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Edgewood Chemical Biological Center

Combat Forensics: Identification of Bad Actors with the Aid of Microfluidic SERS

SET-253 "Surface-enhanced Raman Spectroscopy for Defense Applications"

Bratislava, Slovakia

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Moskovits, Carl Meinhart, Jason Guicheteau

What is ECBC?



Who We Are

We are the nation's primary research and development resource for non-medical chemical and biological defense.



What We Do

We couple research and science with engineering and field operations to create new and effective chemical and biological defense solutions.

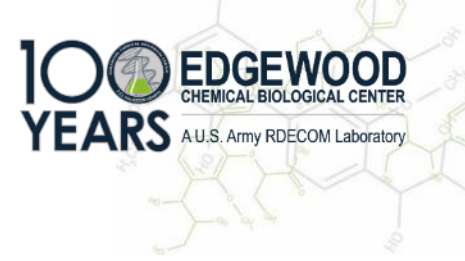


Why We Do It

We do all of this to keep the warfighter, the nation, and the world safe from chemical and biological threats now and in the future.

For almost 100 years ECBC has been a unique national asset. We provide innovative and cost-effective chemical and biological defense technology solutions through our scientific and engineering expertise, coupled with our unique facilities and collaboration with partners.

Strategic Environment through 2040:

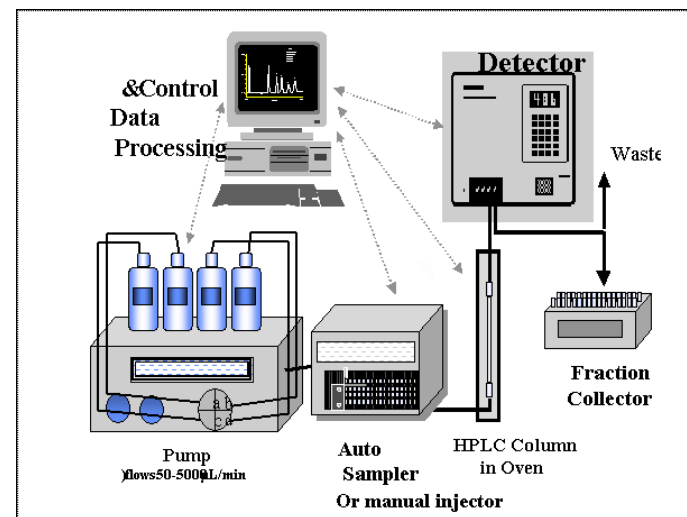


- Rising trend for civil war and internal conflict.
- Rise of larger city states or mega-cities protected by an “empire” will lead to large areas of uncontested or under-governed regions.
- Rise of cities within cities. Within the mega-city we will see self governing regions or autonomous regions with their own security forces and facilities.
- Greater proliferation of knowledge of threats through the internet.
- Rapid innovation and improvisation will make threat prediction difficult.
- **The non-attribution of strategic acts (CBRNE, Cyber...) will make a national response difficult without strong reliance on forensics to narrow down or identify the source.**



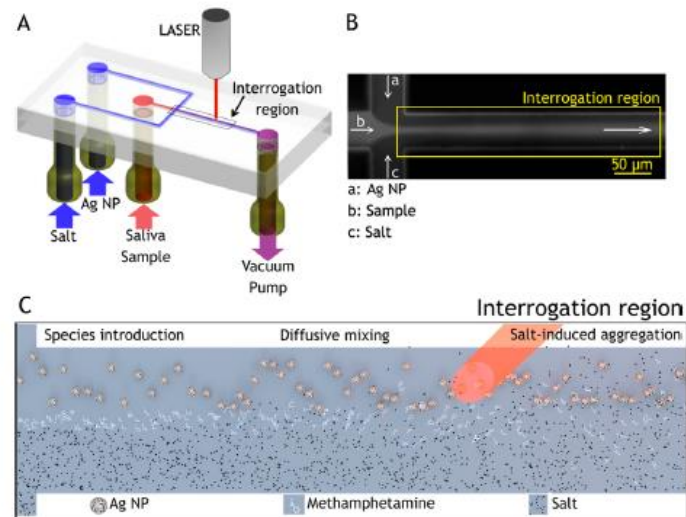
Why Do We Need Field Forensics?

- Obtain “real-time” answers that allow actionable decisions to be made on-the-spot.
- Reduces logistics by moving the analysis closer to the source of the sample.
- Screen materials to identify samples that need to be sent to a lab for additional analysis and minimize the number of these samples.
- Nondestructively analyze large, valuable, or nonmovable objects for which excising samples is not possible.
- **Current methods for drug detection are mainly based on large format laboratory instrumental methods.**

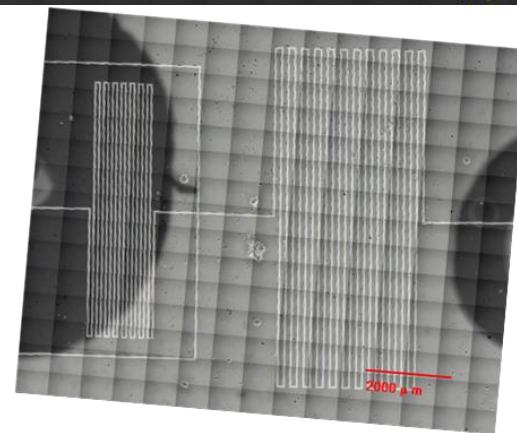


Implementation of SERS onto a Microfluidic Chip

- Potential solution is to combine microfluidics and surface-enhanced Raman spectroscopy (SERS) for a portable detection device
- Microfluidics studies how to manipulate and control fluid flow on the sub-millimeter scale while SERS is a highly sensitive and selective vibrational spectroscopy technique
- The chip functions by flowing colloidal nanoparticles, analyte matrix, and aggregating agent together
- The channels containing the three liquids come together and achieve diffusive mixing across the laminar flow barriers created via hydrodynamic focusing



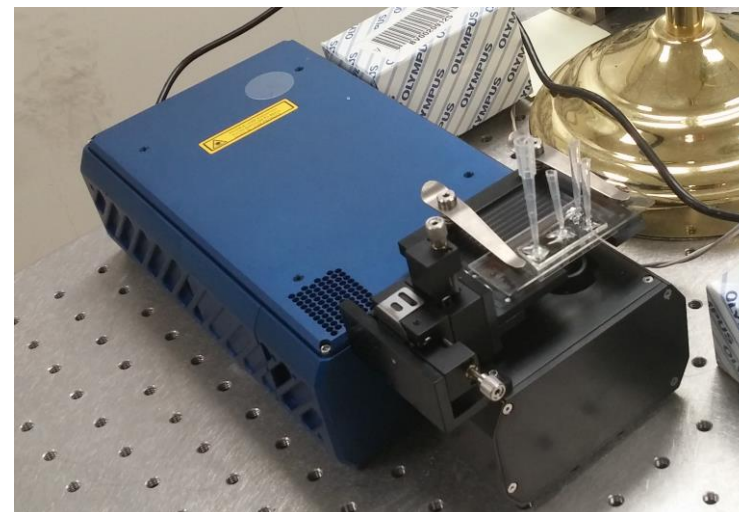
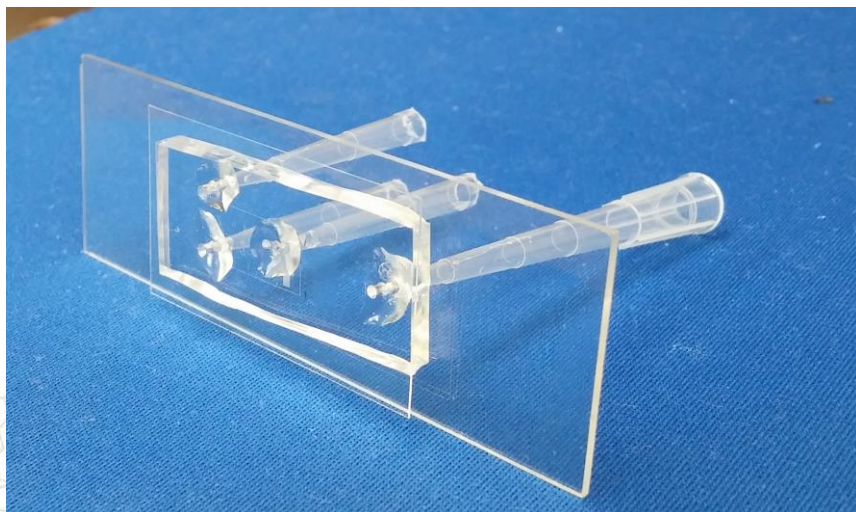
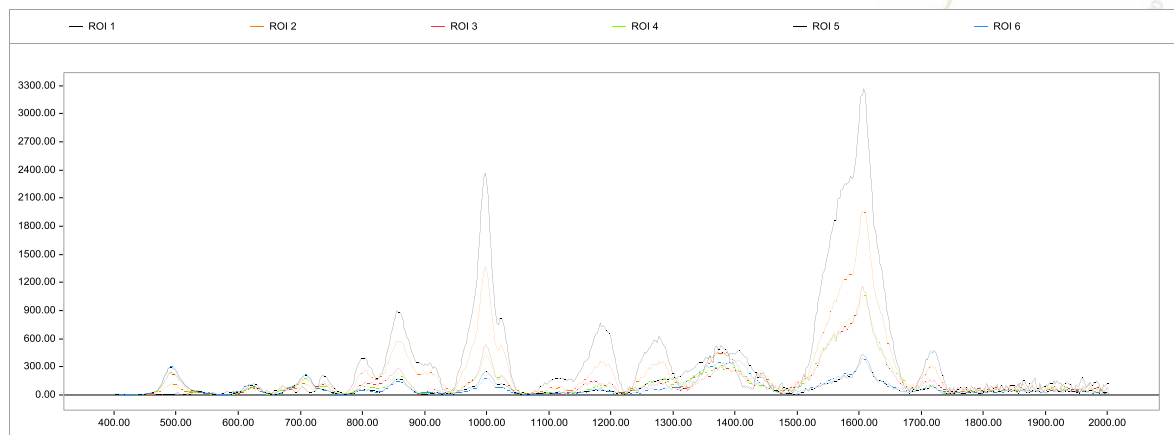
Rapid Detection of Drugs of Abuse in Saliva Using Surface Enhanced Raman Spectroscopy and Microfluidics
Chrysafis Andreou, Mehran R. Hoonejani, Meysam R. Barmi, Martin Moskovits, and Carl D. Meinhart
ACS Nano 2013 7 (8), 7157-7164 DOI: 10.1021/nm402563f



Sierra 2.0, Snowy Range Instruments

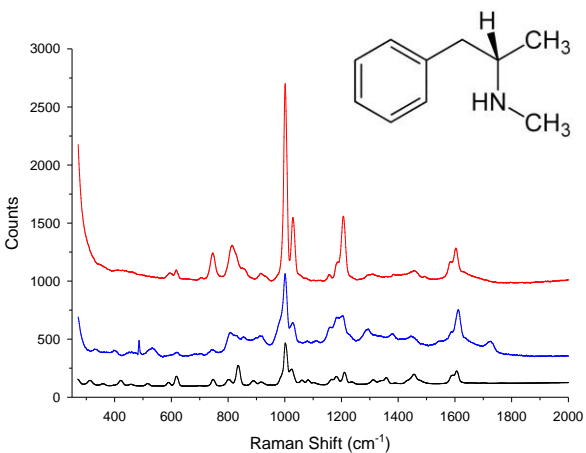
- Snowy Range Instruments has produced a prototype spectrometer to mount the microfluidic chip
- The chip will be inverted and mounted on a fine adjustment stage for alignment

5×10^{-4} M Cocaine

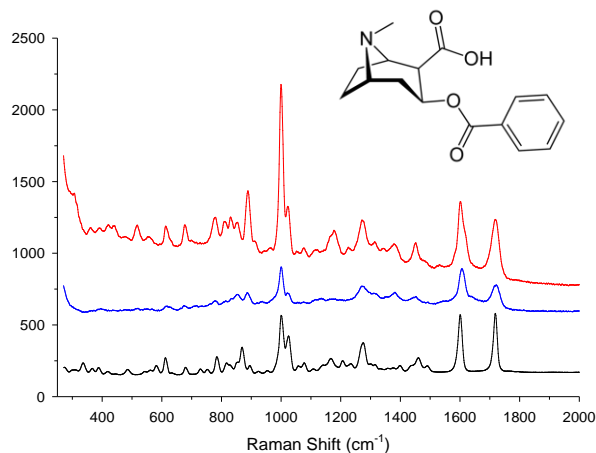


SERS of Probe Analytes

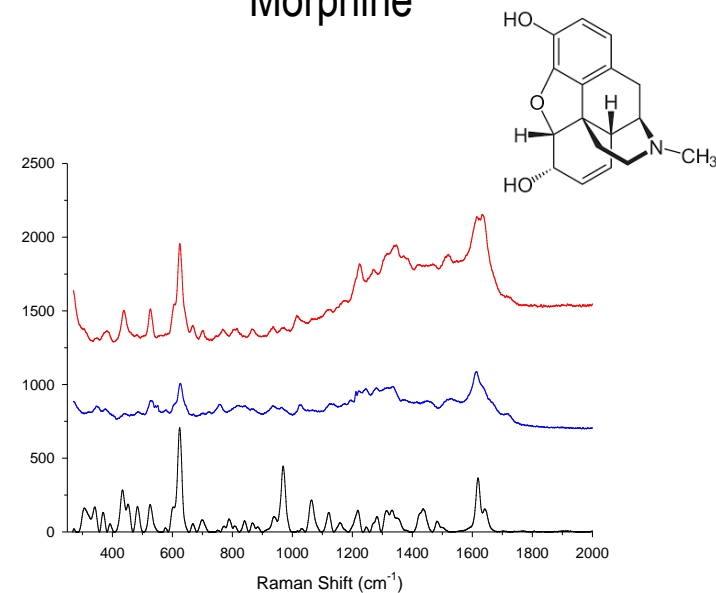
Methamphetamine



Cocaine



Morphine



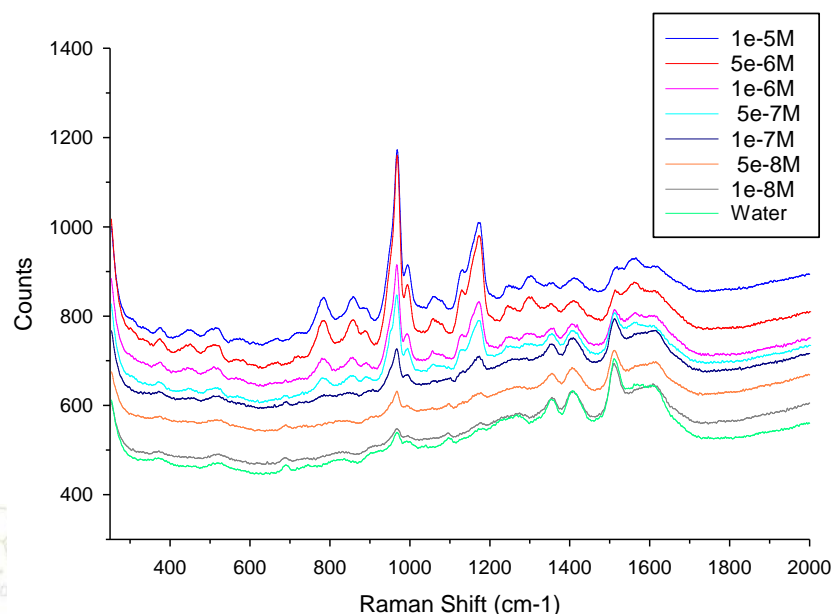
- 1 x 10⁻³M solutions of each analyte
- SERS spectra was collected with 50 nm Ag and Au nanoparticles with 633 nm radiation

— Ag nanoparticles
— Au nanoparticles
— Powder

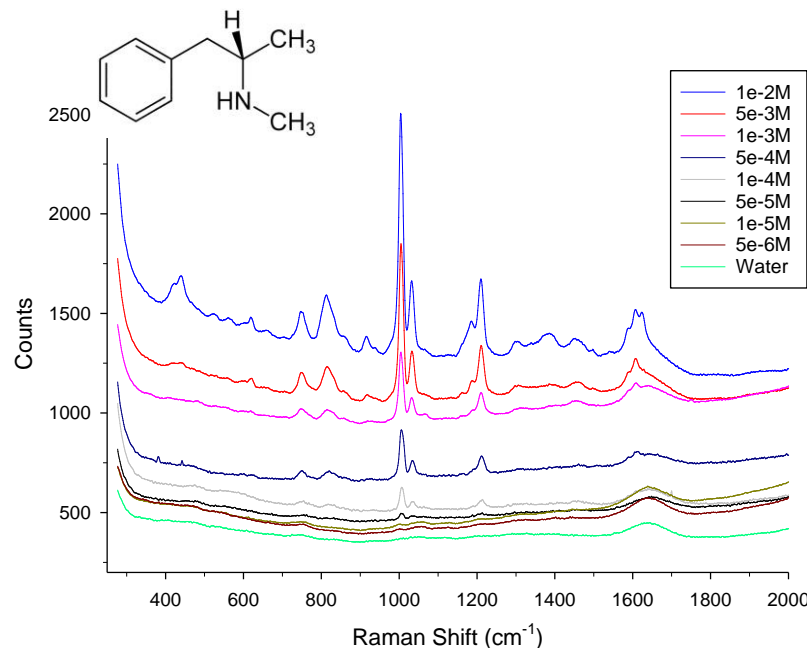
Why Better LOD with AuNPs and Not AgNPs?

- Ag is one of the lowest loss plasmonic materials in the visible and NIR ranges; AgNPs exhibit a larger SERS enhancement than AuNPs due to greater plasmonic efficiency
- However, we obtain a higher LOD with AuNPs
- Studies examining the binding of nitrogen containing compounds to different metals including Ag and Au show that these kinds of molecules have a higher propensity to bind to Au surface over Ag

Methamphetamine



Methamphetamine with AuNPs



Methamphetamine with AgNPs

Experiments in Bodily fluid Matrices

- We have identified the optimal spectroscopic conditions to design the microfluidic/SERS detection platform.
- To establish the efficacy of our spectroscopic technique, detection in bodily fluid matrices needs to be demonstrated.
- Experiments were conducted in artificial saliva and artificial urine purchased from Pickering Test Solutions.

Ingredients for Artificial Saliva:

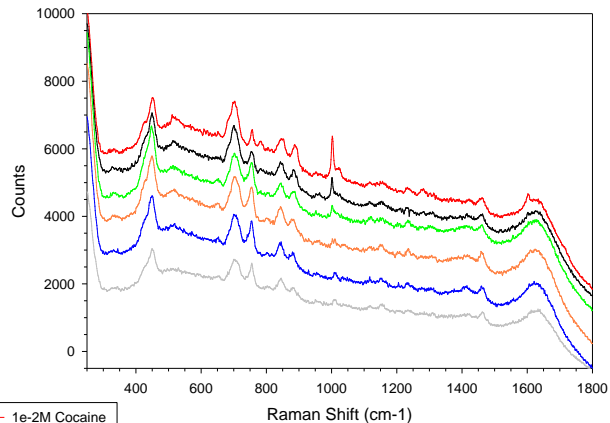
Sodium Chloride
Potassium Phosphate Monobasic
Potassium Chloride
Potassium Thiocyanate
Urea

Ingredients for Artificial Urine:

Peptone	1.0 g/L
Yeast extract	0.005 g/L
Lactic Acid	0.1 g/L
Citric Acid	0.4 g/L
Sodium Bicarbonate	2.1 g/L
Urea	10.0 g/L
Uric Acid	0.07 g/L
Creatinine Hydrochloride*	0.9 g/L
Calcium Chloride, dihydrate	0.37 g/L
Sodium Chloride	5.2 g/L
Iron II sulphate * 7H ₂ O	0.0012 g/L
Magnesium Sulphate anhydrous**	0.24 g/L
Sodium Sulphate *10H ₂ O	3.2 g/L
Potassium Phosphate monobasic	0.95 g/L
Potassium Phosphate Dibasic	1.2 g/L
Ammonium Chloride	1.3 g/L

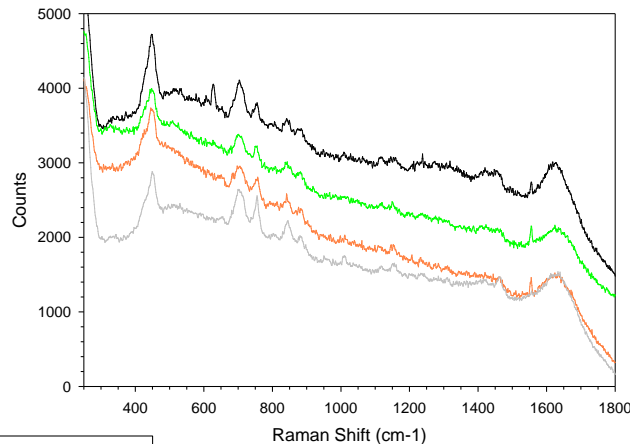
Detecting Drugs with Au Borate Capped Colloid in Artificial Saliva

Detecting Cocaine in Artificial Saliva



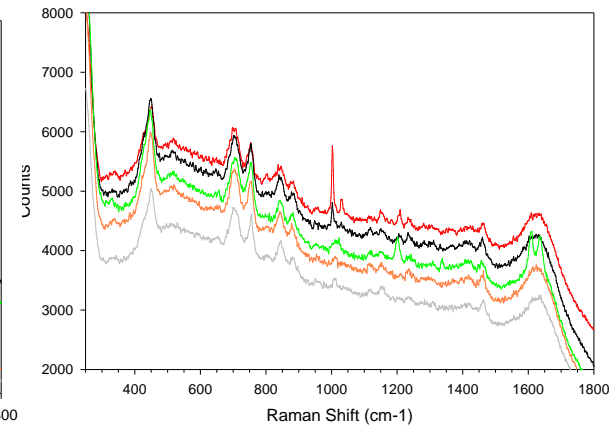
- 1e-2M Cocaine
- 1e-3M Cocaine
- 1e-4M Cocaine
- 1e-5M Cocaine
- 1e-6M Cocaine
- Background

Detecting Morphine in Artificial Saliva



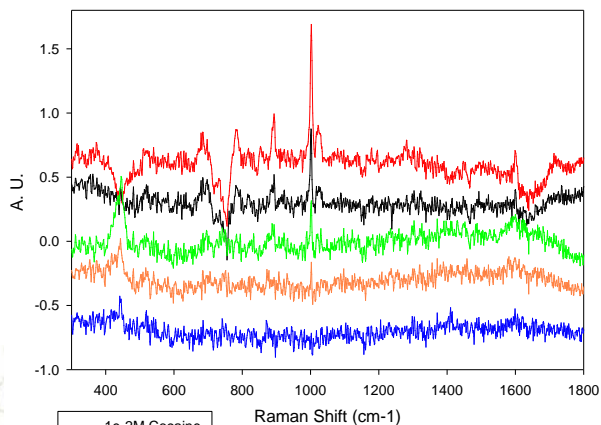
- 1e-3M Morphine
- 1e-4M Morphine
- 1e-5M Morphine
- Background

Detecting Meth in Artificial Saliva



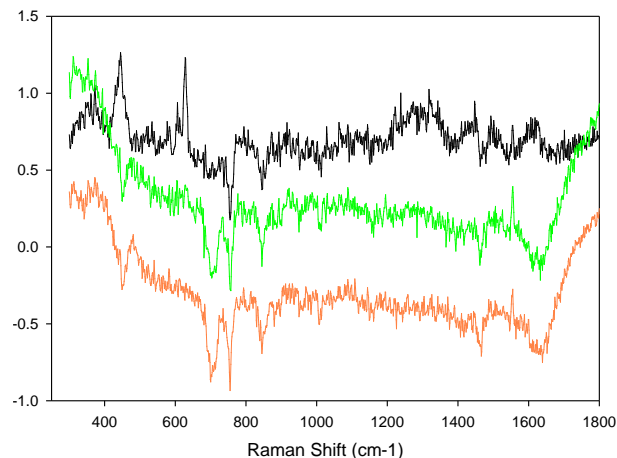
- 1e-2M Meth
- 1e-3M Meth
- 1e-4M Meth
- 1e-5M Meth
- Background Art. Saliva

PLS Subtracted Cocaine Au Borate in Art. Urine



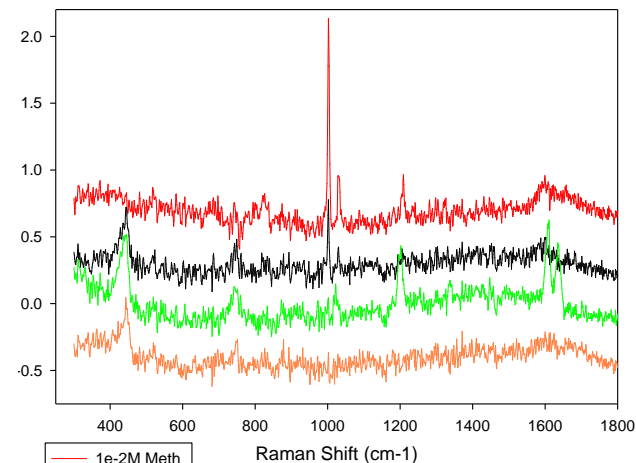
- 1e-2M Cocaine
- 1e-3M Cocaine
- 1e-4M Cocaine
- 1e-5M Cocaine
- 1e-6M Cocaine

PLS Subtracted Morphine Au Borate in Art. Saliva



- 1e-3M Morphine
- 1e-4M Morphine
- 1e-5M Morphine

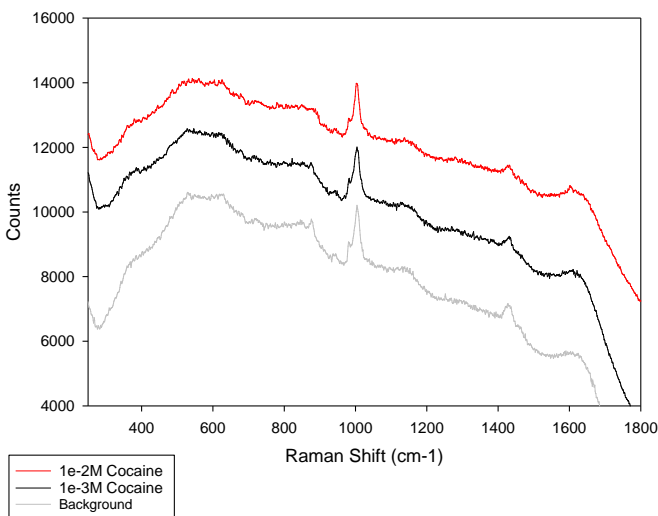
PLS Subtracted Meth Au Borate in Art. Saliva



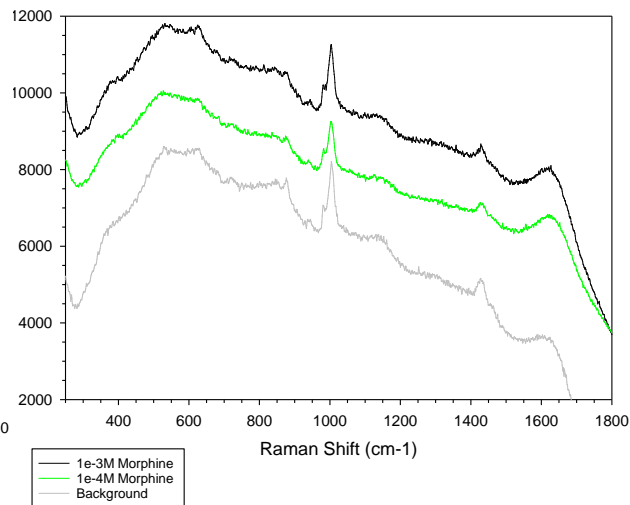
- 1e-2M Meth
- 1e-3M Meth
- 1e-4M Meth
- 1e-5M Meth

Detecting Drugs with Au Borate Capped Colloid in Artificial Urine

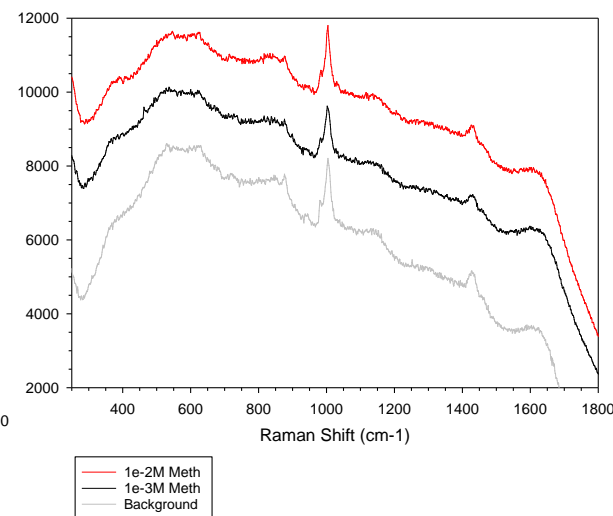
Cocaine in Artificial Urine with Au Borate Capped



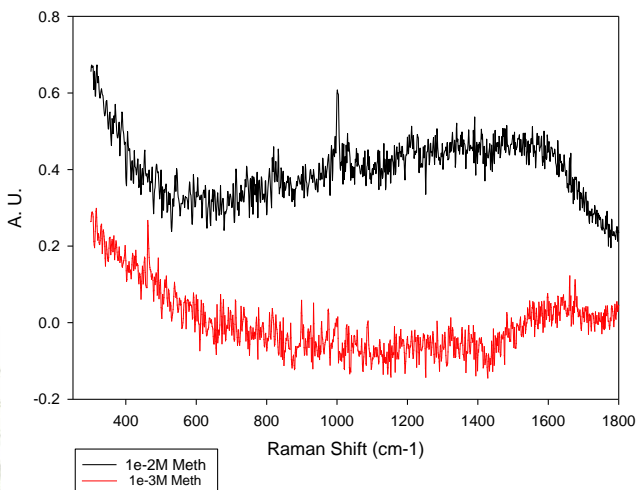
Morphine in Artificial Urine with Au Borate Capped



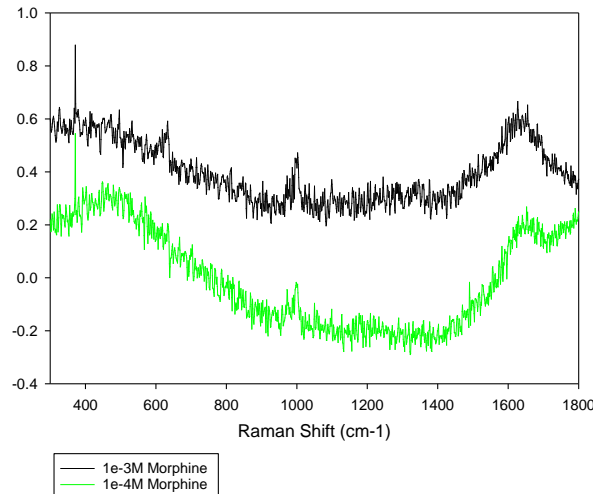
Meth in Artificial Urine with Au Borate Capped



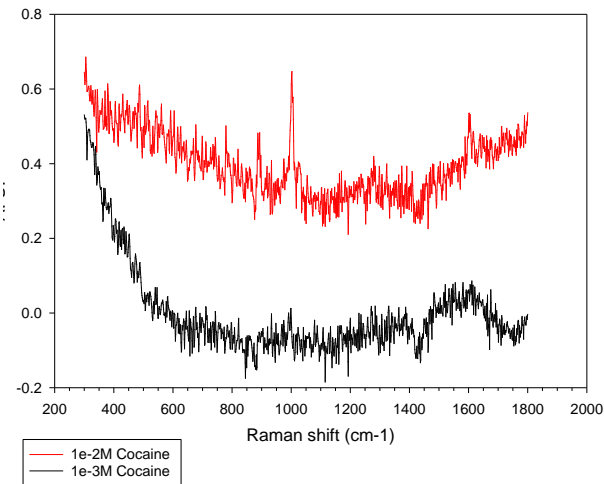
PLS Subtracted Meth Au Borate in Art. Urine



PLS Subtracted Morphine Au Borate in Art. Urine



PLS Subtracted Cocaine Au Borate in Art. Urine



Addressing Problems of Detection in Bodily Fluids

- Limits of detection are substantially lowered in bodily fluid matrices
- Possible solutions to overcome this problem
 - Capture agent: cover nanoparticles with an aptamer specifically designed to target desired analyte
 - Extraction: attempt to extract desired analytes from the bodily fluid into an aqueous solution
 - Diffusive based separation: fabricate a microfluidic chip specifically designed to exploit the mass difference and diffusion rate of the drug analytes vs. the biological interferents in the bodily fluid matrix

Conclusions and Future Work

- We have demonstrated the proof of concept of microfluidic SERS detection of drugs in aqueous solutions.
- Detection in artificial body fluid matrices are significantly worse and challenged by increased scattering baseline and adsorption competition at the nanoparticle interface.
- We will continue to partner with academia and industry on the microfluidics and spectrometer interface to improve the overall sampling.
- We hope to have a more refined prototype in FY19.

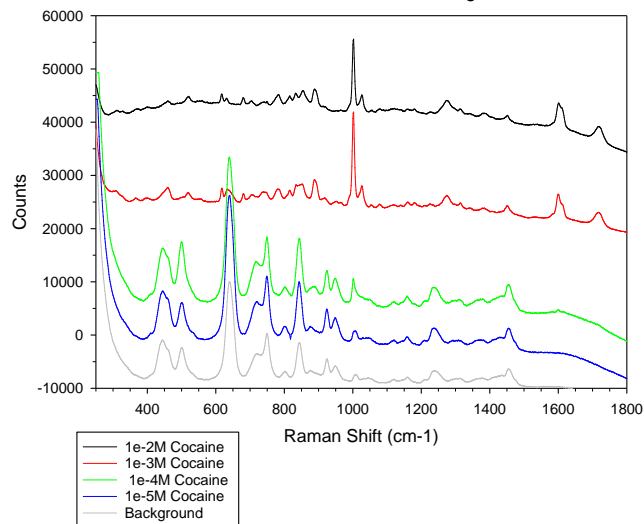
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Technology Driven
Warfighter Focused

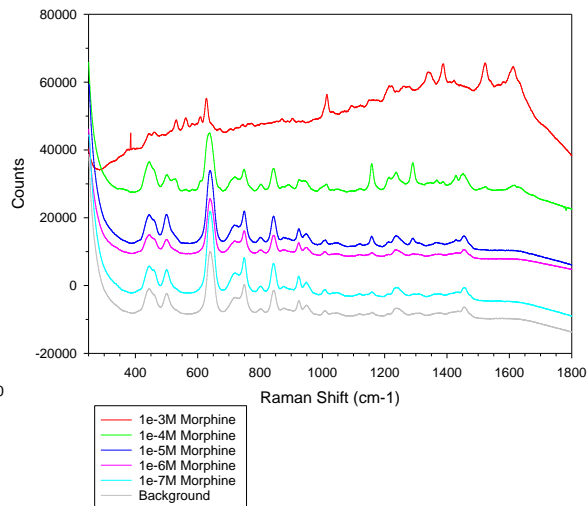


Detecting Drugs with Ag Citrate Capped Colloid in Artificial Saliva

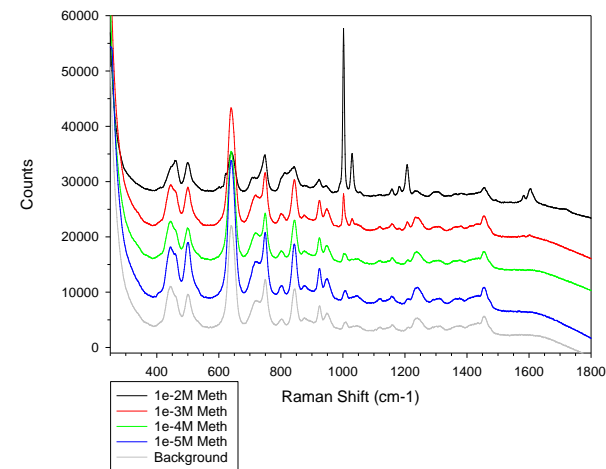
Cocaine in Art.Saliva with 50 nm Ag Citrate



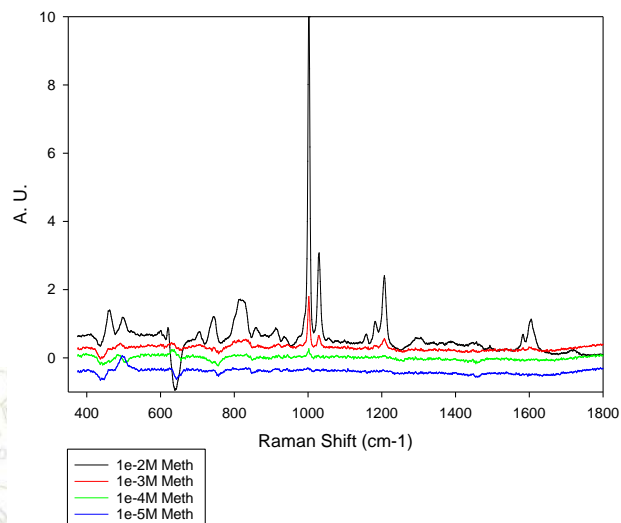
Morphine in Art. Urine with 50 nm Ag Citrate



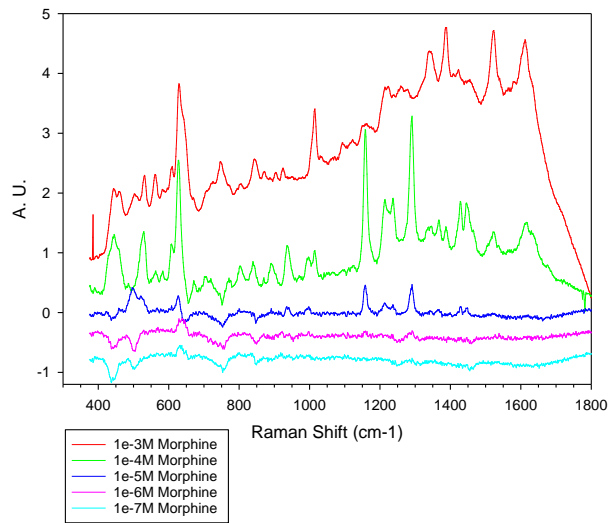
Meth in Art.Saliva with 50 nm Ag Citrate



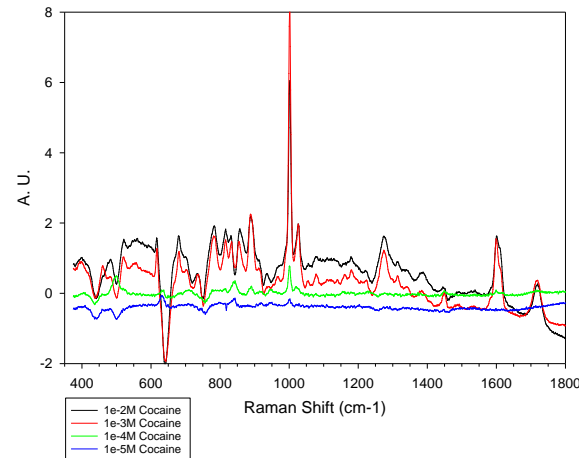
PLS Subtracted Meth Ag Citrate in Art. Saliva



PLS Subtracted Morphine Ag Citrate in Art. Saliva

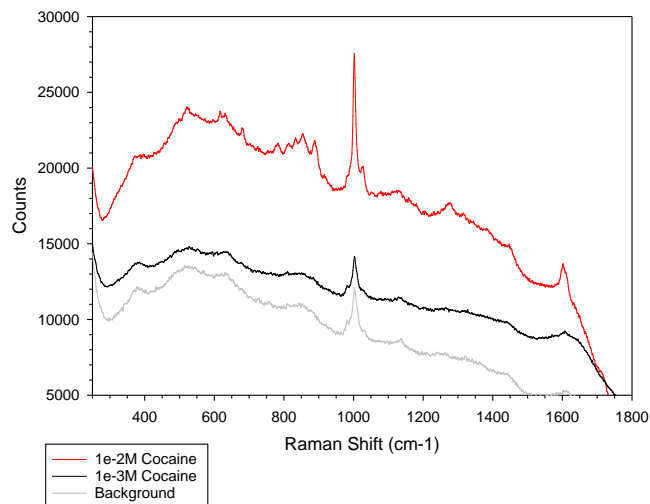


PLS Subtracted Cocaine Ag Citrate in Art. Saliva

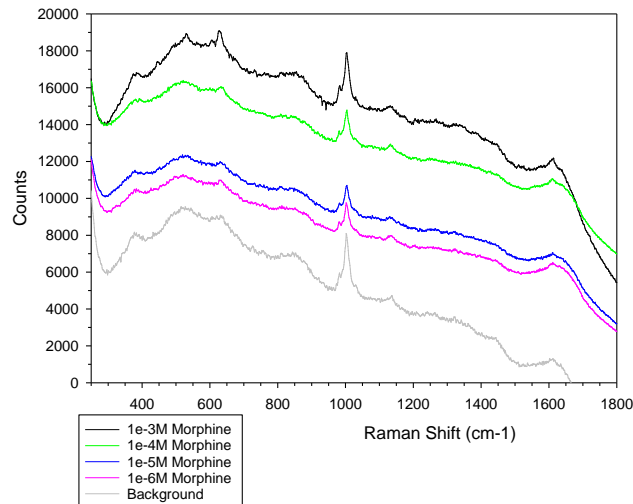


Detecting Drugs with Ag Citrate Capped Colloid in Artificial Saliva

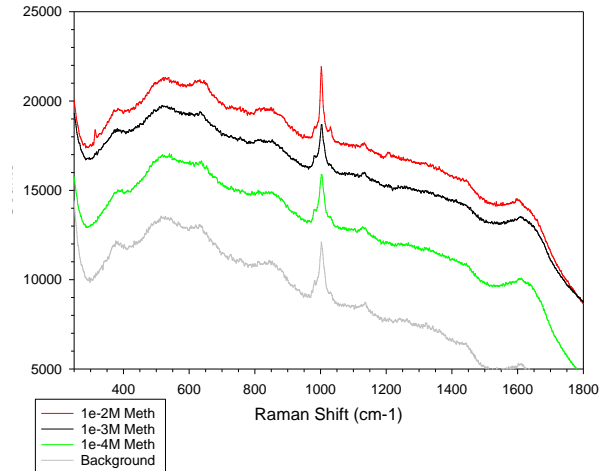
Cocaine with 50 nm Ag Citrate in Artificial Urine



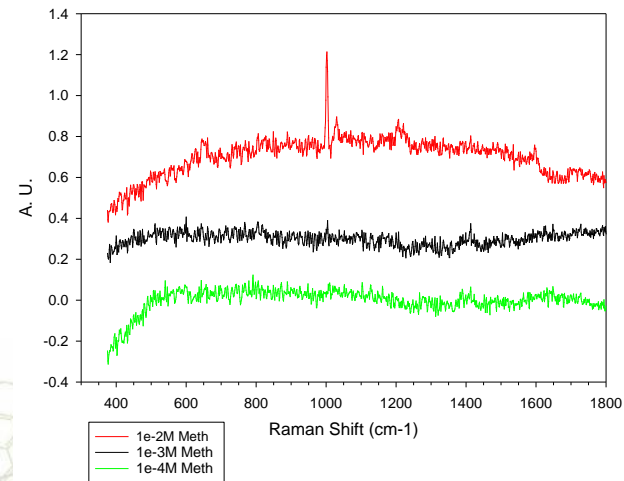
Morphine 50 nm Ag Citrate with Artificial Urine



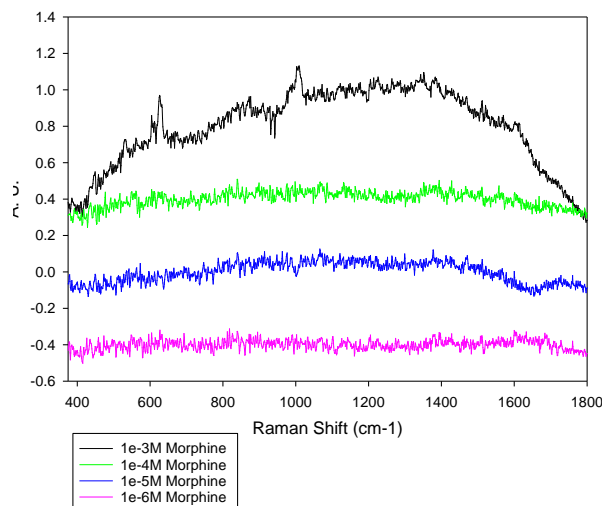
Meth with 50 nm Ag Citrate with Artificial Urine



PLS Subtracted Meth Ag Citrate in Art. Urine



PLS Subtracted Morphine Ag Citrate in Art. Urine



PLS Subtracted Cocaine Ag Citrate in Art. Urine

