

Identification of Inorganic Ions Found in Homemade Explosives Using Microcrystalline Tests and Raman Microspectroscopy

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Abstract

While the combination of microcrystalline tests and Raman spectroscopy have been used in the detection and identification in forensic drug analysis, no such method has been attempted with materials commonly present in the inorganic portion of explosives. Many other techniques have been used in the analysis of components of explosives, but none are as rapid, require little preparation, reproducible, and require trace amounts as the method to be described. In this method, Raman microspectroscopy is paired with microcrystalline tests to identify seven cations (ammonium, barium, calcium, potassium, silver, sodium, and strontium), six anions (chlorate, nitrate, nitrite, oxalate, perchlorate, and tartrate) and urea commonly found in homemade explosives or improvised explosive devices, specifically, those found in fertilizers, fireworks, and pyrotechnics. Raman spectra were generated from microcrystals produced in aqueous test samples prepared with commercially available inorganic salts and reacted with three common reagents used to develop microcrystals: squaric acid, nitron, and chloroplatinic acid. The combination of microcrystal shape/physical characteristics and Raman spectra used in this study serves as a useful model for the incorporation of this type of methodology for the identification of inorganic ions typically found in homemade explosives.

Keywords: *microcrystalline tests, Raman microspectroscopy, inorganic ions, homemade explosives*

Introduction

Inorganic compounds and materials are often used to produce homemade explosives or improvised explosive devices (IED). There are many catastrophic events in the past that have showcased the devastating consequences of IEDs, most notably the World Trade Center Bombing in 1993 with urea nitrate and the Oklahoma City bombing in 1995 with ammonium nitrate fuel oil (ANFO) [1]. Though these events happened over twenty years ago, improvised explosive devices are still

a problem today. In 2019, the Association of Firearm and Toolmark Examiners (AFTE) issued an incident report documenting that out of 715 explosion incidents that year, 84 were IED's [2]. Since this type of crime continues to be committed, it is pertinent that techniques and methods to analyze explosive residues continue to improve. Although IEDs can contain organic compounds, this study will focus on a strategy for the detection of inorganic ions using microcrystalline tests coupled with Raman microspectroscopy.

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Inorganic materials used to make IEDs are available through many commercially available products. Pyrotechnics such as fireworks contain many inorganic compounds to create streams of colors upon detonation. For instance, strontium chloride can be used to create red, sodium chloride or oxalate for yellow, and calcium chloride or sulfate for orange [3, 4]. Firecrackers are composed of potassium nitrate acting as an oxidizer and sparklers contain potassium perchlorate [4]. Common garden and farm fertilizers and food preservatives provide oxidizers for IEDs in the form of nitrates (e.g. ammonium nitrate, calcium ammonium nitrate, sodium nitrate, urea nitrate) and nitrites [5]. Among these examples, ammonium nitrate poses a relatively larger threat since it can be combined with fuel to create a larger explosion [6]. Potassium chlorate can be made from sodium hypochlorite bleach or swimming pool cleaner and can be used to make an IED when combined with other materials such as wax, petroleum jelly, and aluminum powder [6]. Finally, illuminating candles and flares contain sodium nitrate, calcium oxalate, and ammonium perchlorate [5].

Numerous instrumental techniques for the analysis of explosive residues can be found in literature, all of which have advantages and disadvantages. Volatile materials can be examined with gas chromatography, which offers the benefit of short analysis times, high resolution, good sensitivity and low cost. However, explosive residues are easily degraded in the instrument when the sample is converted to a gas [7]. High performance liquid chromatography (HPLC) is accurate, precise, and can analyze both volatiles and non-volatiles; however, the method is only commonly used in the detection of organic residue components of explosive evidence and has poor mass transfer efficiencies with mixtures [8]. Ion chromatography can analyze both inorganic and organic components of explosive residues but identification of inorganic materials may require tandem analysis with capillary electrophoresis [7, 9]. Lastly, X-ray diffraction requires minimal sample preparation, provides high selectivity, and can analyze both inorganic and organic components. However, a large amount of sample is required and when used for explosive analysis can suffer from a lack of sensitivity and long analysis times [8].

Although less commonly used today, microcrystalline tests date back to the 19th century. The classical

text produced by Chamot and Mason in 1931 described several techniques for generating microcrystals, some of which were used in this research; but generically are performed by taking the substance of interest and combining it with a reagent to obtain a characteristic crystalline shape [10].

Many reagents have been used to perform these tests including 1,4-diphenyl-3-(phenylamino)-1H-1,2,4-triazolium (nitron), silver nitrate, 3,4-dihydroxycyclobut-3-ene-1,2-dione (squaric acid), uranyl acetate, barium chloride, methylene blue, and chloroplatinic acid [10, 11]. In particular, squaric acid has been shown to form inorganic crystalline complexes with 23 different cations while nitron has been employed in the detection of common anions associated with oxidizers [12, 13].

Microcrystalline tests have been extensively reviewed for the identification of common drugs of abuse as well as selective designer drugs [14, 15], but the technique has been criticized as having poor discriminating ability and requiring extensive expertise [16]. Furthermore, the Scientific Working Group for the Analysis of Seized Drugs (SWGDM) lists microcrystalline tests as a Category B intermediate technique of analysis [17]. Category B techniques have less confirmatory potential than those methods listed as Category A although more confirmatory than those in Category C [17].

One potential option to improve the perceived lack of discriminating ability of microcrystalline tests is to couple it with a spectroscopic analysis technique such as Raman microspectroscopy. Raman spectroscopy has been used in the examination of explosive residues as well as many other types of forensic evidence [18-21]. Diaz et al. used confocal Raman spectroscopy to detect ammonium nitrate, fuel oil, ammonium nitrate water solutions, and component mixtures in soil on various substrates [22]. Zapata et al. used Raman spectroscopy and infrared spectroscopy to identify 44 of 73 salts, 25 of which could be identified solely by Raman spectroscopy [23]. Further research looked at a portable Raman spectroscopy system to detect a mixture of seven oxyanions: carbonate, sulfate, nitrate, phosphate, perchlorate, chlorate, and thiosulfate [24]. They had one individualizing band for each of the oxyanions and were able to successfully identify the components of three unknown fertilizers that were used to validate the method [24].

Microcrystalline tests have been used in conjunction with Raman microspectroscopy and multivariate statistics

to identify drug analogs. Quinn et al. used gold chloride microcrystalline tests to detect phencyclidine (PCP) and four of its analogs. Raman spectra were generated from resultant microcrystals and discriminated using principal component analysis and linear discriminant analysis [25]. Elie et al. also used microcrystalline tests in combination with Raman microspectroscopy to identify 4-methylmethcathinone (mephedrone) and 5,6-methylenedioxy-2-aminoindane (MDAI) [26].

Similarly, this study will show how microcrystalline tests combined with Raman microspectroscopy can be used in a sensitive and time efficient manner to detect thirteen inorganic ions often encountered in the examination of explosive residues. Of the thirteen, most are common to homemade explosives. Two ions, tartrate, and silver are included on the list of explosive materials in the Federal Register [27].

Overall, the purpose of this research is to determine if microcrystalline tests combined with Raman microspectroscopy can be used as a method to identify inorganic components of explosive residue.

Materials and Methods

Microcrystalline Tests

Microcrystalline tests were performed on quartz or aluminum microscope slides using Method 1 as described by Chamot and Mason [10]. In this method, 3 μL of an aqueous solution of the material containing the ion to be tested (approximately 8 mg/mL) is placed next to 3 μL of an aqueous solution of the test chemical (test reagent) on the slide (all solutions are prepared in wells in spot plates; in the case of nitron, the solution is acidified with one drop of glacial acetic acid). Using a toothpick, the test reagent is brought into the sample reagent on the slide forming a channel between both reactants. Individual microcrystalline tests were run in replicates of five to show robustness of crystal growth. In some cases, different salts of the same ion were used among the five replicates. Microcrystals were observed at 200x using an Olympus BX53 polarized light microscope (Center Valley, PA) with image capture using CellSens imaging software (Olympus, Center Valley, PA). Tests chemicals used to detect particular ions are found in Table 1.

Table 1 Test chemicals and ions.

	Squaric Acid	Nitron	Chloroplatinic Acid
Test Ions	Ag ⁺ , K ⁺ , Na ⁺ , NH ₄ ⁺ (including from urea), Ba ²⁺ , Ca ²⁺ , Sr ²⁺	ClO ₃ ⁻ , ClO ₄ ⁻ , C ₂ O ₄ ⁻ , C ₄ H ₄ O ₆ ⁻ , NO ₂ ⁻ , NO ₃ ⁻	K ⁺ , NH ₄ ⁺ (including from urea)

Test chemicals were purchased from Aldrich Chemical Company (nitron, 98.0%), Sigma-Aldrich (3,4-dihydroxy-3-cyclobutene-1,2-dione or squaric acid, $\geq 99.0\%$); (chloroplatinic acid hexahydrate, $>99.9\%$ trace metal basis). Chemicals used as controls for particular ions included aluminum nitrate (Sigma Aldrich), ammonium calcium nitrate (Greenway Biotech Inc.), ammonium nitrate (Sigma Aldrich), barium chloride (Fisher Scientific), calcium nitrate (Sigma Aldrich), iron (III) nitrate (Sigma Aldrich), potassium chlorate (Fisher Scientific), potassium oxalate (Sigma Aldrich), potassium nitrate (Fisher Scientific), potassium nitrite (Sigma Aldrich), potassium perchlorate (Sigma Aldrich), silver nitrate (VWR), sodium nitrate (Sigma Aldrich), sodium nitrite (Sigma Aldrich), sodium tartrate (Baker Analyzed), strontium chloride (J.T. Baker), and urea (Sigma Aldrich).

Urea Microcrystalline Test

To detect urea, an aqueous solution of urease (Sigma Aldrich) (approximately 1.5 mg of urease was added to water in a well of a spot plate) must be added to the test reagent and allowed to incubate for twenty minutes at room temperature prior to testing. Urease causes hydrolysis of urea to form the ammonium ion which is then detected.

Raman Microspectroscopy

Raman spectra were collected from microcrystals produced with test reagents with a Thermo Fisher Scientific DXR2 Raman microscope (Waltham, MA) equipped with a 785 nm laser at 100x using parameters listed in Table 2. Parameters were optimized for individual ions. Collection was obtained using OMNIC 9.8.372 software. Spectra were corrected for fluorescence, baseline, and smooth.

The Raman microscope was re-aligned and re-calibrated on a weekly basis to ensure no drift was being observed in the spectra. All tests were run in replicates of five for each salt tested to ensure reproducibility of the Raman spectra. Percent correlation of variation

(%CV) of Raman shifts was determined from microcrystals generated from squaric acid and nitron gathered throughout the study. The %CV did not exceed 0.1 for any Raman shift in the study, demonstrating reproducibility of data.

Table 2 Raman DXR2 parameters.

Ion	Reagent	Slide	Aperture	Scan Number	Laser Power
Ammonium (NH ₄ ⁺)	Squaric Acid	Quartz Slide	50 μm Pinhole	20 scans	30 mW
Barium (Ba ²⁺)	Squaric Acid	Aluminum Slide	50 μm Slit	128 scans	20 mW
Calcium (Ca ²⁺)	Squaric Acid	Aluminum Slide	50 μm Slit	64 scans	20 mW
Potassium (K ⁺)	Squaric Acid	Quartz Slide	50 μm Slit	64 scans	30 mW
Silver (Ag ⁺)	Squaric Acid	Quartz Slide	50 μm Pinhole	20 scans	30 mW
Sodium (Na ⁺)	Squaric Acid	Aluminum Slide	50 μm Slit	64 scans	30 mW
Strontium (Sr ²⁺)	Squaric Acid	Quartz Slide	50 μm Pinhole	20 scans	30 mW
Ammonium (NH ₄ ⁺)	Chloroplatinic Acid	Quartz Slide	50 μm Pinhole	20 scans	20 mW
Potassium (K ⁺)	Chloroplatinic Acid	Quartz Slide	50 μm Pinhole	20 scans	20 mW
Chlorate (ClO ₃ ⁻)	Nitron	Quartz Slide	50 μm Slit	128 scans	30 mW
Nitrate (NO ₃ ⁻)	Nitron	Quartz Slide	50 μm Pinhole	20 scans	20 mW
Nitrite (NO ₂ ⁻)	Nitron	Quartz Slide	50 μm Pinhole	20 scans	20 mW
Oxalate (C ₂ O ₄ ²⁻)	Nitron	Quartz Slide	50 μm Pinhole	20 scans	20 mW
Perchlorate (ClO ₄ ⁻)	Nitron	Quartz Slide	50 μm Slit	64 scans	15 mW
Tartrate (C ₄ H ₄ O ₆ ²⁻)	Nitron	Quartz Slide	50 μm Pinhole	20 scans	20 mW

Validation

A blind study including fourteen single source and three mixtures was performed to test the accuracy and repeatability of the combination of microcrystalline tests with Raman microspectroscopy of the thirteen inorganic ions and urea. Single source and mixed samples were given to the primary researcher with no prior knowledge of what the unknowns contained. Raman spectra were developed for the microcrystal(s) produced with squaric acid and nitron and compared to standard spectra. Results indicating the presence of potassium or ammonium were further tested with chloroplatinate acid.

Results

Nitron and squaric acid were tested with each of the thirteen inorganic ions and urea. Potassium and ammonium ions and urea were tested with chloroplatinic acid. Images of characteristic crystal formation and corresponding Raman spectra can be found in Fig. 1-3 (squaric acid), 4 (chloroplatinic acid), and 5-6 (nitron) for all ions that produced positive results.

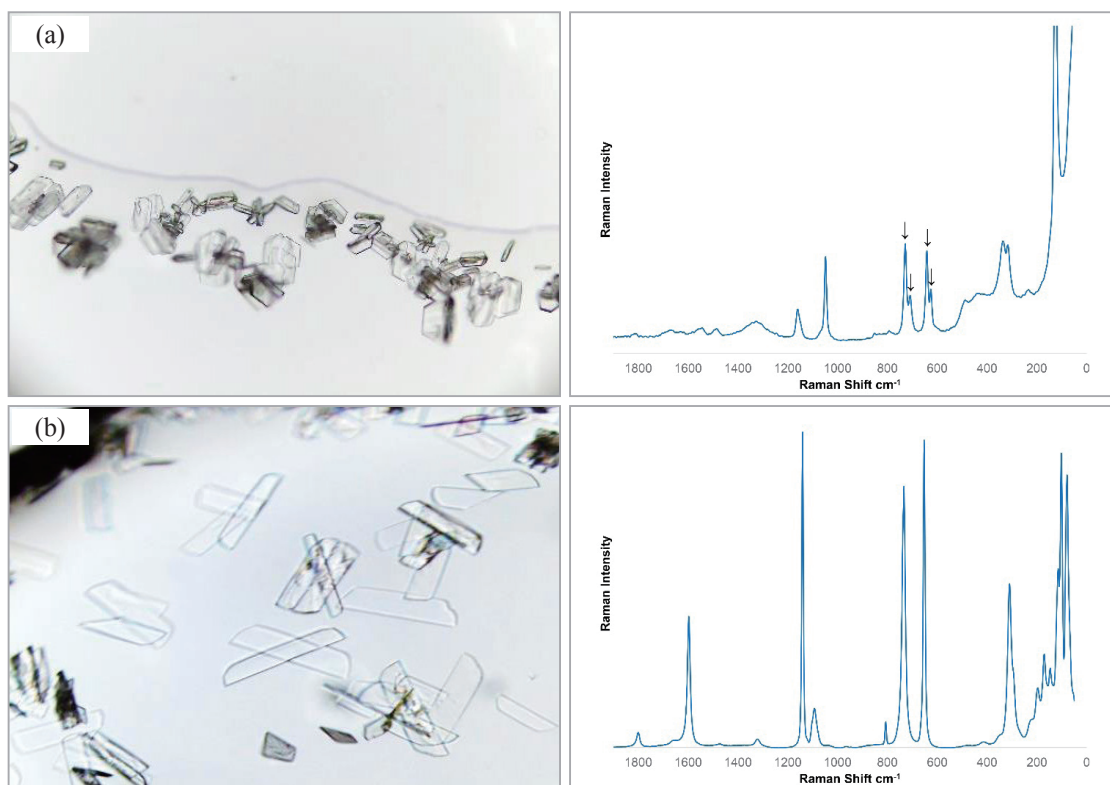


Fig. 1 Squaric acid crystals at 100X with corresponding Raman spectra: (a) ammonium—arrows point to peaks referenced in text at 728 cm⁻¹, 709 cm⁻¹ (shoulder), 641 cm⁻¹, and 625 cm⁻¹ (shoulder); (b) barium.

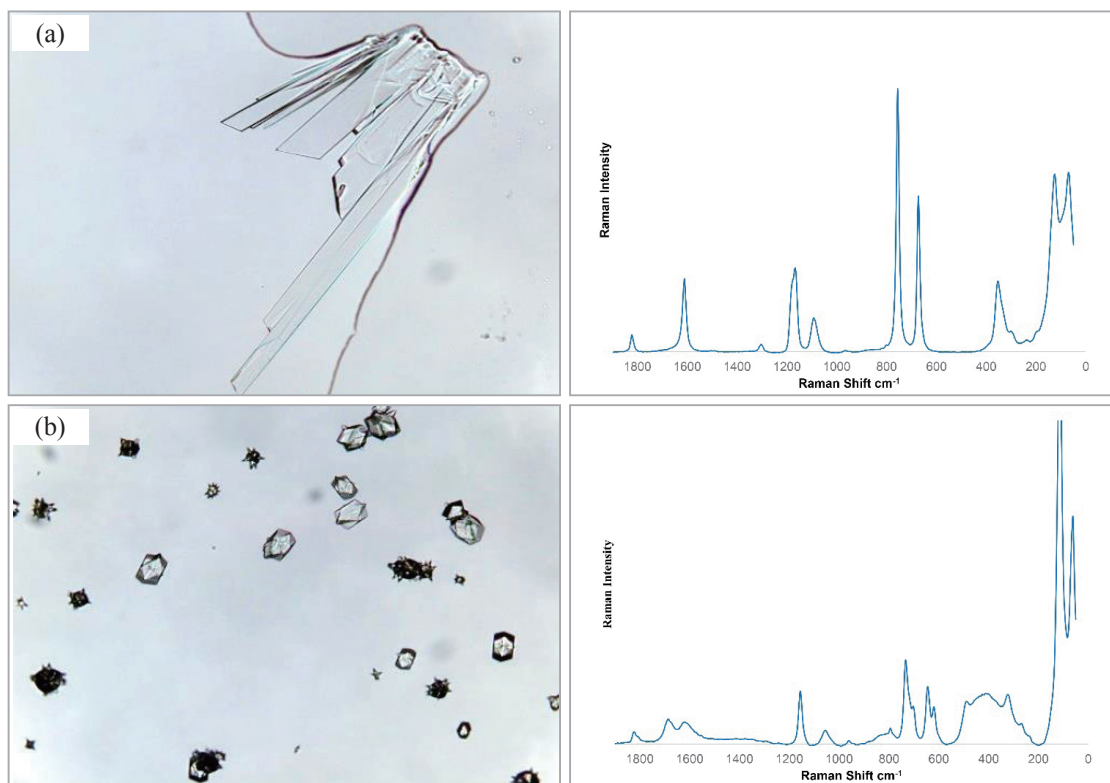


Fig. 2 Squaric acid crystals at 100X with corresponding Raman spectra: (a) calcium; (b) potassium.

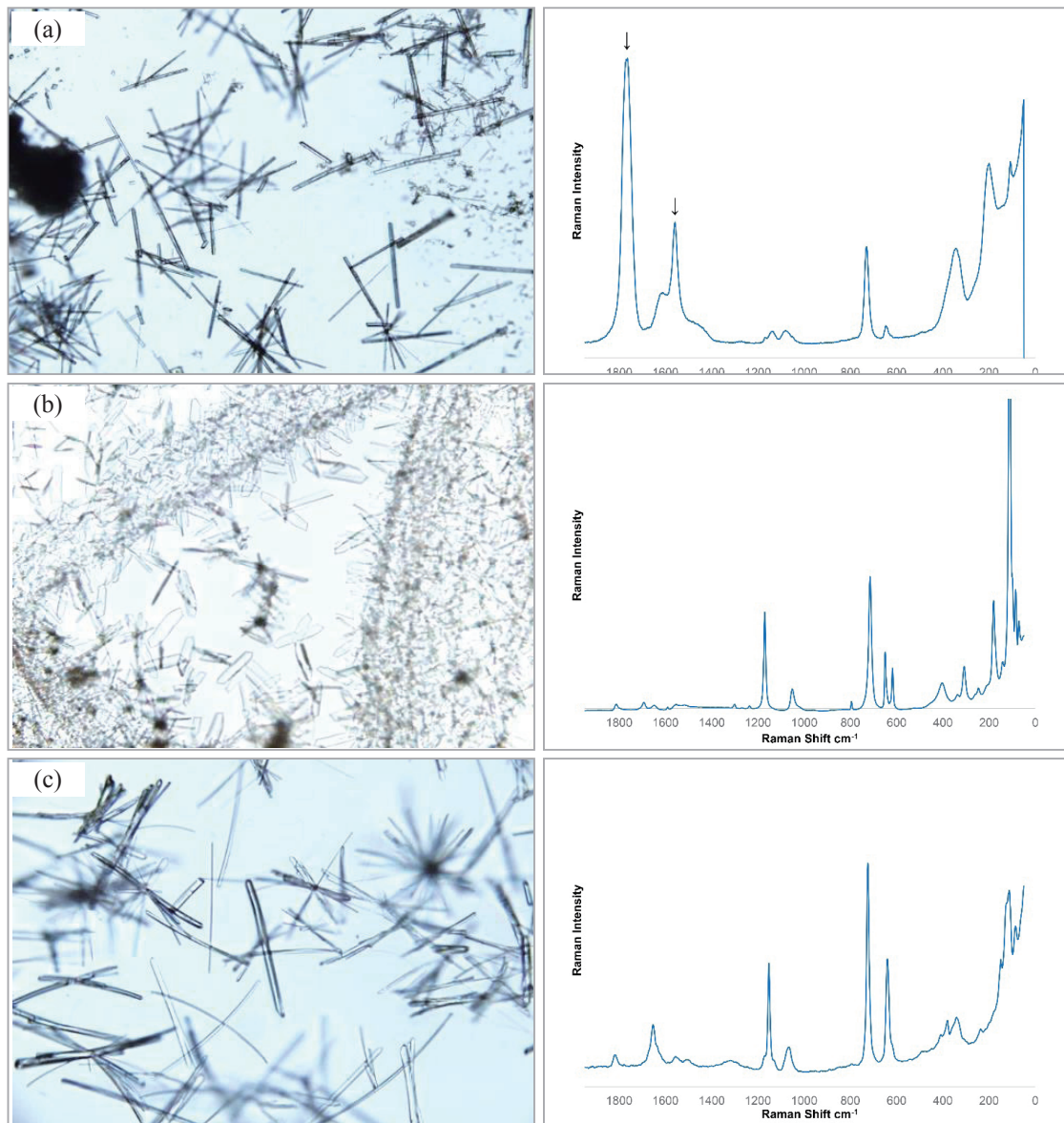
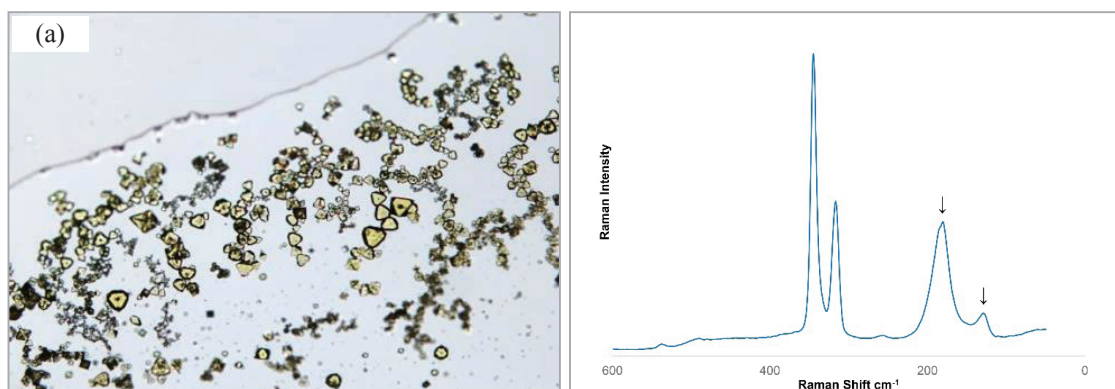


Fig. 3 Squaric acid crystals at 100X with corresponding Raman spectra: (a)silver-arrows point to peaks referenced in text at 1764 cm⁻¹ and 1558 cm⁻¹; (b)sodium; (c)strontium.



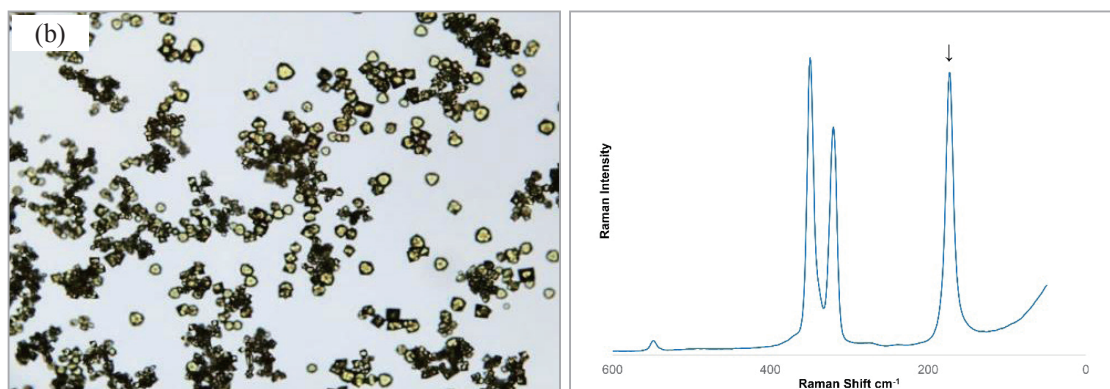


Fig. 4 Chloroplatinic acid crystals at 100X with corresponding Raman spectra: (a) ammonium—arrows point to peaks referenced in text at 180 cm^{-1} and 129 cm^{-1} ; (b) potassium—arrow points to peak referenced in text at 172 cm^{-1} .

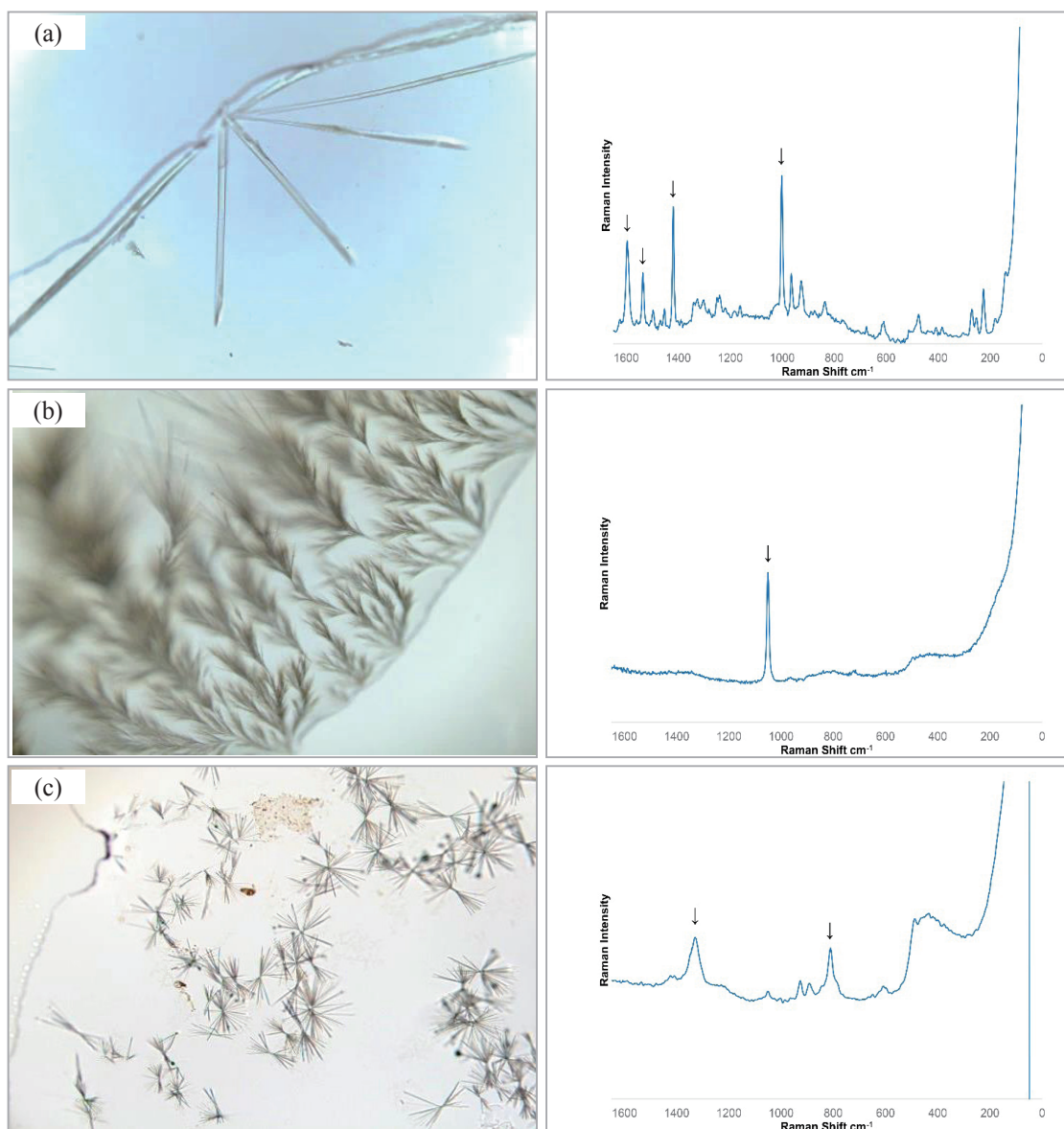


Fig. 5 Nitron crystals at 100X with corresponding Raman spectra: (a) chlorate—arrows point to peaks referenced in text at 1594-1596 cm^{-1} , 1534-1536 cm^{-1} , 1416-1419 cm^{-1} , and 1002 cm^{-1} ; (b) nitrate—arrow points to peak referenced in text at 1050 cm^{-1} ; (c) nitrite—arrows point to peaks referenced in text at 1325 cm^{-1} and 811 cm^{-1} .

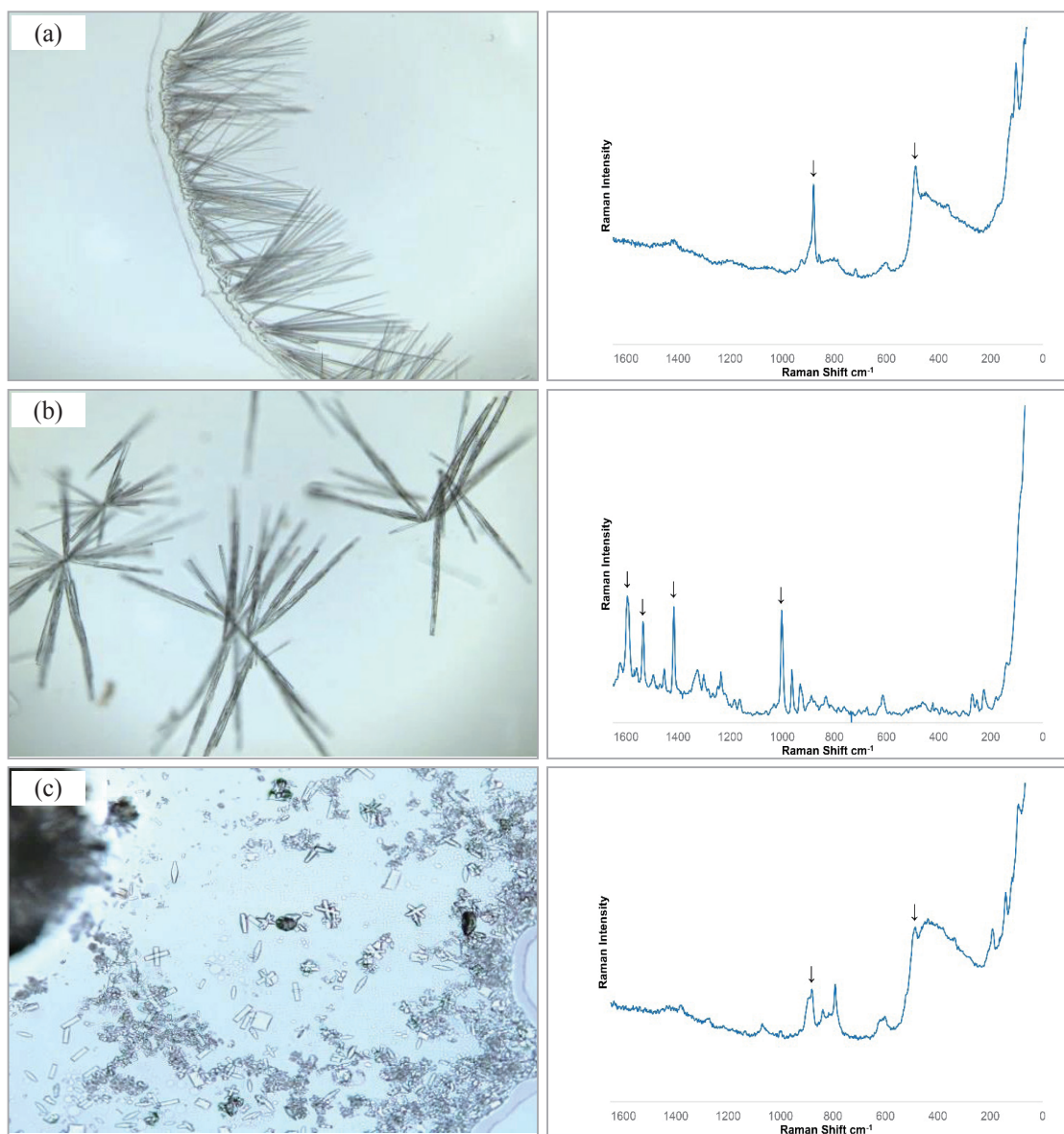


Fig. 6 Nitron crystals at 100X with corresponding Raman spectra: (a)oxalate-arrows point to peaks referenced in text at 880 cm^{-1} and 488 cm^{-1} ; (b)perchlorate-arrows point to peaks referenced in text at 1594-1596 cm^{-1} , 1534-1536 cm^{-1} , 1416-1419 cm^{-1} , and 1002 cm^{-1} ; (c)tartrate-arrows point to peaks referenced in text at 881 cm^{-1} and 791.

Although nuanced differences existed for all crystals produced, crystal habit could be categorized as blades or plates (ammonium squarate, barium squarate, calcium squarate, silver squarate), rods (sodium squarate, strontium squarate), four-pointed stars/ellipsoids (potassium squarate), dendritic needles (nitron nitrate), needles (nitron nitrite, nitron oxalate), needles to rods (nitron chlorate, nitron perchlorate), octahedral to cubic (ammonium hexachloroplatinic acid, potassium hexachloroplatinic acid) and X-shape (nitron tartrate).

Examination of the Raman spectra from crystals with similar habit shows spectra that in most cases are clearly distinguishable from each other. Silver squarate is clearly the most distinctive among squaric acid crystals with shape of blades or plates showing distinctive Raman shifts at 1764 and 1558 cm^{-1} (Fig. 3(a)). Ammonium squarate displays two Raman shifts with shoulders, one found at 728 cm^{-1} (shoulder at 708 cm^{-1}) and the other at 641 cm^{-1} (shoulder at 625 cm^{-1}) (Fig. 1(a)). Although the crystal habit is different, the ammonium squarate

spectrum is very similar to that of potassium squarate. Of all the cations tested with squaric acid, calcium squarate, barium squarate, and strontium squarate yielded Raman spectra showing the most similarity to solid squaric acid. Although difficult to distinguish by pattern recognition, changes in polarizability would still be expected to occur with different cations resulting in variation in peak shifting. Fig. 7 shows the variation in Raman spectra for squaric acid, barium squarate, calcium squarate, and

strontium squarate from 400-1200 cm^{-1} . Given the %CV found in the study (none greater than 0.1%), the Raman shift differences observed in Fig. 4 are not likely to have occurred simply due to experimental fluctuation of drift. Crystal morphology, however, can distinguish strontium squarate from barium squarate and calcium squarate. Another distinguishing characteristic is that the sign of elongation is negative for barium squarate and positive for calcium squarate and strontium squarate [12].

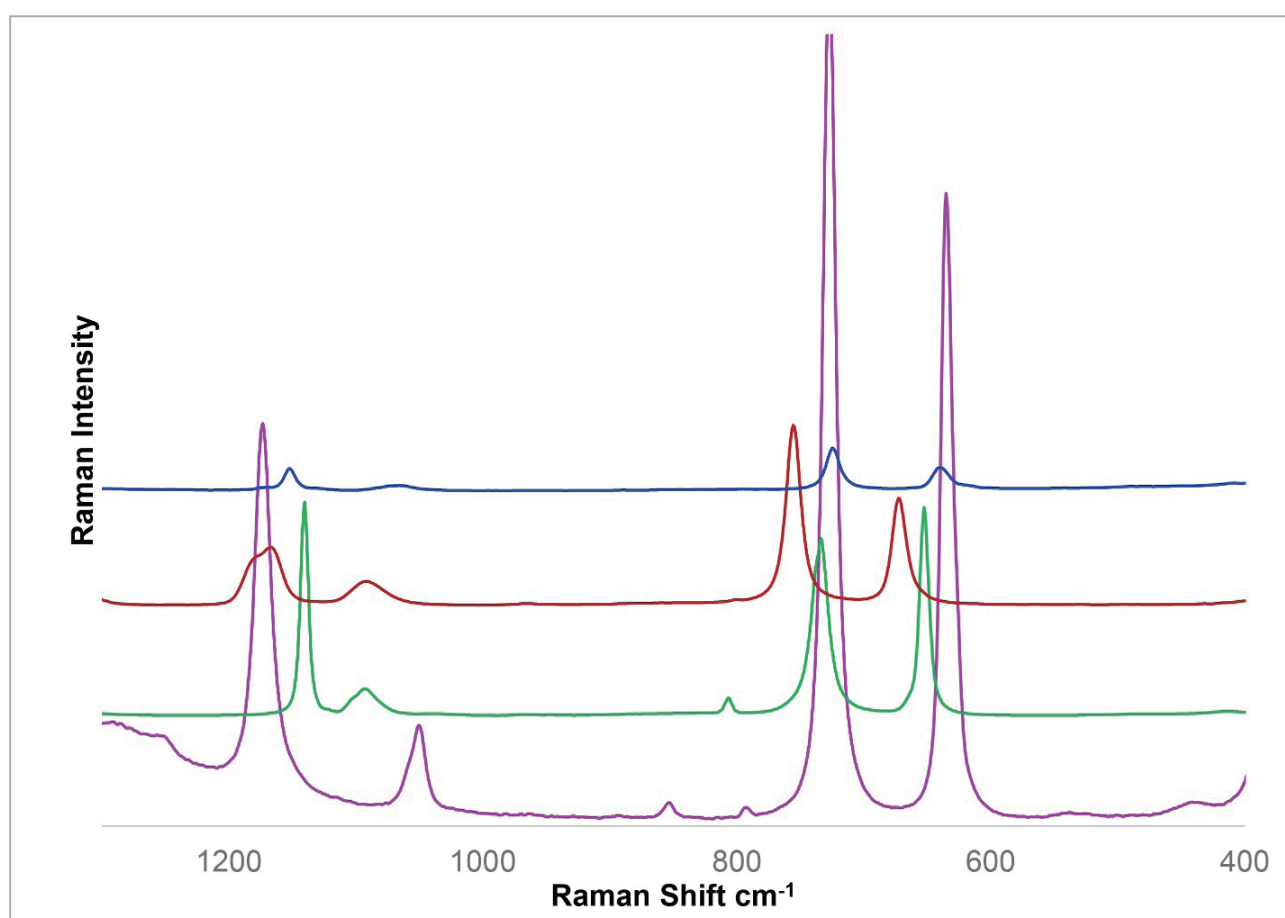


Fig. 7 Raman spectra for squaric acid (purple), barium squarate (green), calcium squarate (red), and strontium squarate (blue) from 400-1200 cm^{-1} .

Although the Raman spectra cannot be differentiated between ammonium squarate and potassium squarate, the spectra are clearly different for ammonium hexachloroplatinic acid and potassium hexachloroplatinic acid (Fig. 4). Ammonium hexachloroplatinic acid displays a peak at 180 cm^{-1} followed by a smaller one at 129 cm^{-1} while potassium hexachloroplatinic acid displays a single peak in this area of the Raman spectrum at 172 cm^{-1} .

The potassium hexachloroplatinic acid also displays a Raman spectrum closer to solid chloroplatinic acid than ammonium hexachloroplatinic acid (Fig. 8). Unlike squaric acid which produces crystals with different habits with ammonium and potassium, ammonium hexachloroplatinic acid and potassium hexachloroplatinic acid cannot be differentiated by crystal shape or color (yellow-green) under the microscope.

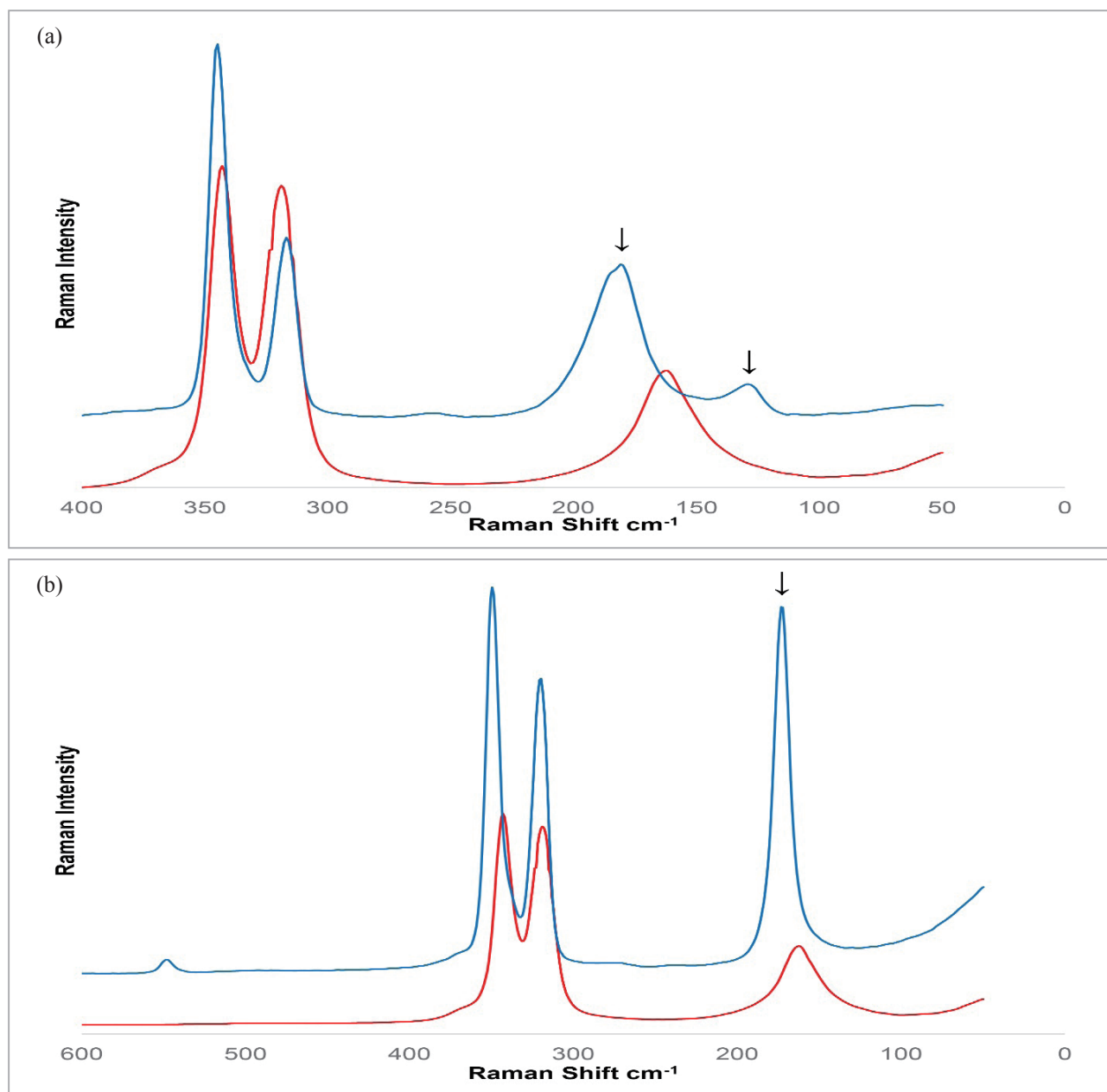


Fig. 8 Comparison of Raman spectra between ammonium hexachloroplatinic acid (arrows point to peaks at 180 cm^{-1} and 129 cm^{-1} referenced in text) and chloroplatinic acid (a) and potassium hexachloroplatinic acid (arrow points to peak at 172 cm^{-1} referenced in text) and chloroplatinic acid (b). Chloroplatinic acid is in red and ammonium hexachloroplatinic acid and potassium hexachloroplatinic acid are in blue.

Of the anions tested in the study, tartrate produced X-shaped crystals with nitron that showed Raman shifts at 881 cm^{-1} and 791 cm^{-1} (Fig. 6(c)). The dendritic needles of nitron nitrate show a characteristic Raman shift at 1050 cm^{-1} while the needles of nitron nitrite and nitron oxalate show Raman shifts at 811 cm^{-1} and 1325 cm^{-1} , and 488 cm^{-1} and 880 cm^{-1} respectively (Fig. 5(b) and 5(c)). The strong intensity peak at 1050 cm^{-1} for nitron nitrate has been previously reported in published data [23, 24].

Differentiation of chlorates and perchlorates both yielded similar crystal habit (needles to rods) with nitron and Raman spectra with defined peaks around 1002 cm^{-1} , $1416\text{--}1419\text{ cm}^{-1}$, $1534\text{--}1536\text{ cm}^{-1}$, and $1594\text{--}1596\text{ cm}^{-1}$. Previous published work also reported difficulty in differentiating chlorate and perchlorates by Raman spectroscopy. Zapata reported that perchlorate demonstrates a shift at 935 cm^{-1} while chlorate shows a peak at 932 cm^{-1} [24]. This may correspond to peaks in the study at 932 cm^{-1} (perchlorate) and 927 cm^{-1} (chlorate). Of the anions tested with nitron, only chlorate and perchlorate produced Raman spectra showing similarity to the Raman spectrum of solid nitron.

Urea did not produce crystals with any test reagents. The addition of urease, however, allowed for the detection of ammonium ion by squaric acid and chloroplatinic acid through the enzymatic digestion of urea.

Blind study results with both single-source and mixed samples yielded the correct results.

Discussion

The possibility of adding different test reagents to the same sample drop to create different microcrystals may exist. Fig. 9 shows three test reagents used to detect three ions in the same test drop. The sample reagent contains calcium ammonium nitrate, and three test reagents are added in succession (chloroplatinic acid for ammonium, squaric acid for calcium, and nitron for nitrate) to the sample reagent. Microcrystals for each ion are highlighted in the figure. Confirmation with Raman spectroscopy was achieved with three different microcrystals. With the use of multiple test drops, the proper sequence of addition must be considered depending on the ion to be detected. For example, ammonium crystals made from squaric acid were not observed after the addition of chloroplatinic acid.

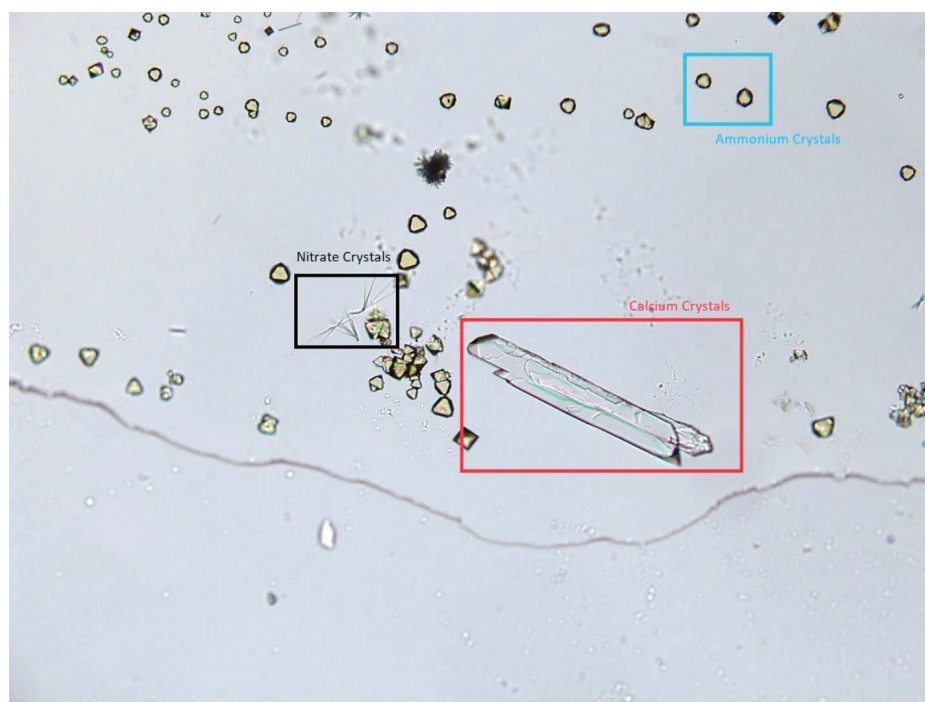


Fig. 9 Microcrystals at 100X obtained after the successive addition of chloroplatinic acid, squaric acid, and nitron to an aqueous drop of calcium ammonium nitrate. Crystals for ammonium hexachloroplatinic acid, calcium squarate, and nitron nitrate can be observed in the photomicrograph.

The list of ions examined in this study is in no way exhaustive of the possible inorganic and organic constituents in homemade and other types of explosives. Given that nitron and squaric acid can produce microcrystals with many different types of ions (as well as other test reagents not part of this study such as silver nitrate), the development of an analytical flow chart for identification of particular ions is premature but is a future and achievable goal. Furthermore, chemometrics may need to be employed for definitive identification of ions.

A more specific advantage to the presented method of analysis is the detection of urea. Though it requires an enzymatic reaction, microcrystalline tests followed by Raman microspectroscopy can detect urea where methods described in previous studies cannot. Although pre-blast analysis of urea nitrate is easy to analyze using color tests, chromatography, or spectroscopy, it is difficult to detect in post-blast debris because urea breaks down by thermal desorption to form ammonium [28]. In one study, urea was extracted with hot acetone and analyzed by HPLC/Atmospheric Pressure Chemical Ionization (APCI)/MS to detect urea, but this method is time consuming and expensive [29]. Similarly, XRD and IR spectroscopy cannot be used successfully to detect in post-blast analysis due to the impurities in the samples [30].

An advantage of microcrystalline tests is that it allows for isolation of components in mixtures which then can be examined individually. Although it is not immune from interference from substrate contamination (such as endogenous inorganic ions in soil), background interferences and resolution problems commonplace with techniques such as ion chromatography and capillary electrophoresis are not evident. In addition, the method does not suffer from reproducibility issues as there were no shifts in Raman peaks.

Another advantage is the ability to use small volumes of test sample. Positive results on 3 μL aliquots prepared from 8 mg/mL test samples were easily obtained. Thus, the amount of solid test material needed for examination was approximately 0.02 mg. Although the sensitivity of other methods in the analysis of explosives has been reported to be better [31-32], this method still allows for the analysis of trace samples.

Since the limit of sensitivity was not examined in this study, it could in fact be much lower. One study found that γ -hydroxybutyrate combined with $\text{AgNO}_3/\text{La}(\text{NO}_3)_3$ produced crystal growth with a detection

limit of 0.5 mg/mL [33]. Furthermore, microcrystalline growth of certain designer drugs was achieved with concentrations as low as 0.2 g/L [14].

Finally, a Raman microscope does not require large outlays of consumables as in other types of instrumentation. The only additional material needed is quartz and aluminum microscope slides which can be reused repeatedly after cleaning.

Conclusion

The combination of microcrystal shape and Raman spectra was used to identify urea and thirteen ions commonly found in homemade explosives. The combination of microcrystalline tests and Raman microspectroscopy offers advantages such as simplicity, low cost, minimal sample preparation, short analysis time, and the ability to detect urea. The combination of both Raman microspectroscopy and microcrystalline tests offers the potential for the identification of inorganic ions particularly in situations where each technique alone is less than discriminating.

Future Work

Although the method described is robust and offers several advantages to existing techniques, its practical application can only be proven through validation with actual casework samples which were not available to the authors. If similar results can be achieved with actual casework samples, then the methodology proposed in this study will serve as a suitable alternative to other analytical methods for the detection of inorganic explosive residues and will be of value for forensic laboratories with limited resources and instrumentation.

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