Analysis of Inorganic Oxidizing Salts in Intact and Chemically Reacted Consumer Fireworks Using Microscopical and Spectroscopic Approaches

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ABSTRACT

The present study describes an analytical scheme using light microscopy, micro-Raman, ATR-FTIR, and SEM-EDS for the identification of inorganic oxidizing salts in both intact and chemically reacted firework samples. Using light microscopy, a lower amount of inorganic oxidizing salts and unhindered growth of subhedral crystals were observed in chemically reacted samples. Using micro-Raman spectroscopy, some spectral changes were noted that did not impact identification. ATR-FTIR allowed for the differentiation of anions present in inorganic oxidizers. Elements found using SEM-EDS indicated constituents of inorganic oxidizing salts found in intact and chemically reacted samples as well as fuel components.

INTRODUCTION

The use of explosive mixtures containing inorganic salts in improvised explosive devices (IEDs), such as commercial fireworks, in events such as the 2013 Boston Marathon Bombing and the 2025 explosion of the Trump hotel in Las Vegas, have led to a greater need to understand compositions of pyrotechnics to assist forensic practitioners in rapid analysis and identification. This study demonstrates an analytical scheme using light microscopy, micro-Raman spectroscopy, ATR-FTIR spectroscopy, and SEM-EDS for forensic investigators to identify and discriminate inorganic oxidizing salts in both intact and chemically reacted consumer fireworks.

MATERIALS & METHODS

<u>Samples & Preparation-</u> Twelve consumer firework samples and six inorganic oxidizers reference samples were analyzed (**Table 1.**).

Table 1. Fireworks and reference inorganic oxidizers analyzed in this study.

Type	*Brand*	*Name*	*Attributed Sample Label*
Artillery	Winda Fireworks	Super Bombs	A1
	Monkey Mania	Artillery Shells	A2
	Brothers Pyrotechnics	Artillery Shells	A3
Fountain	Red Rhino	Garden in Springs	F1
	Bright Star	Hello, Summer	F2
	Cutting Edge	Magical Crystal	F3
Firecracker	Mega Pyrotechnics	Bayou Dynamite	FC1
	Red Rhino	Red Hot Dynamite Hot Crackers	FC2
	Cutting Edge	Mighty Cracker	FC3
Roman Candle	Monkey Mania	Color Pearls	R1
	Winda Fireworks	Dragon Tails	R2
	Monkey Mania	Roman Candles	R3

Inorganic oxidizing salts reference sample					
Potassium perchlorate ($KClO_4$)	Potassium chlorate ($KClO_3$)	Lead nitrate ($Pb(NO_3)_2$)	Strontium nitrate ($Sr(NO_3)_2$)	Barium nitrate ($Ba(NO_3)_2$)	Potassium nitrate $K(NO_3)$

For chemically reacted samples, fireworks were ignited, and remaining particles were collected. A decantation method was used to separate inorganic oxidizers in intact samples before recrystallization. Inorganic oxidizers were collected and recrystallized from slides for reacted samples using a wet swabbing technique. Intact fireworks were cut and crushed into powder for FTIR and SEM-EDS analysis. Residues from chemically reacted samples were scraped from the remnants and placed on the ATR crystal and carbon stubs for ATR-FTIR and SEM-EDS analysis.

<u>Instrumentation</u>: <u>Microscopy</u>: Photomicrographs were collected at 20x using a Leica DM 2700 P microscope and an AmScope WF200 digital camera with Amscope camera software v4.11. *<u>Micro-Raman spectroscopy</u>*: A Renishaw inVia™ InSpect confocal Raman microscope was used to collect three replicate Raman spectra for each sample. Spectra were collected using a 532 nm laser. *<u>ATR-FTIR</u>:* Spectra were collected using a Thermo Scientific Nicolet 6700 FT-IR spectrometer with a Diamond ATR crystal. Each sample was scanned 64 times with a range of 4000-650 cm^{-1}. Averages of five replicate spectra of each sample and standard were used for data analysis. *<u>SEM-EDS</u>:* Hitachi SU3500 Scanning Electron Microscope coupled to Bruker Electron-Dispersive X-ray Spectroscopy Detector was utilized with an acceleration voltage of 20 kV, minimum of 20 kcps, and integration time of 50 s for elemental analysis.

RESULTS & DISCUSSION

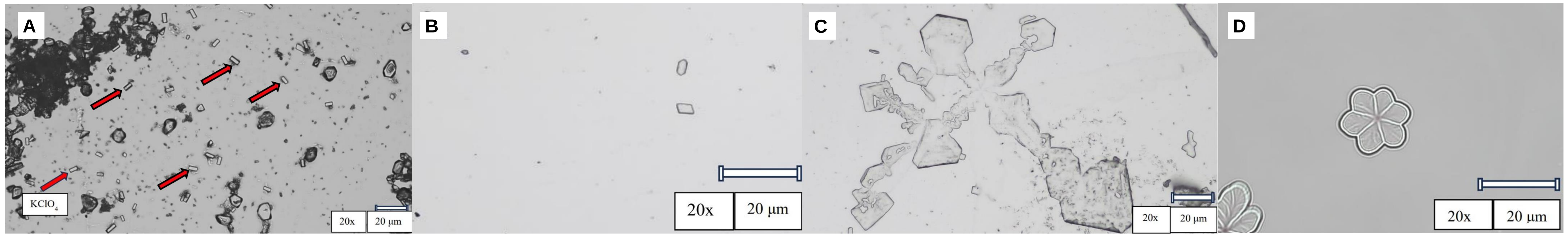

Figure 1. Photomicrographs of **A)** recrystallized intact sample F3, **B)** recrystallized chemically reacted sample A3, **C)** unhindered subhedral crystal growth observed in recrystallized chemically reacted sample A3, **D)** unidentified crystal morphology seen in chemically reacted sample F1.

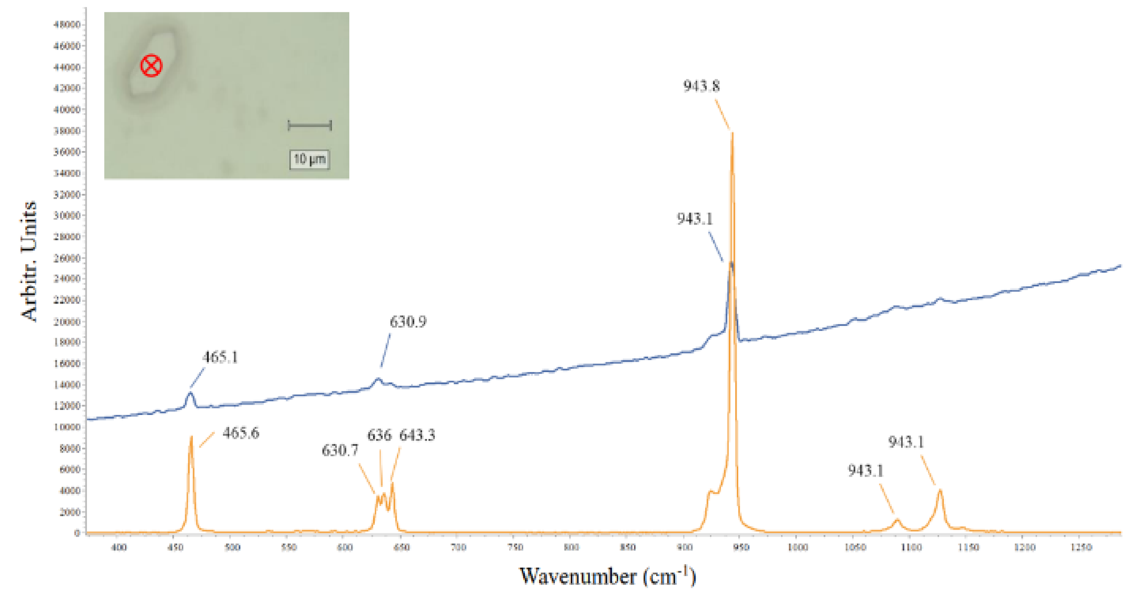

Figure 2. Raman spectra of recrystallized potassium perchlorate standard (orange) and chemically reacted fountain 1 (blue).

- A greater amount of recrystallized inorganic oxidizing salt was observed in the intact samples (**Figure 1A**) than in the chemically reacted samples (**Figure 1B**) via light microscopy.
- The unhindered subhedral growth of crystals at the conclusion of the recrystallization process (**Figure 1C**) posed challenges in identifying inorganic oxidizers using micro-Raman spectroscopy, due to the lack of euhedral crystals available for analysis.
- Unidentified crystal morphology was observed in chemically reacted samples (**Figure 1D**), except for firecrackers.

Table 2. Inorganic oxidizing salts identified using light microscopy and micro-Raman spectroscopy for each type of chemically reacted consumer fireworks (35 swabs for Artillery, 36 swabs for Fountain, and 27 swabs for Roman Candle and Firecracker)

	$KClO_4$		KNO_3		$Ba(NO)_3)_2$		$KClO_3$	
Type	Microscopy	Raman	Microscopy	Raman	Microscopy	Raman	Microscopy	Raman
Artillery	16	12	10	0	3	0	5	0
Roman Candle	10	2	3	0	2	0	1	0
Firecracker	26	25	17	0	1	0	9	0
Fountain	20	14	9	1	5	0	10	0

0-25% 25-50% 50-75% 75-100%

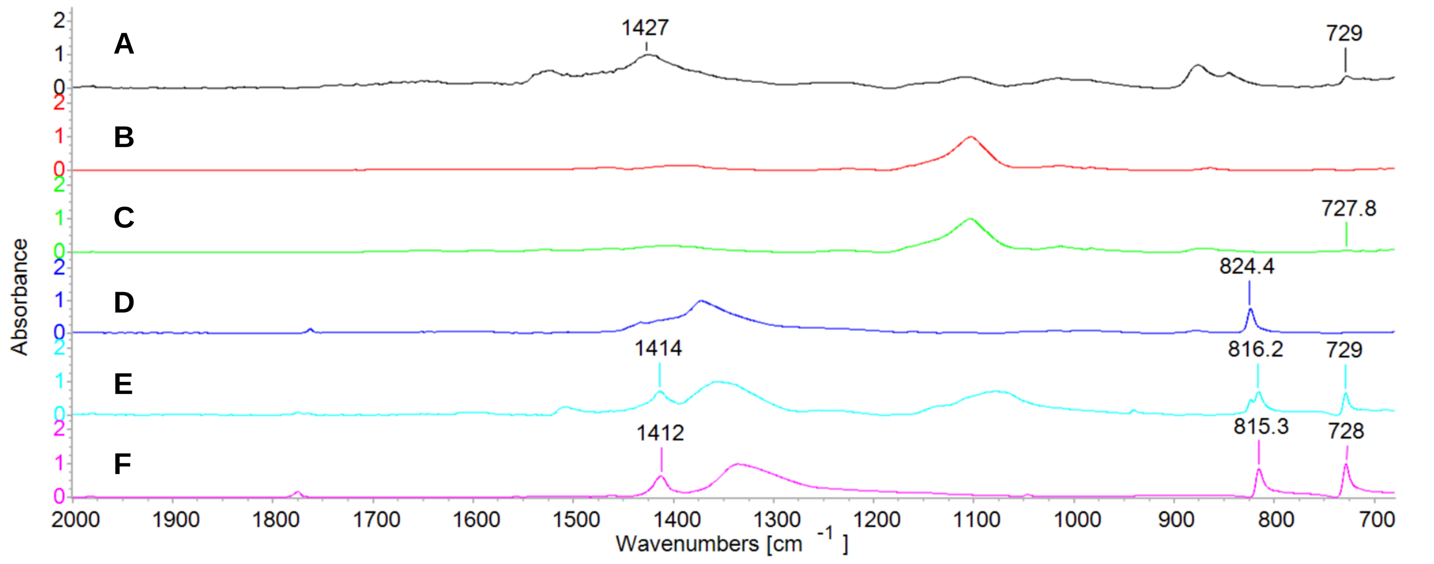

Figure 3. ATR-FTIR spectra of (R1) Roman Candle chemically reacted samples (**A, B and C**), intact samples from the tube propellant (**D**) the spheres (**E**), and Barium Nitrate standard (**F**).

- Potassium perchlorate was the most identified inorganic oxidizing salt using micro-Raman spectroscopy (**Figure 2**).
- Changes in Raman spectra such as shifting and peak dropout were observed when standards were recrystallized in comparison to chemically reacted samples.
- Using ATR-FTIR allowed for the identification of the anions and the determination that samples often contained multiple types of inorganic oxidizers, such as nitrates, chlorates and perchlorates.
- Roman candles were often found to contain Barium Nitrate for both chemically reacted and intact samples (**Figure 3.**).
- Chlorine and potassium, which were observed in both intact and chemically reacted samples using SEM-EDS are indicative of the inorganic oxidizing salts also identified using light microscopy and micro-Raman spectroscopy.
- SEM-EDS also allowed for the detection of magnesium, aluminum, and sulfur, which are fuel components.

CONCLUSIONS

- Micro-Raman spectroscopy allowed for the identification of individual crystal's anion and cation in inorganic oxidizers, while ATR-FTIR mostly allowed for identification of anions within inorganic oxidizing salts present in samples and allowed for the determination of mixtures.
- Using light microscopy, smaller and thinner crystals were observed following recrystallization of the chemically reacted samples, which hindered micro-Raman analysis.
- While the SEM-EDS identified similar elements in intact and chemically reacted samples, fewer elements were observed in chemically reacted samples as supported by their microscopical examination.

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