WHITE PAPER

Fluorescence-free 785 nm material identification with MIRA XTR DS

In Raman spectroscopy, accurate and sensitive identification of chemicals and materials can be compromised by fluorescence from laser excitation of the target substance itself and/or interferents in the sample matrix. Fluorescence emission in Raman spectra reduces the signal-to-noise ratio and can obscure signature peaks assigned to the unique Raman-active vibrational modes of molecules. This restricts the breadth of illicit and hazardous materials that can be identified for actionable intelligence by first responders, law enforcement agents, as well as military and customs personnel. Recent advances have had some success in mitigating the impact of fluorescence on data quality; however, **compact commercially available Raman devices that provide a universal solution for suppressing fluorescence are lacking**. MIRA XTR DS fills this void with a state-of-the-art handheld Raman system that revolutionizes material identification in complex environments.

Metrohm
Raman

Survey of Fluorescence Suppression Methods

Developers have focused on mechanical and computational solutions for reducing or eliminating spectral interference, resulting in a small handful of fluorescence-free portable Raman devices that perform with varying levels of success **[1–3]**. A notable example is the Bruker Bravo™, which uses patented Sequentially Shifted Excitation, or SSE, technology and employs a DBR (distributed Bragg reflector) diode laser that shifts excitation wavelength as a function of temperature **[4,5]**. The Raman signal shifts with incident wavelength, but fluorescence emission does not, and on-board data processing can distinguish the spectrum of elastically scattered light. This system produces high-quality information, but sacrifices cost and size in order to accommodate a DBR laser. It also suffers from shortened operational lifetimes due to constant temperature cycling of the laser.

A second example of fluorescence mitigation in handheld Raman devices is the Rigaku Progeny ResQ™. This instrument utilizes a 1064 nm laser to excite samples below the UV-visible electromagnetic range in which fluorescence occurs. The disadvantage of long wavelength excitation is that the intensity of the Raman response is inversely proportional to incident wavelength according to λ^{-4} or $1/\lambda^4$ **[6]** and the resulting signal is 3.4× weaker for 1064 nm than for 785 nm excitation. High-power lasers (420 +/– 30 mW) are employed to compensate for poor signal-to-noise, while lower power lasers (≤ 100 mW) are sufficient for good Raman signal acquisition at 785 nm. In addition, the capture of scattered wavelengths outside of the silicon detection range requires expensive, cooled InGaAs (Indium Gallium Arsenide) detectors. The result is a bulky device that suffers from reduced operational times in the field due to the increased power requirements. Additionally, test samples (particularly those of dark coloration) are susceptible to damage such as burning when exposed to a high-power laser.

Finally, while 785 nm excitation is less prone to fluorescence interference than lasers operating in the 400–700 nm range of the spectrum (e.g. green 532 nm lasers), many samples emit levels of background fluorescence that are sufficiently strong to conceal Raman signals when excited in the red to near-infrared (IR) region.

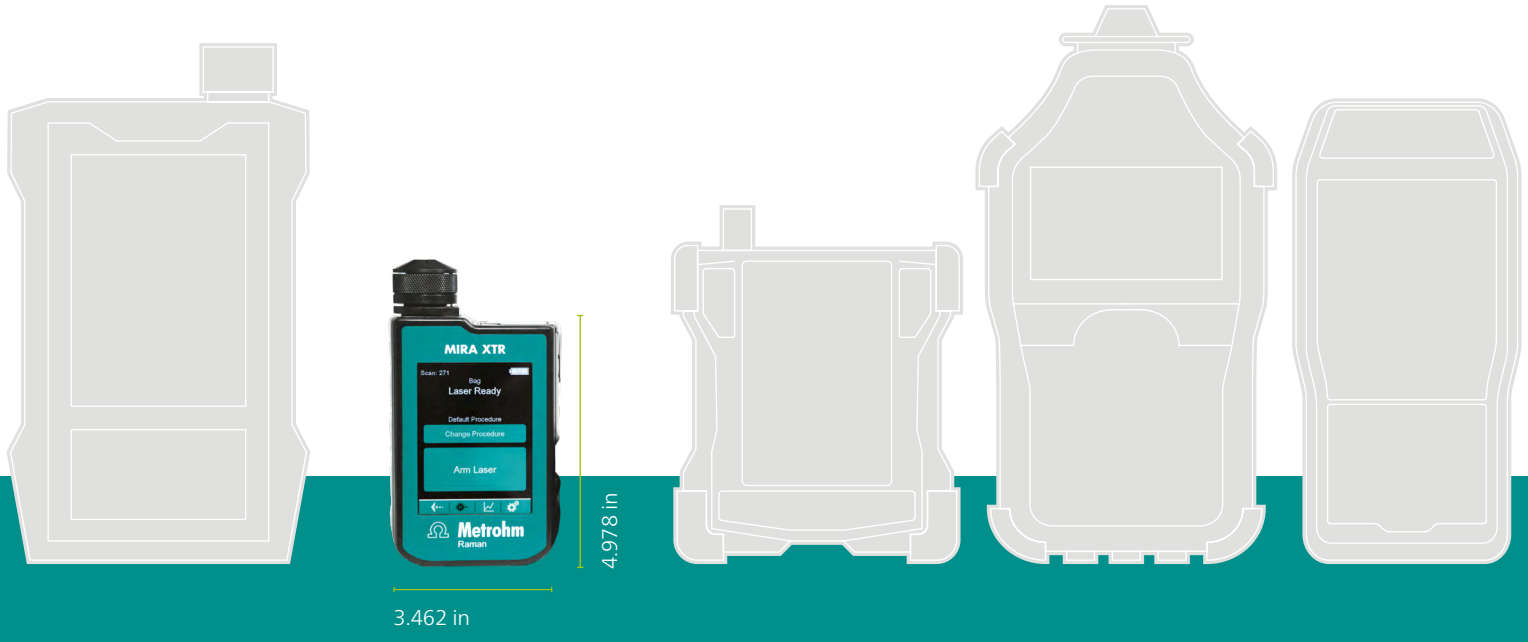

Figure 1. Relative scale of commercially available "handheld" Raman devices.

RAMAN EXTRACTION

Fluorescence in a Raman spectrum contributes undesirable noise that distorts the baseline and obscures Raman peaks. This can be seen in **Figure 2**, both as a partial effect at 1064 nm and fully at 785 nm. It creates a baseline that cannot be described mathematically, and therefore cannot be subtracted mathematically.

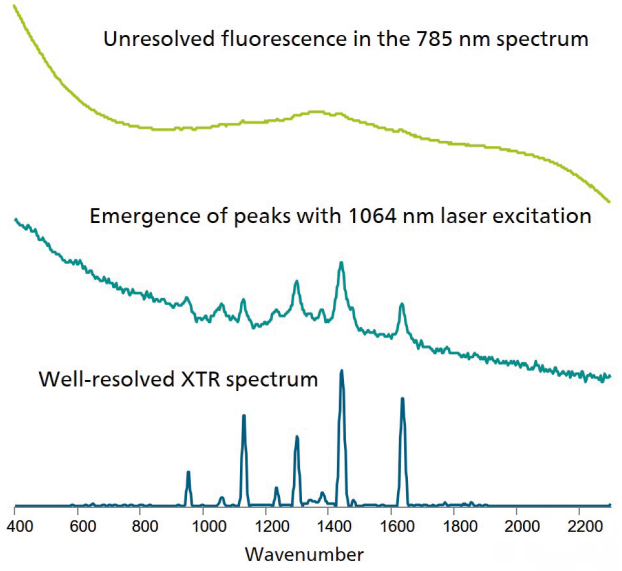

Figure 2. Fluorescence in the Raman spectrum.

In terms of instrumentation, the detector cannot distinguish between Raman scattered light and fluorescence. Very large and expensive Raman systems can be built that use the time difference of Raman scattering (instantaneous) and fluorescence (nanoseconds) to separate the signals **[7]**. However, this is impractical for handheld Raman systems.

XTR® (which stands for «Raman eXTRaction») is Metrohm Raman's patent-pending proprietary method to differentiate the signals stemming from fluorescence and Raman scattering and bin them into two distinct spectra. MIRA XTR DS produces a fluorescence spectrum with its corresponding intensity and shape, and it generates a pure Raman spectrum of just the Raman scattered light.

MIRA XTR DS

The appropriate instrument for diverse on-site applications balances integrated design and functional features. While progress has been made in the performance of portable Raman devices, compact and cost-effective solutions for fluorescence mitigation are still lacking. MIRA XTR DS fills this gap with a handheld Raman system that uses a low cost, low power 785 nm laser with silicon detectors for sensitive fluorescence-free detection.

MIRA XTR DS rapidly eXTRacts the Raman signal from spectra complicated by fluorescence with advanced, patent-pending algorithms. Built on the MIRA DS platform, MIRA XTR DS maintains all the benefits of its predecessor for chemical and material identification.

MIRA XTR DS: A handheld Raman system that uses a low cost, low power 785 nm laser with silicon detectors for sensitive fluorescence-free detection.

MIRA XTR DS

- Achieve sensitive, fluorescence-free detection using adjustable low power lasers.
- Enjoy the rugged, compact footprint designed for field-based defense and security professionals.
- Experience flexible sampling with inter-changeable SmartTips for contact, through packaging, and standoff data acquisition.
- Interrogate materials accurately and thor-oughly, with reduced risk of sample burning with Orbital Raster Scanning (ORS).
- Have confidence in a broad scope of applications and extensive material ID with a library of >21,000 substances.
- Get actionable intelligence with HazMasterG3™ software, and share results instantly with the MIRA Cal M mobile app.
- Analyze complex mixtures with mixture matching and trace detection capabilities.

Fluorescence-free Material Identification

Test materials evaluated for fluorescence mitigation with MIRA XTR DS included hazardous chemicals, illicit drugs, ingredients and products commonly used in the food and beverage industry, and an assortment of manufactured materials. Liquids were examined in glass vials using the vial-holder attachment, and solids were directly interrogated with the iUA- intelligent Universal Attachment. Proprietary SmartAcquire routines automatically optimized acquisition parameters for collection of the highest quality data, including laser power, integration time, and spectral averaging. For comparison, 785 nm and 1064 nm Raman spectra were collected with MIRA DS and a commercially available handheld Raman device, respectively.

MIXTURE ANALYSIS AT 785 NM

Figure 3 contains overlaid 785 nm and XTR spectra that illustrate both the extraordinary ability of MIRA XTR DS to eXTRact Raman data from a mixture of highly fluorescent hydrocarbons and the resolution that permits visual confirmation of both solvent and solute. MIRA XTR DS yields high information content with excellent peak resolution. The characteristic flat baselines contribute to excellent signal-to-noise and are superior to spectral processing using baseline-correction. In contrast, 785 nm laser excitation without XTR is dominated by fluorescence emission across the spectrum, which obscures weaker Raman signals.

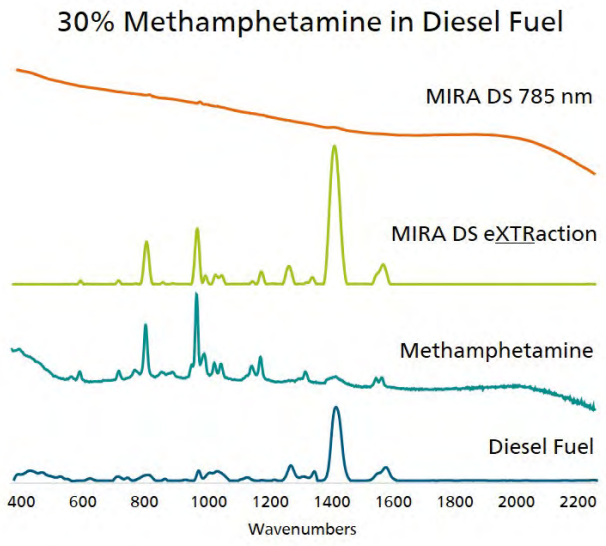

Figure 3. Each component in a methamphetamine and diesel fuel mixture can be distinguished in the MIRA XTR DS spectrum.

FLUORESCENT EXCIPIENTS AT 785 NM AND 1064 NM

MIRA XTR DS demonstrates superior resolution in comparison with traditional handheld 785 nm and 1064 nm systems in Raman analysis of two common excipients found in food and drug products (**Figure 4**).

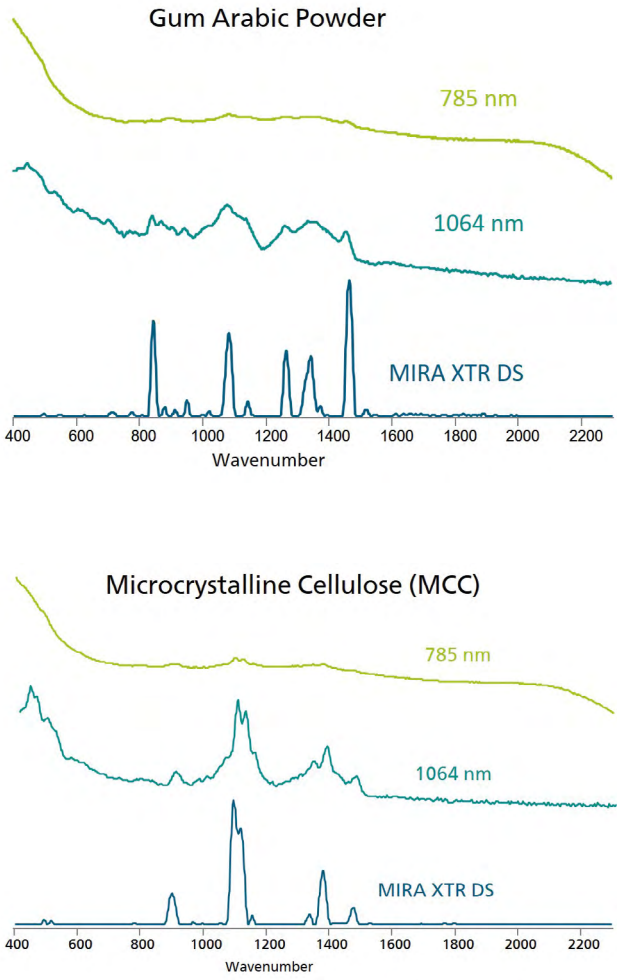

Figure 4. MIRA XTR DS demonstrates improved signal and resolution over traditional handheld 785 nm and 1064 nm systems.

Excitation at 1064 nm shows some improvement over traditional 785 nm interrogation, but even at this wavelength, spectra for both excipients lack sufficient signal-to-noise and peak resolution for confident library matching. Gum Arabic and microcrystalline cellulose (MCC) are excellent examples of fluorescent excipients that could potentially obscure the signal of other target ingredients in a mixture.

FLUORESCENCE AT 785 NM AND BURNING AT 1064 NM

Strongly colored materials, such as a black plastic cap and blue cardboard, traditionally pose a challenge for measurement with 785 nm Raman systems. High quality data is obtained with MIRA XTR DS, which is in stark contrast to interrogation using both 785 and 1064 nm lasers, as seen in **Figure 5**. The spectra of both materials at 785 nm showed the broad, characteristic emission of fluorescence. Excitation at 1064 nm resulted in immediate burning of both plastic and paper cardboard. It is well known that this can be an issue, and the manufacturer of the system used here offers a large spot adapter (LSA), designed to spread out incident laser light and reduce sample damage. However, high laser powers are notorious for causing burns.

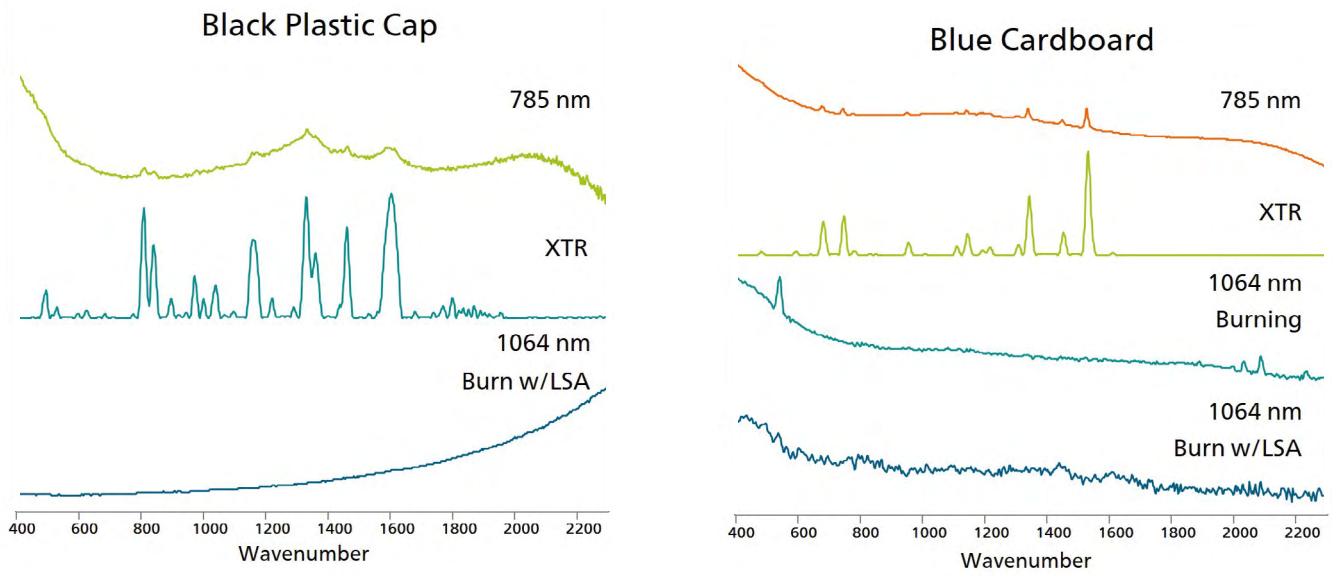

Figure 5. Raman spectra for two colored materials tested at different wavelengths and with MIRA XTR DS.

THE POWER TO AUTHENTICATE MATERIALS

Food authentication is highly desirable when it comes to traditional, certified products like meat, cheese **[8]**, olive oil, and honey. Because Raman has the sensitivity to distinguish between different sugars **[9]** and even grass-fed vs. grain-fed beef **[10]**, it is posited as a method for instant, on-site interrogation of other food products. A more illustrative application of fluorescence eXTRaction can be seen in **Figure 6**.

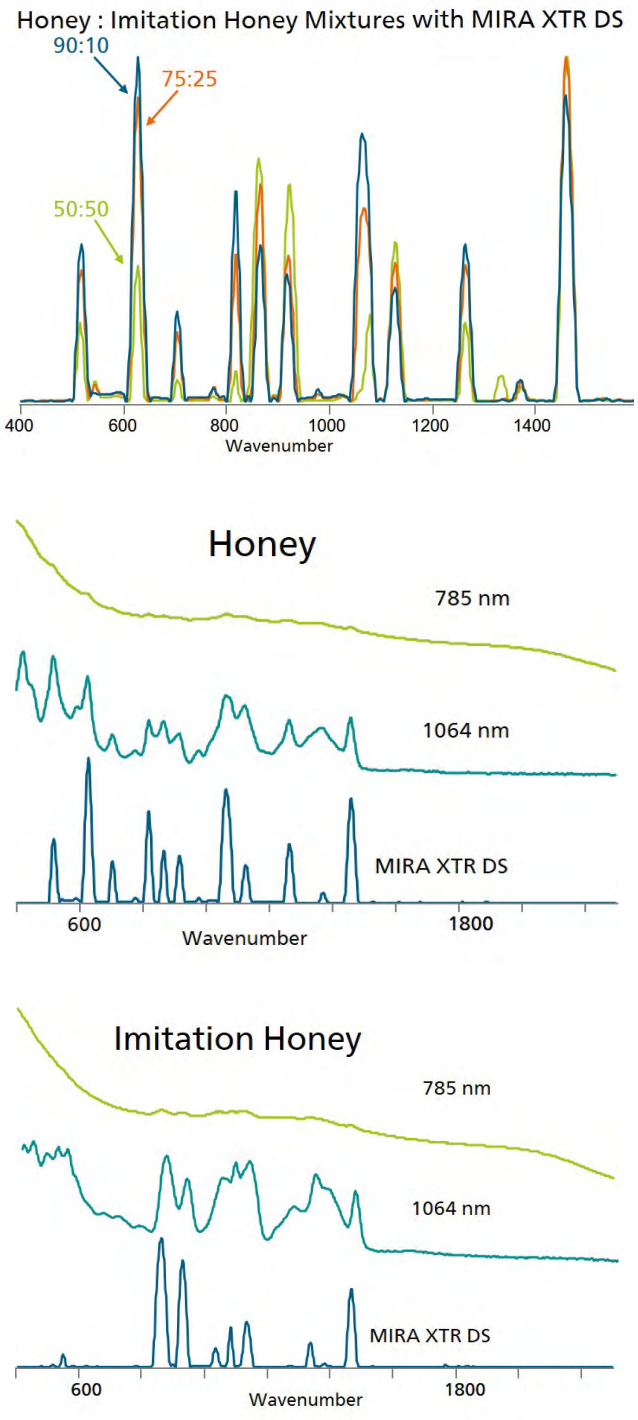

Figure 6. The difference between real and imitation honey can be detected with MIRA XTR DS at sufficient sensitivity to perceive different mixtures of the two substances.

FENTANYL ANALYSIS WITH MIRA XTR DS

Capabilities of MIRA XTR DS for eXTRacting Raman spectra from background fluorescence can also be essential in the detection of narcotics and illicit drugs. Butyryl fentanyl and acetyl fentanyl are both «designer drug» analogues of fentanyl **[11]** and reveal signature peaks of low intensity with 785 nm laser excitation that are difficult to resolve in spectra dominated by fluorescence interference.

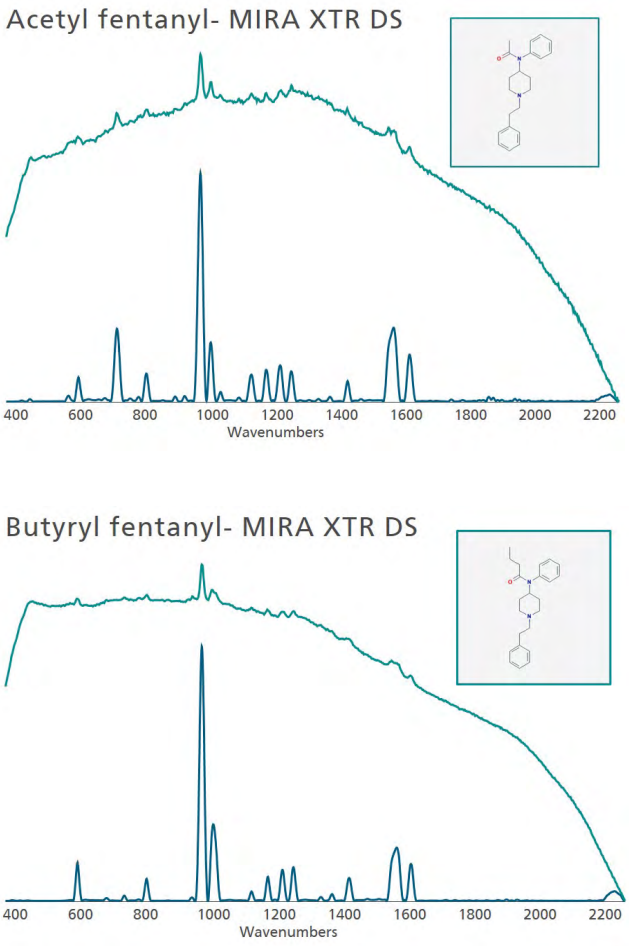

Figure 7. MIRA XTR DS can distinguish very similar molecular analogues of fentanyl.

Any ambiguity regarding their accurate identification and clear discrimination is easily overcome with XTR spectral processing. Although very similar in their chemical composition and structure, the implementation of XTR spectral processing reveals a Raman peak positioned within the 600–800 cm^{-1} range in **Figure 7** (top) that is unique to acetyl fentanyl.

SUMMARY

MIRA XTR DS is the evolution of handheld Raman spectroscopy. It overcomes the longstanding limitation of fluorescence interference and integrates this capability into one of the most affordable and compact instruments available on the market. Now users can proceed with enhanced confidence in both data quality and the ability to make informed decisions in the field.

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