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FT-Raman: an invaluable addition to the forensic arsenal to combat the opioid epidemic

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Introduction

Illicitly manufactured fentanyl is becoming a major driver of opioid overdose. According to the Centers for Disease Control and Prevention (CDC), illegal, lab-made fentanyl was involved in more than 50% of opioid overdose deaths in 2016.[1] The growing opioid epidemic presents multifaceted challenges for law enforcement, first responders, and forensic lab personnel. In particular, the high potency of fentanyl and fentanyl analogues makes accidental exposure life-threatening, with ingestion, inhalation, and absorption through the skin as possible exposure routes. With a lethal dose of only a few milligrams, fentanyl is considered 50-100 times more potent than morphine. Carfentanil, a fentanyl analogue, is approximately 100 times more potent than fentanyl. Consequently, the CDC has issued a health alert on the rise of unintentional overdoses of clandestinely produced and trafficked fentanyl in the form of counterfeit pills and heroin adulterants.[1-2] The situation is further exacerbated by the waves of new synthetic opiates. Through chemical modification, new potent fentanyl analogues are created at a fast pace in underground labs, keeping authorities constantly on their toes to identify these emerging chemical entities and to understand their pharmacology and toxicology.

The challenges in the detection, identification, and screening of synthetic opioids mandate the use of multiple analytical techniques and instrumentation, both field-deployable and laboratory-based, in a concerted and holistic manner. For example, The CDC advises two-tiered testing, an enzyme-linked immunosorbent assay (ELISA) screen followed by gas chromatography/mass spectrometry (GC/MS) to identify the fentanyl compound in blood and urine in the cases of suspected overdose. In the meantime, liquid chromatography / mass spectrometry (LC/MS), LC/MS/MS, ion mobility spectrometry (IMS), and thermal desorption direct analysis in real time mass spectrometry (TD-DART-MS) are being explored to meet the demand on low detection limit for many case samples where fentanyl is present with other drugs and cutting agents at low concentration.[2]

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Raman spectroscopy has long been used for the detection and identification of illicit drugs and adulterants, and offers a valuable addition to the forensic toolbox for the analysis of fentanyl and fentanyl analogues. FT-Raman utilizes a long-wavelength laser (1064 nm) which greatly reduces fluorescence and produces high signal-to-noise spectra, making it well suited for many narcotic samples that fluoresce. It also enables sampling through glass vials, polymer blister packs, and plastic evidence bags; hence, often requires little to no sample preparation. It is nondestructive and allows the custody chain to be maintained, given the possibility of qualitative and quantitative evaluation of the sample to confirm its integrity from its seizure until the sample is placed in the evidence file.[3]

In this application note, analyses of fentanyl as well as other illicit drugs using FT-Raman spectroscopy are presented. The advantages of FT-Raman for the detection and identification of illicit drugs are also discussed.

Materials and methods

All samples analyzed in this study were prepared at Albuquerque Police department. Samples were analyzed in double bags, blister packs or glass vials, and handled in compliance with Schedule I controlled substance handling protocols. A Thermo Scientific™ Nicolet™ iS50 FT-IR spectrometer equipped with a calcium fluoride beam splitter and an FT-Raman module with a 1064 nm laser was used for all analyses (Figure 1). A total of 64 scans were co-added for each spectrum at 8 cm-1 resolution, with a total acquisition time of ~75s. The laser power was set at 0.5 mW. The spectra were searched against Thermo Scientific Law Enforcement and Security (LEnS) Raman and DEA Raman libraries using OMNIC library search and Specta multicomponent search options.

Figure 1: An iS50 Raman module for the Thermo Scientific Nicolet iS50 FT-IR spectrometer.

Results and discussion

Figure 2A shows the Raman spectrum of bulk fentanyl in a double bag, directly acquired without any sample manipulation. Since the laser spot size is approximately 60 µm, small quantity of samples, such as a few granules, can be analyzed with ease. An example is shown in Figure 2B. While Figure 2B exhibits a slightly higher noise level compared to Figure 2A, both samples were nonetheless positively identified as fentanyl citrate through library search.

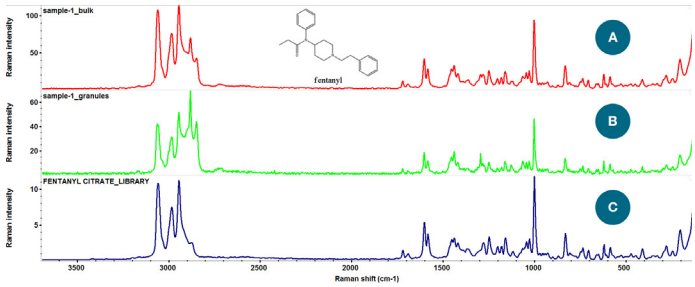

Figure 2: Raman spectra of (A) seized bulk fentanyl in a double-bag; (B) a few fentanyl granules in a double-bag; and (C) fentanyl citrate from DEA Raman library.

Raman spectroscopy is sensitive to both chemical and physical properties. Its unique selection rules generate a molecular fingerprint that is well suited to the differentiation between many illicit drug compounds and their analogues. Figure 3 shows the Raman spectra of a tablet as well as the 3,4-methylenedioxyamphetamine (MDA) and 3,4-methylenedioxymethamphetamine (MDMA) standards from the library. Despite the minute structural difference between MDA and MDMA (inset of Figure 3), Raman spectroscopy can unambiguously distinguish the two. In this case, the tablet was identified as MDA with a match score of 83, as opposed to a match score of 66 for MDMA.

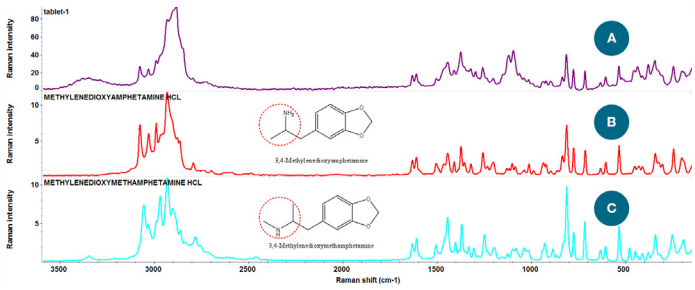

Figure 3: Raman spectra of (A) a tablet; (B) 3,4-methylenedioxyamphetamine (MDA) standard from the library; and (C) 3,4-methylenedioxymethamphetamine (MDMA) standard from the library.

Seized street drugs are often present in the form of mixtures. Figure 4 shows the Raman spectrum of an off-white powder sample in an evidence bag. Initial library search showed similar match score for lactose and cocaine, suggesting that the sample contains multiple components. The spectrum was then subjected to the OMNIC Specta multi-component search, and the sample was identified as a mixture of cocaine and β-D-lactose, a commonly used cutting agent.

Conclusions

The Nicolet iS50 FT-IR spectrometer equipped with the iS50 Raman module offers an invaluable tool for the forensics labs to combat the growing opioid epidemic. Raman analysis requires little to no sample preparation and allows for direct measurements through glass vials and evidence bags, greatly reducing the risk of lab personnel's accidental exposure to high potency drugs such as fentanyl and fentanyl analogues. While the measurement of bulk narcotic samples is fast and straightforward, with a laser spot size of 60 µm, acquisition of high quality Raman spectra from as little as few granules is also possible. Combined with DEA and LEnS Raman libraries, OMNIC Specta enables identification of multi-component illicit drugs with confidence. Raman spectroscopy using the iS50 Raman module is a safe, fast, and complementary technique for the screening, detection and identification of illicit drugs.

References

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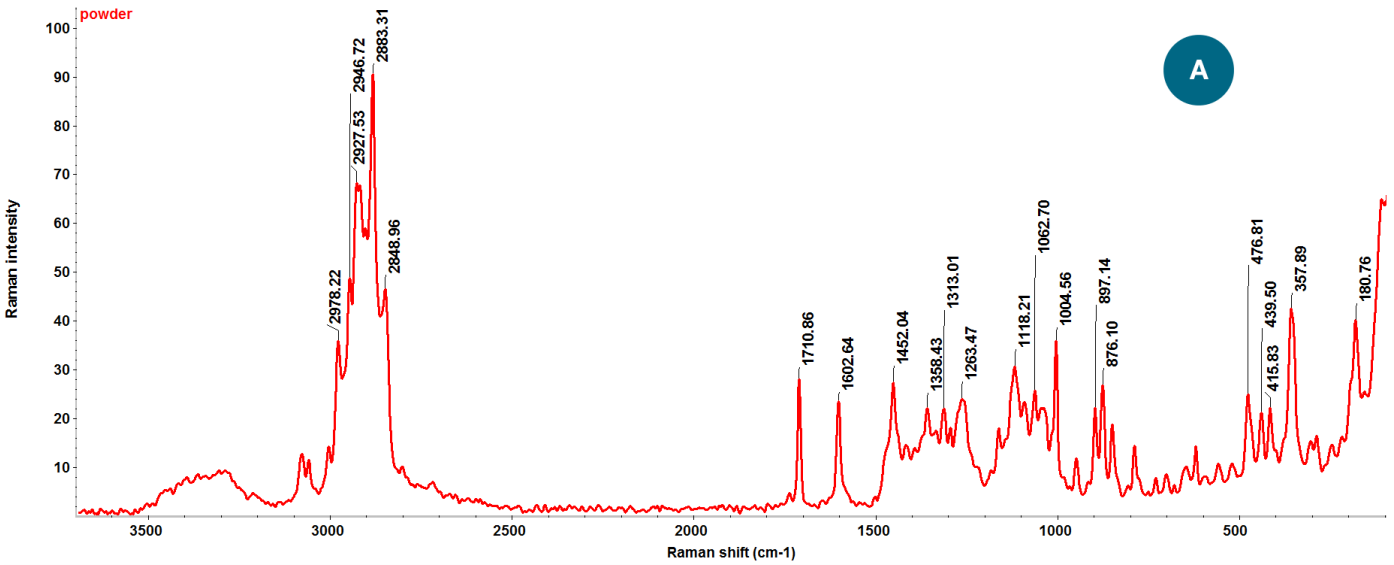
2. Edward Sisco, Jennifer Verkouteren, Jessica Staymates, Jeffrey Lawrence, Forensic Chemistry, Volume 4, June 2017, Pages 108-115,
3. Ciro Augusto Fernandes de Oliveira Penido, Marcos Tadeu Tavares Pacheco, Igor K. Lednev, Landulfo Silveira Jr., Journal of Raman Spectoscopy, 47 (1), January 2016, Pages 28–38.



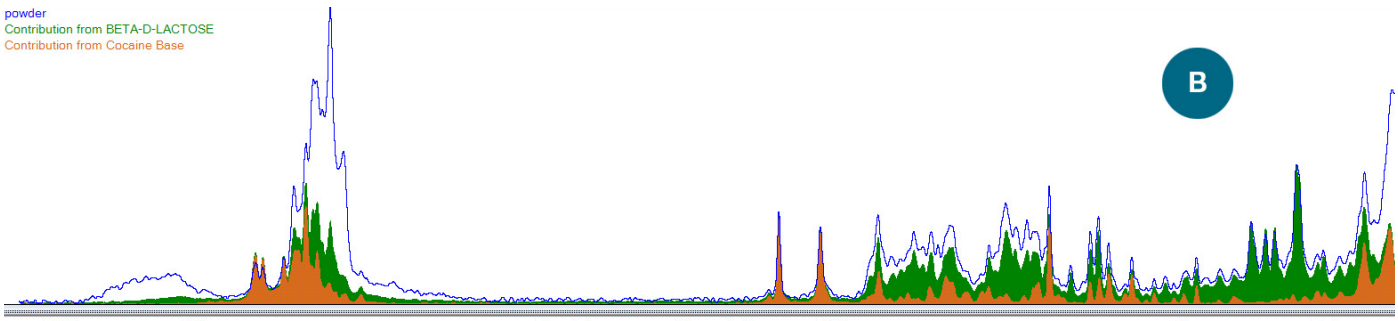


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Figure 4: Raman spectra of a seized street drug sample containing cocaine and β-D-lactose.

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