



B123 Raman Microscopy of Low Explosives and Their Combustion Products

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After attending this presentation, attendees will learn the use of Raman microspectrophotometry on trace level detection of common ingredients of low explosives and their combustion products

This presentation will impact the forensic community and/or humanity by illustrating the usefulness of Raman for trace level detection of low explosives and their combustion products with minimal sample preparation.

Background: Inorganic low explosives usually consist of oxidiser/fuel mixtures. They can be made using ordinary laboratory chemicals, ammonium nitrate fertilizer, black powder, and pyrotechnic materials from sparklers, flash powders, and fireworks. Formulations and recipes are readily available on the Internet. Common oxidising agents used are nitrates, perchlorates, and chlorates of sodium, potassium, and ammonium. Fuels include sulphur, finely divided aluminium, magnesium, titanium, zinc, charcoal, sugar, red gum and shellac.

This paper illustrates the usefulness of dispersive Raman microspectrophotometry for the detection of low explosives and their combustion products. Major techniques for the analysis of low explosives include stereomicroscopy to mechanically separate individual particles and crystals, scanning electron microscopy with energy dispersive x-ray analysis (SEM/EDX) to determine elemental composition and morphology of particles, polarised light microscopy (PLM) to screen and differentiate crystals, microchemical (spot) tests, ion chromatography (IC) for soluble ions in water extracts, and Fourier Transform infrared (FT-IR) microspectrophotometry for molecular structure elucidation.

Current techniques however suffer from several limitations. SEM/EDX is non-destructive and extremely sensitive and powerful for elemental composition but cannot identify molecular and ionic species. Microchemical tests are destructive and often lack sensitivity and specificity; expected color changes may also be masked by interferences. Ion chromatography is a destructive separation technique and although sensitive, is based on matching retention times since conductivity detectors do not discriminate ionic species. In recent years, advances in Raman spectrometer design, improved lasers and detectors, faster acquisition of Raman spectral data, increased sensitivity, easier optical alignment and instrument operation, new approaches to reduce fluorescence masking, and greater affordability have led to the growing popularity of Raman spectrometry as an alternative vibrational spectroscopic technique.

Raman spectroscopy has widely been reported as having several advantages over infrared spectroscopy. Raman analysis requires minimal or no sample preparation. Unlike IR spectroscopy, the Raman technique is not affected by atmospheric moisture. Glass cells and aqueous solutions may be used to obtain Raman spectra and the sample can often be examined *in situ* non-intrusively. The Raman spectrum covers a wider range from 150 to 4000 cm^{-1} , compared to micro-FT-IR which often uses a mercury cadmium telluride (MCT) detector limited to the range 750-4000 cm^{-1} . The far-IR region below 750 cm^{-1} often has absorption bands with useful molecular information. The IR and Raman spectra of a sample may differ considerably and hence each technique can provide additional, complementary information regarding the sample. Infrared-inactive bands may be observed by Raman spectroscopy, and bands that are weak in IR spectra are often strong in Raman spectra.

Materials and Methods: Analyses were performed on a Renishaw RM1000 Raman spectrometer. The spectrometer was calibrated using a silicon standard.

- A) General comparison of oxidisers and combustion products To ascertain whether oxidisers and their combustion products can be differentiated using Raman microscopy, the following solid phase salts were analysed and their spectra compared: potassium nitrate, potassium chlorate, potassium perchlorate, sodium nitrite, potassium chloride, potassium carbonate, and potassium sulphate. The specificity of Raman spectra for solid phase nitrates, chlorates, and perchlorates were also studied by varying the cation and monitoring Raman shifts for the different vibrational modes. Small amounts of the solids were placed on ordinary glass slides. Samples mounted on graphite stubs for SEM/EDX analysis could also be directly analysed in the Raman microscope.
- B) Repeatability of Raman shift measurements
Repeatability of Raman shifts was studied by performing two runs a day over three successive days. Up to 4 principal peaks were monitored for the six runs. The mean, standard deviation and coefficient of variation were then calculated. This study was applied to 8 oxidisers and 4 combustion products.
- C) Analysis of aqueous solutions
As water is often used to extract post-blast debris for analysis, aqueous solutions of the oxidisers and combustion products were also analysed using the technique. Solutions of 1% and 5% (w/v) of 24 salts prepared using DI water. A sample volume of 15 μL (0.15 - 0.7 mg solute) of solution was drawn into and sealed in a capillary tube (3.5 cm long x 1.5 mm outer diameter.). The tube was placed directly in the path-length of the laser beam. The effects on Raman shifts from hydration of ions dissolved in aqueous solution were investigated.
- D) Analysis of mixed salts recrystallised from aqueous solutions Ion exchange upon crystallisation of mixed salts



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from the evaporation of aqueous solutions was studied. A small volume (30 μL) of 1% or 5% solution (containing 0.3-1.5 mg solute) was placed in a cavity slide and evaporated to dryness using the "quick dry" approach or the "slow dry" approach. "Quick dry" consisted of drying on a hotplate at 60°C for 5-10 minutes. "Slow dry" was carried out under natural unforced conditions at ambient humidity and 22°C for 6-8 hours. The crystals were sampled in the same way as for original solid materials. A small amount of the solid was placed on glass slide or mounted on a carbon stub.

Results and Discussion:

- A) General comparison of oxidisers and combustion products The number of peaks, Raman shifts and peak intensities and widths of common oxidisers and combustion products were found to be significantly different, allowing the different oxyanions, sulphate nitrate, chlorate, perchlorate, nitrite, chloride, carbonate, and sulphate to be readily differentiated. Raman spectra are unique for the different functional groups (anions). For each anion, the solid phase Raman spectra were found to be specific for each mating cation.
- B) Repeatability of measurements
Good repeatability was obtained for Raman measurements. The worst case occurred for sodium salts; slight irregularities in peak shapes contributed to the apparent shifts. Since identifications are based on several peaks in the spectrum, this repeatability was sufficient for conclusive identification of oxidisers and their combustion products.
- C) Analysis of aqueous solutions
In aqueous solution, the Raman spectra of nitrates of ammonium, barium, sodium, and potassium could not be differentiated. The effect of cations disappeared for the salts in solution. The spectra showed higher base-line, peak broadening, loss of small peaks and shoulders, shorter peaks, and lower resolution. Shifts were observed in the peaks between solid state and dissolved salts. Raman spectra of recrystallised oxidisers were indistinguishable from those of the original solid salts.
- D) Analysis of mixed salts recrystallised from aqueous solutions Ion exchange was observed in some cases but not in others. Crystallisation is influenced by the relative solubilities and ionic radii of the competing ions in solution.

Conclusion: Results indicate that Raman microscopy is a very powerful non-destructive technique that can easily identify oxidisers at low detection limits. Spectral resolution was of the order of 1 cm^{-1} , and Raman spectroscopy was found to conclusively identify ionic species, even in aqueous solutions. High spatial resolution was achieved; a microscope objective of 50x gave a laser spot size of 2 microns on the sample, indicating a high sensitivity of approximately 20 picograms of material. Combined with elemental information from SEM/EDX, the new Raman technique allows quick identification of both the cationic and anionic moieties of oxidisers with minimal sample preparation.

Raman Microscopy, Low Explosives, Oxidisers