In a new series Dr Christina Baxter, of Emergencyresponsetips.com, offers helpful advice for first responders. This issue is Raman spectroscopy.

Keeping you safe!

This new column is intended to provide operational guidance to the hazmat/ **CBRNE** community regarding the selection and performance of equipment and tactics. For this first edition, we are focussing on Raman spectroscopy and instrument selection.

There are many Raman spectroscopy instruments on the market today. When selecting the appropriate device for your team, several important factors should be considered. One of these is the wavelength of the laser - ultraviolet (UV), visible (VIS) and near-infrared (NIR) lasers are all available today with nearinfrared being the most common. There are trade-offs which the user must balance when choosing the wavelength; these include scattering efficiency, photon energy, fluorescence, spectral resolution and

> detector availability. Generally, as the wavelength increases from UV (ie 325-nm) to VIS (ie 532nm) to NIR (ie 785-nm, 1064nm), signal intensity, photon energy, fluorescence and spectral resolution decrease while detector complexity increases.

Risk of deflagration

The safety concern that has received the highest level of attention over the years has been the potential for excessive heating of samples due to the energy of the illuminating laser. Work performed by Harvey and Wright at the Pacific Northwest National Laboratory (report PNNL-13942) demonstrated that 12 seconds of illumination from the commonly used 300mW 785-nm NIR laser resulted in sample temperatures ranging from 28.0°C for white samples to 146.8°C for black samples. These thermography experiments led to the recommendation that grey or black samples, or samples on a dark background, should not be analysed using the standard 300-mW 785-nm systems. In addition, the report recommends that explosives, explosive mixtures and propellants only be analysed in milligram quantities as unacceptable risk could be posed by larger sample sizes. One way in which many commercial instruments attempt to avoid these issues is by using raster scanning of the sample. In this way, the energy is dispersed across an area of the sample versus a point in the sample.

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Eve safety

Another significant safety concern when using Raman spectroscopy instruments, especially those with lasers in the NIR region, is that the power densities are high enough to damage the user's eyes. Just one glance into the direct or reflected laser can cause irreversible ocular damage. The eye's natural way of protecting itself using the blink reflex is not fast enough to protect against the power of lasers in the NIR region (greater than 1mW). When using non-eye safe Raman systems, it is imperative that eye safety is maintained by wearing appropriate safety goggles, avoiding reflective surfaces, and using sample containment devices, when available.

Fluorescence

Fluorescence interference may be caused by either the compound being analysed or impurities in the sample. In this case, molecules absorb the laser energy causing the molecule to be excited to a higher electronic state. As the molecules relax to the lower energy level, fluorescent light is emitted. This phenomenon is dependent upon the excitation wavelength. In the UV region, sample fluorescence can often mask the entire Raman signal. As the wavelength of the laser is increased towards the NIR region, the fluorescence decreases. In fact, this lack of fluorescence interference is one of the main selling points of 1064-nm Raman systems over the traditional 785-nm systems or those of lower wavelengths.

Future systems will likely take advantage of time-resolved spectroscopy as a means of removing much of the fluorescence signal, especially at the lower wavelengths. A common example of

fluorescence interfering with sample adjudication on a 785-nm instrument is seen with heroin which naturally fluoresces.

The Future: proximity and stand-off detection

While most Raman spectroscopy instruments used by the emergency response community are point detectors, there are two systems currently working towards proximity, or stand-off, detection. The Mira DS has an optical attachment designed for remote identification from up to 1.5metres (4.92ft) away. The Pendar X10 system provides a dedicated remote identification capability from up to 1metre. Both systems utilise raster scanning to disperse the laser energy while also providing enhanced mixture identification. The Pendar X10 also has the added benefit of limited fluorescence interference and lower laser energy than most NIR products. Other systems focus on utilising UGV and UAV interfaces to achieve stand-off capability.



Finally, it is imperative that you try any instrument that you are considering procuring. Make sure that the libraries are suitable for the threats of interest, the software is simple yet powerful, and that detector maintenance, logistics, and upkeep are within your capability, technically and financially. Until next time,



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