

GSR analysis with inVia™ InSpect



Forensics

Gunshot residues

Gunshot residue (GSR) is an important class of trace evidence, relevant to investigations involving the alleged use of a firearm.

Firing a weapon creates a complex mixture of chemical species. A subset of these compounds, both organic and inorganic, are crucial to forensic investigations of shootings. Multiple studies have shown these key materials are highly unlikely to be found in the environment but are known to be created during the conditions that exist when a weapon is fired^{1,2}.

The combination of well-established science and long-standing practice makes this class of evidence compelling to the courts; so targeted forensic analysis focuses on revealing these key materials³.

At present, the analysis of metallic residues and inorganic species is dominated by SEM-EDS, with bespoke benchtop solutions for GSR analysis available commercially. However, the increasing number of ammunitions containing lower levels of certain metals, especially lead, have resulted in some of the key inorganic GSR ('IGSR') markers being far less ubiquitous or even completely absent. It's a problem that's been recognised worldwide⁴.

Other analytical techniques are therefore needed, to access a broader range of high-fidelity markers – including those found in organic GSR ('OGSR') residues. Raman microscopy—a fusion of Raman spectroscopy with optical microscopy—provides highly specific chemical analysis of GSR.



Figure 1. The inVia™ InSpect confocal Raman microscope.

Raman spectroscopy

In this note we explore some of the key characteristics of the Raman technique for GSR analysis, and their benefits. For instance, Raman microscopy is already well-known and widely accepted for the analysis of organic and inorganic particulates and is highly complementary to existing methods. Also, Raman spectroscopy is a non-contact and non-destructive technique—normally requiring very little sample preparation—so there's minimal time lost to sample prep, minimum sample loss, and a low risk of cross-contamination.

These benefits, along with its ability to focus at the diffraction limit of visible light to analyse micrometre sized particles and features, are why Raman spectroscopy is being more widely adopted^{5,6,7}. It is increasingly clear that Raman microscopy can be added to an existing forensic laboratory and included within existing analytical pathways.

inVia InSpect Raman microscope

inVia InSpect (Figure 1) is a member of Renishaw's inVia line of confocal Raman microscopes, designed for use in forensic laboratories. It draws together all of Renishaw's experience in developing instrumentation for forensic scientists.

Renishaw has configured InSpect to be ideal for supporting the research, development, and routine analysis requirements of forensic investigations.

Analysing cartridge case GSR

We can illustrate some of inVia InSpect's key features for GSR studies using mechanically recovered residue from a spent cartridge case, which we deposited onto a clean stainless-steel microscope slide. GSR collected at a crime scene is more usually recovered from a suspect or victim's body or clothes, from the weapon involved, or from the immediate environment in proximity to the weapon at the point of discharge. Suitable methods of recovery are well documented, and include wet or dry swabbing, tape lifting and gravitational deposition - as well as direct analysis *in situ*.

The ammunition used is lead (Pb)-free: basic details of its composition are known from the manufacturer's data sheet. The round was fired from a breach/barrel combination that had previously been used for multiple other firings; as such, a degree of cross-contamination could be expected.

As Figure 2 shows, the residue varied dramatically in particle size and shape. Morphologies range from spherical particles a few micrometres in size, to complex multifaceted particles many hundreds of micrometres across. Clearly heterogeneous, the larger particles tend to be agglomerates of OGSR with inclusions of IGSR.

The first task during analysis was to find areas of interest. The microscope slide was loaded onto the InSpect's MS30 high-speed encoded stage, using the EasyMove sample loading system that allows easy transition between manual, trackball, and software sample positioning. Then the integrated microscope eyepieces and high-resolution video camera were used to survey the sample at lower magnification before refining and targeting suspect particles at a higher magnification.

The Leica DM-series microscope at the heart of every InSpect system is fitted with a range of long working distance microscope objectives, as well as being equipped with multiple contrast methods. You can switch rapidly between brightfield, darkfield and polarisation contrast options, choosing different magnification objectives to balance field of view, depth of focus, and numerical aperture, to optimise your image.

The integration between InSpect's high performance 5MP video camera and the MS30 stage also allows seamless creation of extended images, covering a larger area than a single frame of the video camera, using the montage feature of the WiRE™ (Windows-based Raman Environment) software; you can also account for tilt using the Surface correction feature.

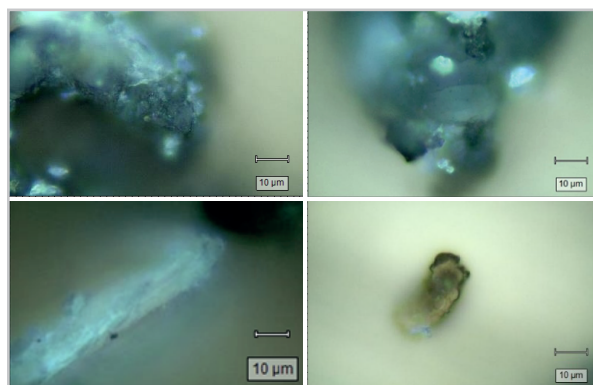


Figure 2 – images of four different particles (all using 100x objective).

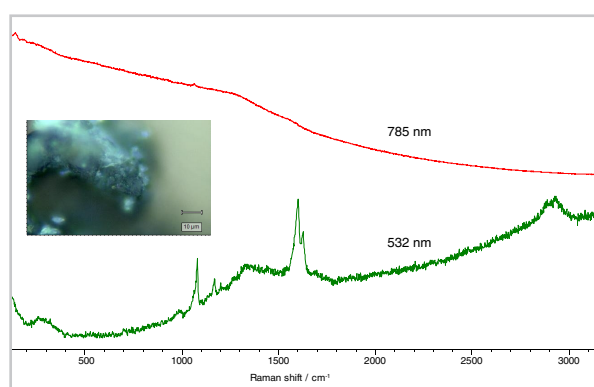


Figure 3 – in this case, 532 nm excitation yields a Raman spectrum revealing both organic and inorganic components, as well as unresolved signal from carbonaceous species; in contrast 785 nm excitation yields very little recognisable data.

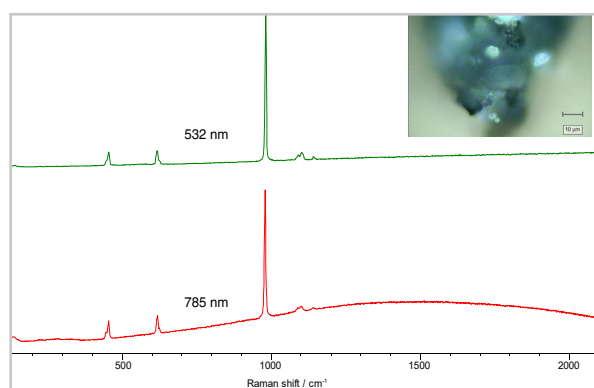


Figure 4 – in this case, both 532 nm and 785 nm yield excellent spectra of a dominant inorganic component, with excitation at 532 nm avoiding the luminescence background generated at 785 nm.

The WiRE software suite allows you to define single points, clouds or swarms of discrete points, or regular arrays. You simply choose the preferred option and the software interprets your requirements.

Having decided where to analyse, a preferred excitation wavelength was selected and the four particles were analysed.

You'll notice that the figures contain two sets of data; one collected using green excitation at 532 nm, the other using deep red excitation at 785 nm. This is very common practice: sometimes the data collected at one excitation wavelength has greater information content than the other, whilst comparison of spectra acquired at different wavelengths can show subtle but important differences.

The data (Figures 3 to 7) reveal that detailed signatures from GSR are recoverable from complex residues using inVia InSpect.

The primer (diazodinitrophenol, DDNP), propellant (nitrocellulose), and other additives (strontium and barium nitrates) react with other minor components, the casing, projectile, breach and barrel to yield a rich mixture: Figure 3 shows as much, with amorphous carbon, degraded organic material, an inorganic carbonate species and a highly characteristic doublet at 1605 cm⁻¹ and 1629 cm⁻¹ shift with a single peak of lesser intensity at 1170 cm⁻¹ shift. According to several previous authors, the bands at these positions are strongly associated with conserved markers for OGSR, related to compounds such as centralites, used in small quantities.

Figure 4 shows the distinct contrast occasionally observed; in this case dominated by and likely representing a single phase of barium sulphate. Barium salts could be expected, based on its composition - however, previous studies have shown that other reasons (potential contaminants) could also be possibilities.

Figure 5 offers ample evidence for needing two lasers; whilst limited features are visible in the 532 nm spectrum, 785 nm excitation provides a far richer and more detailed picture.

The data in Figure 6 are also 785 nm-excited, for the same reason: the inherent variability of composition as a function of position is clearly seen, as well as clear conservation of key features, such as the peaks at 1605 cm⁻¹ and 1629 cm⁻¹ shift. At least one of the spectra has an additional phase, giving strong characteristic bands.

Finally, the simplicity of Figure 7 belies the complexity of the composition; the two distinct bands at around 1065 cm⁻¹ and 1080 cm⁻¹ are either due to distinct carbonate species, or due to a high-temperature mixed mineral phase.

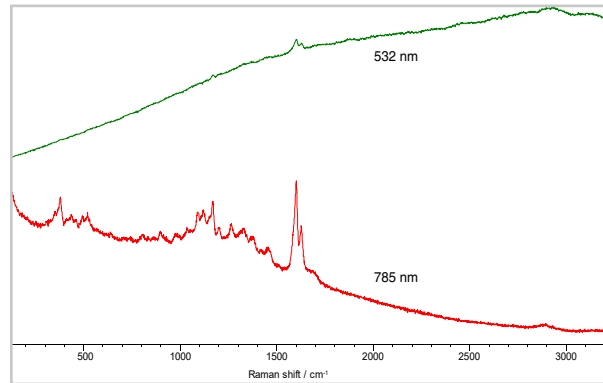


Figure 5 – 532 nm reveals the presence of an organic component over a strong fluorescence background, whilst 785 nm reveals much more detail with minimal interference.

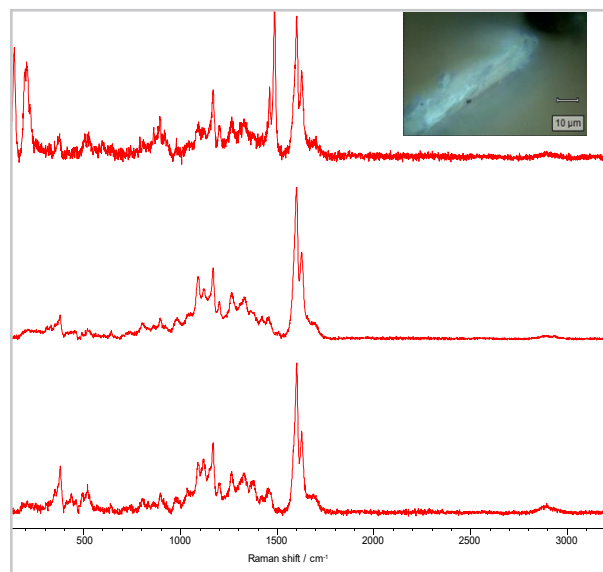


Figure 6 – three spectra taken from different positions highlight the inherent heterogeneity observed; being able to control the point of analysis allows different contributions, organic and inorganic, to be noted.

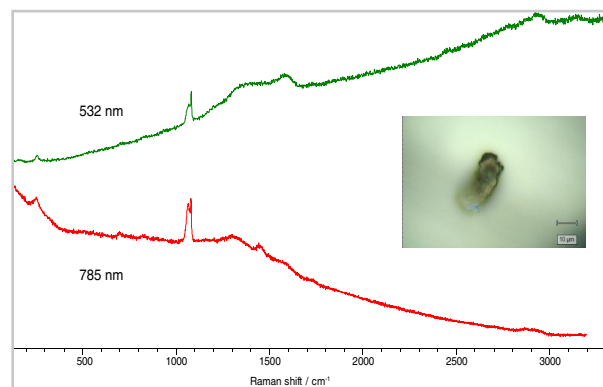


Figure 7 – in this case, a broad background showing signs of amorphous carbon also contains the Raman signal indicating a mixed inorganic phase, either a mix of distinct species or a complex species with mineral-like structure.

Analysis and assignment of the spectra is a key point, whether researching the composition or analysing for the presence of GSR. A range of reference sources are available for the components seen here – from general spectral reference libraries, such as those commercially available with InSpect, to more comprehensive and bespoke reference databases created by individual groups from authentic reference standards. The WiRE software supports both approaches; whichever suits the task better.

Having two laser wavelengths is crucial. Every InSpect system comes equipped with two lasers that are permanently mounted. Changing wavelengths is simple and completely automated; there is no need for the user to change any components by hand, or to align the system manually - it is fast and automated, with built-in optimisation. And because the two lasers are permanently mounted and the MS30 motorised stage is precision feedback controlled, it's possible to return to the same point on the sample, even after changing laser wavelengths, without manual intervention.

An integrated solution

InSpect also offers powerful capabilities for particle analysis, and for combining Raman data with imagery from other microscopy techniques.

The Particle Analyser software module adds morphology to the basic spectroscopic description of your data. Size and shape information can either be generated using the InSpect's optical microscopy capabilities, or by importing from an alternate source (such as SEM) using the Correlate software module. Morphology can then be used to direct acquisition of Raman data – to focus on particle with characteristics of most interest, saving time.

But you can also use the Correlate™ module to create images that fuse together imagery from elementally-sensitive techniques (such as SEM-EDX) with structural and compositional data from Raman measurements – including Raman images, created from data collected using InSpect's StreamHR mapping capabilities. Fused images can convey complex information more straightforwardly than single images – increasing the impact of your analysis, creating a compelling narrative.

Conclusions

InSpect provides a comprehensive package for the analysis of gunshot residue irrespective of its origin, delivering benefits for detection and identification of both organic and inorganic residues. It complements your existing suite of instruments and extends their capabilities – enhancing the range of analytical options you can bring to bear when analysing GSR.

References

- 1 Dalby et al, **J Forensic Sci** (2010) <https://doi.org/10.1111/j.1556-4029.2010.01370.x>
- 2 Maitre et al, **Foren Sci Int** (2017) <https://doi.org/10.1016/j.forsciint.2016.09.003>
- 3 See, for example, **ASTM 1588-17** "Standard Practice for Gunshot Residue Analysis by Scanning Electron Microscopy/Energy Dispersive X-Ray Spectrometry" DOI:10.1520/E1588-17
- 4 Goudsmits et al **Science & Justice** (2016) <http://dx.doi.org/10.1016/j.scijus.2016.06.007>
- 5 Abrego et al **Analyst** (2014) <https://doi.org/10.1039/C4AN01051E>
- 6 Stich et al **J Raman Spectrosc** 29(9) 787-790 (1998)
- 7 Bueno et al, **Anal Chem** (2012) <http://dx.doi.org/10.1021/ac203429x>

A range of related Renishaw literature is available. Please ask your local Renishaw representative for more information.

Renishaw. The Raman innovators

Renishaw manufactures a wide range of high performance optical spectroscopy products, including confocal Raman microscopes with high speed chemical imaging technology, dedicated Raman analysers, interfaces for scanning electron and atomic force microscopes, solid state lasers for spectroscopy and state-of-the-art cooled CCD detectors.

Offering the highest levels of performance, sensitivity and reliability across a diverse range of fields and applications, the instruments are designed to meet your needs, so you can tackle even the most challenging analytical problems with confidence.

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