

Mass Spectrometry & Spectroscopy

Determination of heroin in street drug samples with printable surface enhanced Raman scattering (P-SERS)

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A new ID Kit, a test for the presence of opioids, was used with the Mira DS handheld Raman analyser to successfully detect heroin in 18 crude street heroin samples. Detection of heroin with ID Kit was accomplished easily and very quickly, with minimal sample clean-up. Solvent studies were also implemented to determine the optimal solvent for crude sample extraction, with results included here.

Samples

A local forensic laboratory provided 18 samples of crude street heroin. The presence of heroin in each of the samples was previously confirmed with GC/MS. Each sample was light brown and powder or crystalline in form and ranged from 1–5 mg by weight.

Instrument

ID Kit	607506400
Mira DS Raman Analyzer	2.926.0020
MiraCal DS Software	606071010
SERS Smart Attachment	607506040

Solvent study

- Water
- Ethanol
- Methanol
- Dichloromethane
- Chloroform
- Ethyl Acetate
- 5% Acetic Acid
- Hexane
- Acetonitrile



Nine 1–2 mg samples were separated from larger volume samples, 250 μL of candidate solvent was added to these 1–2 mg samples, and the test tube was shaken to combine. Solids were allowed to settle and 10 μL of the supernatant was added directly to ID Kit P-SERS substrates and allowed to dry. Each P-SERS substrate was inserted into the slot on the SERS attachment, and a spectrum was acquired.

Parameters	Solvent Study	Heroin Detection
Laser Power	1-2	2-3
Integration Time	0.5 s	1 s
Averages	2	2
Raster	OFF	OFF



Analysis

Desirable attributes for the solvent study were:

- Successful and clean extraction of heroin
- Nanoparticle compatibility
- Volatility (evaporates quickly)
- Solvent fluorescence/background
- Quality of SERS spectrum
- Toxicity
- Domestic and international shipping regulations

Results

Ethanol, dichloromethane, acetonitrile, ethyl acetate, acetic acid, and water all enabled detection of signature heroin peaks at 531, 625, and 1,336 cm^{-1} (Figure 1). Extraction of crude street heroin with ethyl acetate resulted in spectra with the lowest levels of fluorescence, background interference, and contamination.

SERS vs Raman comparison

SERS is a technique that enables detection of trace analytes and can mitigate fluorescence. The heroin spectra in Figure 2 illustrates a common challenge for Raman spectroscopy in the analysis of crude street heroin samples. SERS analysis of a 1 mg/mL heroin standard (green) exhibits low levels of fluorescence. However, street heroin can exhibit high levels of fluorescence under classical Raman analysis (blue). SERS substrates efficiently quench fluorescence, resulting in spectra containing visible heroin peaks (red).

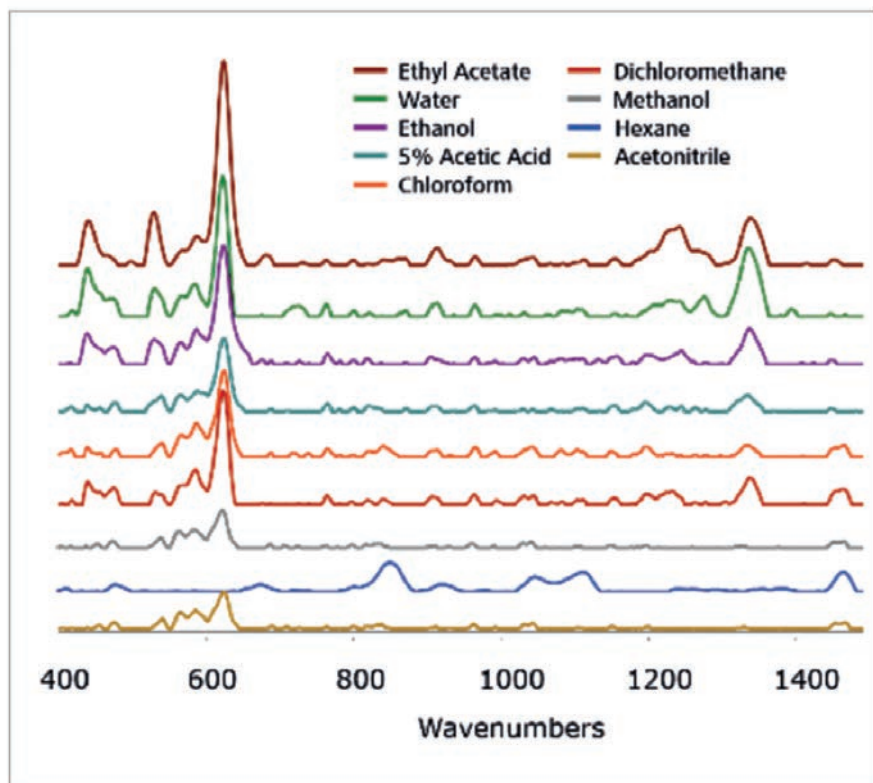


Figure 1. Extraction of heroin from street samples.

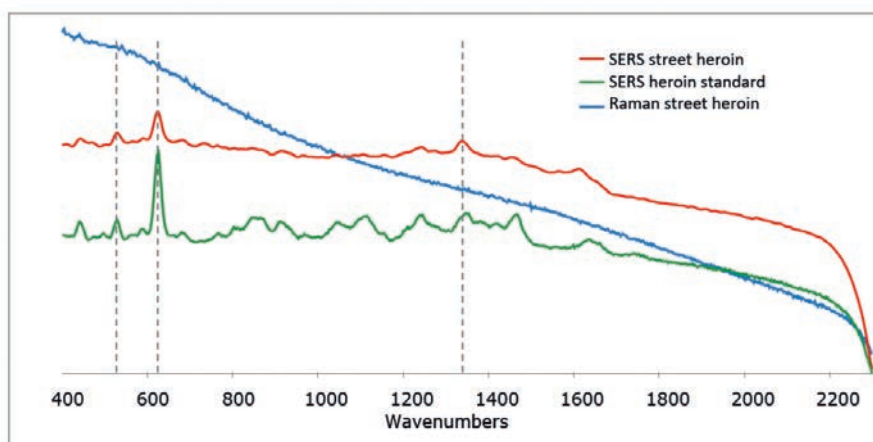
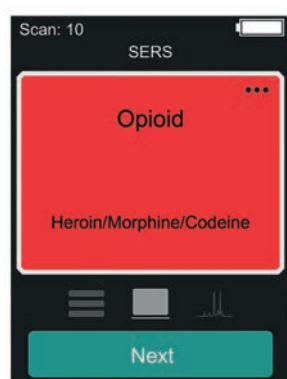


Figure 2. Fluorescence in Raman spectra of heroin.



P-SERS analysis of heroin street samples

Each of 18 street samples were extracted with ethyl acetate and applied to ID Kit substrates in a manner identical to that described earlier. Heroin was positively detected in SERS spectra of all 18 samples (Figure 4). Automated heroin detection algorithms on Mira DS provided quick results, reported as a positive opioid ID on a bright red hazard screen, Figure 3.

Figure 3. Successful detection of opioids with Mira DS.

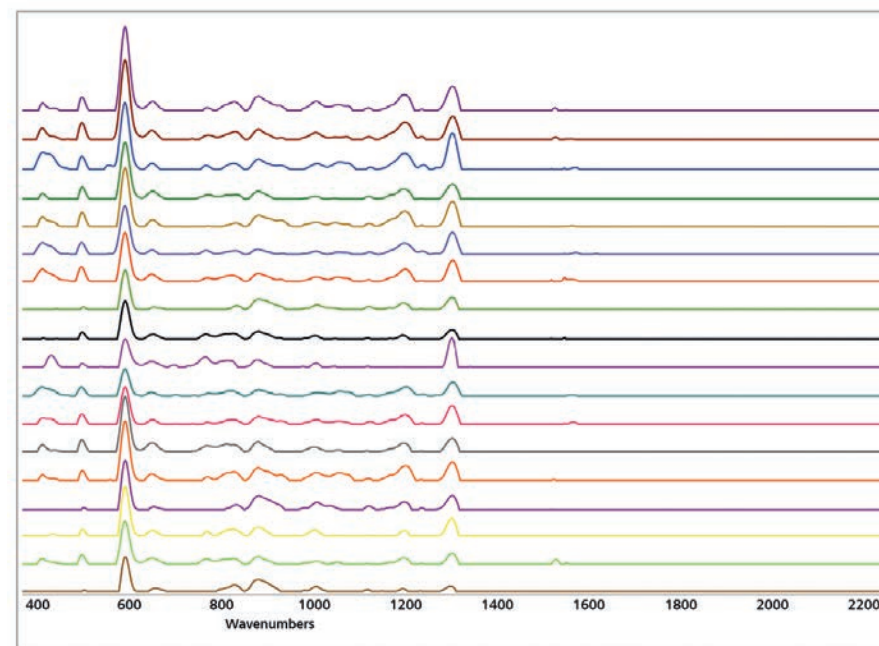


Figure 4. SERS spectra of 18 street heroin samples.



Conclusion

This study is designed to showcase how this new ID Kit is easy to use and provides fast and accurate results with the greatest of ease: a small amount of street sample suspected of containing heroin, morphine, or codeine is added directly to a supplied vial of ethyl acetate. The resulting supernatant is dropped directly onto P-SERS substrates provided with ID Kit. This substrate is inserted into the SERS Smart Attachment on Mira DS, and automated opioid detection algorithms perform the analysis.



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