4$
- Raman confirmed $KClO_4$ in most samples for both explosions
  - Facilitated detection of subhedral and euhedral KNO_3 crystals that precipitated after microscopy (when drop was nearing complete dryness)
- $Ba(NO_3)_2$ detected in only one swab from explosion 1
  - Low abundance compared to other salts present (~5% in the mixture)

	$KClO_4$		***KNO_3***		***$Ba(NO_3)_2$***	
Replicate	*Microscopy*	*Raman*	*Microscopy*	*Raman*	*Microscopy*	*Raman*
Explosion 1	26	27	3	21	0	1
Explosion 2	28	28	6	28	0	0

*30 total swabs per detonation

Conclusions

- Swabbing methodology enabled collection of inorganic oxidizers after explosion
- Recrystallization and subsequent microscopy identified mostly $KClO_4$
  - Minor KNO_3
- Raman analysis identified KNO_3 more readily than microscopy alone
  - Discrepancy due to Raman being conducted on dry recrystallized extracts
- Raman analysis identified more than one inorganic salt in a single crystal
- Subsequent Raman analysis was essential to identify minor constituents

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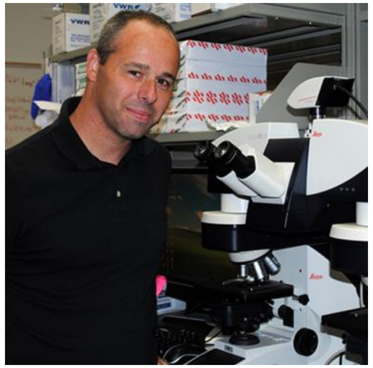

Questions?

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