Smart Substrates for Street Substances: Development of SERS-MIP Sensors for Field Detection of Seized Drugs

[1]Sydney M. Hampton*, BS; [1]Krystal VanHorn, BS; [2]Abuzar Kabir, PhD; [1]Geraldine Monjardez, PhD

[1]Department of Forensic Science, Sam Houston State University, Huntsville, TX 77340

[2]Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199

Sam Houston State University

ABSTRACT

This study represents the initial phase of developing field-portable sensors for detecting seized drugs with high sensitivity and selectivity. The final design will require a substrate that meets both SERS and MIP performance needs. Preliminary results show that SERS fiberglass and SERS nylon swabs successfully detected crystal violet and caffeine. However, further optimization is needed to standardize nanoparticle size and distribution, as current variability reduces reproducibility for target analyte detection.

INTRODUCTION

In 2025, U.S. Customs and Border Protection reported a 10,000-pound increase in seized drugs compared to 2024[1]. Rapid field screening methods can yield false outcomes and require user interpretation, while portable Raman spectrometers, though more reliable, often lack the selectivity needed to detect trace analytes within complex matrices..

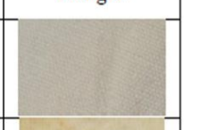
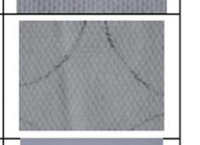
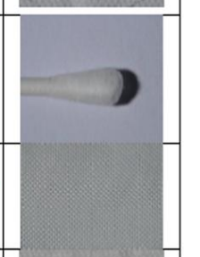
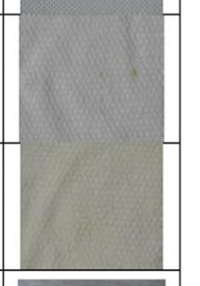
Molecularly Imprinted Polymers (MIPs) feature analyte-specific binding cavities engineered through functional group interactions. While highly selective, MIPs do not enhance analytical sensitivity. Integrating MIP selectivity with SERS-based sensitivity offers a promising approach for accurate, sensitive, and selective drug identification in field settings.

MATERIALS & METHODS

Gold nanoparticle synthesis: Gold nanoparticles (AuNPs) synthesis utilized a modified Turkevich[2] method with sodium hydroxide as the capping agent and sodium borohydride as the reducing agent (**Figure 1**).

Deposition of AuNPs on substrates: Once synthesized, deposited on substrates by pipetting or submersion during synthesis. The substrates utilized can be found in **Table 1**.

Table 1 substrates assessed in phases three of substrate selection.

Substrate	Sorbent	Images
Fabric Phase Sorptive Extraction Membrane	Fabric Phase Sorptive Extraction Membrane	
Titania	Titania	
Zirconia	Zirconia	
Silica	Silica	
Thin Cellulose	Sol-gel Tetramethoxyortho silicate/ CarboWax (PEG) 20M	
Cotton Canvas	Sol-gel Tetramethoxyortho silicate/ CarboWax (PEG 20M	
Cotton Canvas	Sol-gel Tetramethoxyortho silicate/ CarboWax (PEG 20M	
Cotton Bud	Sol-gel Tetramethoxyortho silicate / phenyl triethoxysilane / CarboWax (PEG) 20M	
Fiberglass	Sol-gel tetramethoxyortho silicate	
Cotton Canvas	Sol-gel tetramethoxyortho silicate/ Polycaprolactone Polydimethylsiloxane Polycaprolactone	
Cellulose Canvas	Sol-gel tetramethoxyortho silicate/ CarboWax (PEG) 20M/ Aminopropyl triethoxysilane	
Nylon	Proprietary	

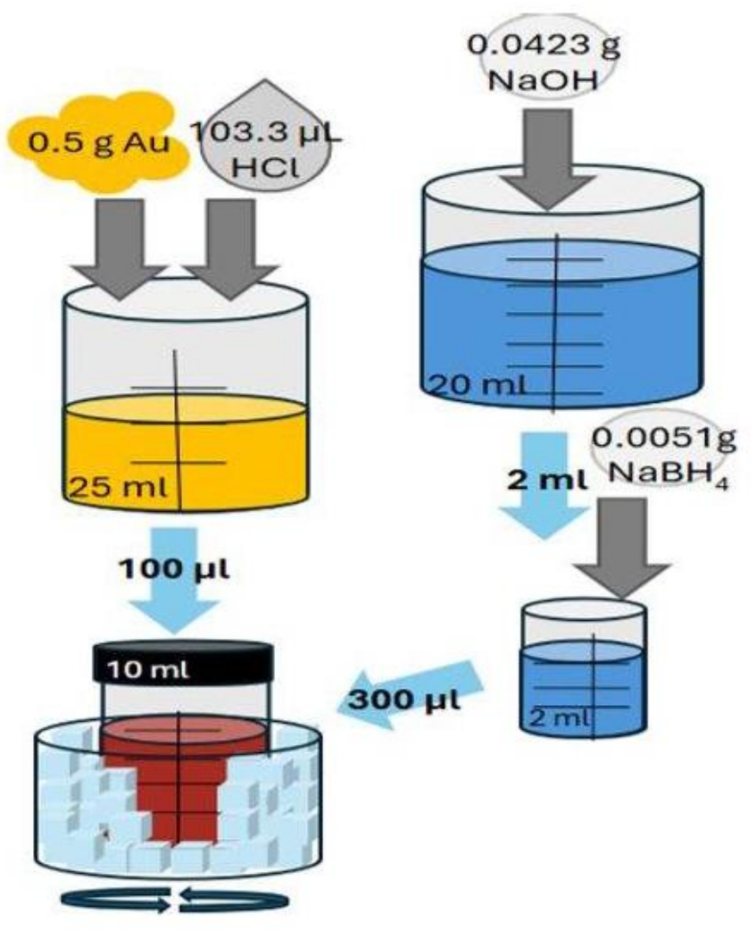


Figure 1. Process showing the water-based AuNPs synthesis

Assessment of SERS substrates: Crystal violet (CV) in DI water solution (2.5- 10 µL 10^{-3} M) and caffeine in chloroform solution (0.5 M) were pipetted onto SERS substrates to to determine their SERS enhancement.

Assessment of illicit drugs: 5 µL of methamphetamine in methanol solution (0.0067 M) were pipetted onto SERS Copan swabs for Raman analysis

Data collection: All Raman spectra were collected using a Renishaw inVia™ InSpect confocal Raman microscope using a 20x objective, 532 nm or 785 nm laser, and a spectral range of 200-2000 cm^{-1}. The parameters varied depending on the substrate and analyte being tested.

Powdered MIP testing: This study compared a 30 mg caffeine in 30 ml chloroform solution absorbance both with and without exposure to MIPs imprinted for caffeine. ~100 mg MIP polymer powder imprinted for caffeine (**Figure 2**) was added to a vial with 10 ml of the caffeine in chloroform solution. This solution was then capped, Parafilmed, and left overnight, along with the caffeine in chloroform solution. The sample was then centrifuged to remove MIP powder from solution. The absorbance of this solution was compared both before and after interaction with the imprinted MIP powder. UV-Vis analysis was completed for solutions using a Thermo Scientific Evolution 60S UV-Visible Spectrophotometer with Thermo ScientificTM VISIONliteTM software in 80:20 Methanol: Water as the solvent.

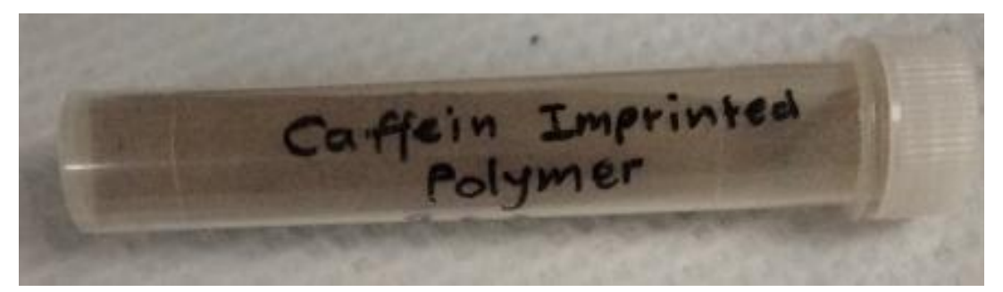


Figure 2. Caffeine imprinted polymer powder

RESULTS & DISCUSSION

Phase 1: Testing hydrophilicity and nanoparticle integration

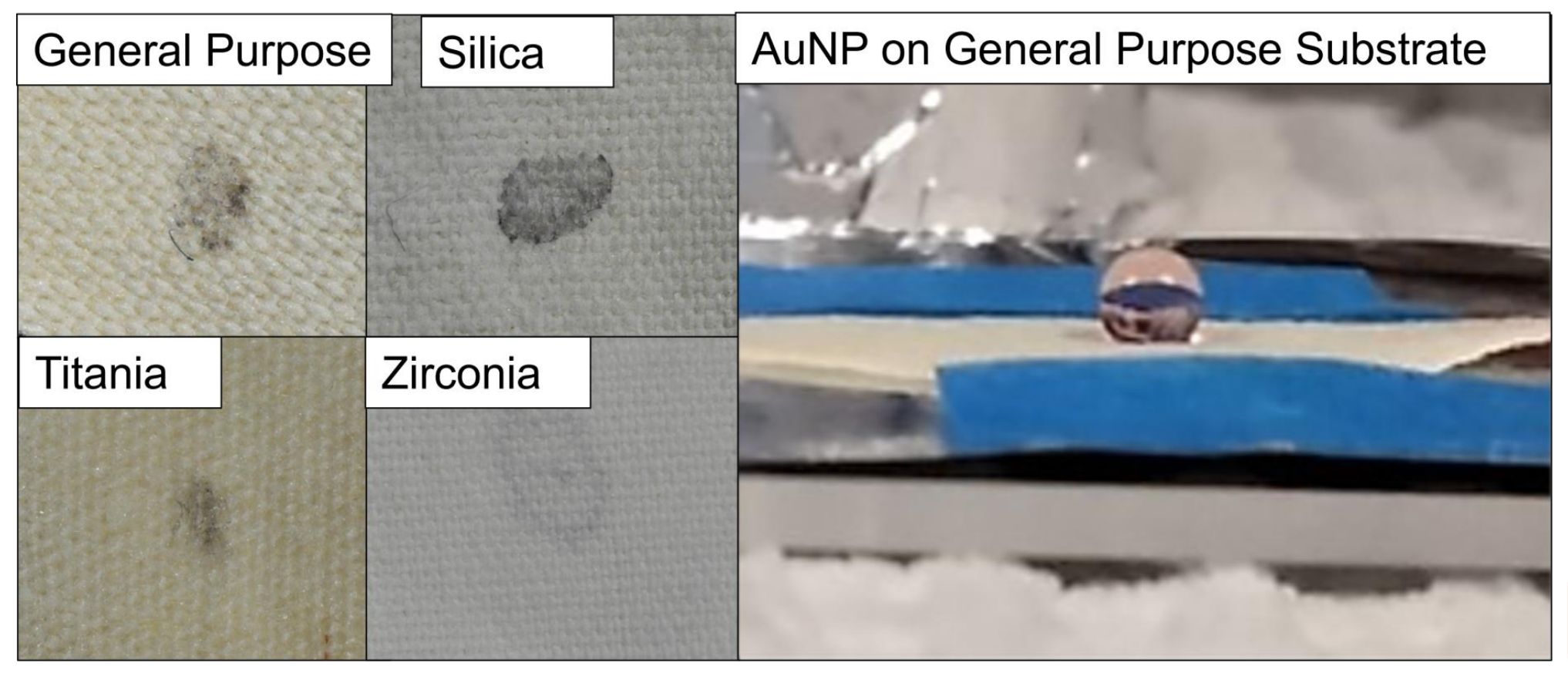


Figure 3 Substrates exhibiting intrinsic hydrophobic behavior: Fabric Phase Sorptive Extraction (FPSE) Membrane (General Purpose)| Silica | Titania | Zirconia

- Four substrates exhibited hydrophobic behavior (general purpose, zirconia, titania, and silica) as high contact angles were observed when AuNP solutions were pipetted onto substrates (**Figure 3**)
- A greater than 90° contact angle was observed on these substrates suggesting there is a limited ability for the AuNPs and substrates to interact
- These substrates were not considered for phase two

Phase 2: Crystal violet identification studies

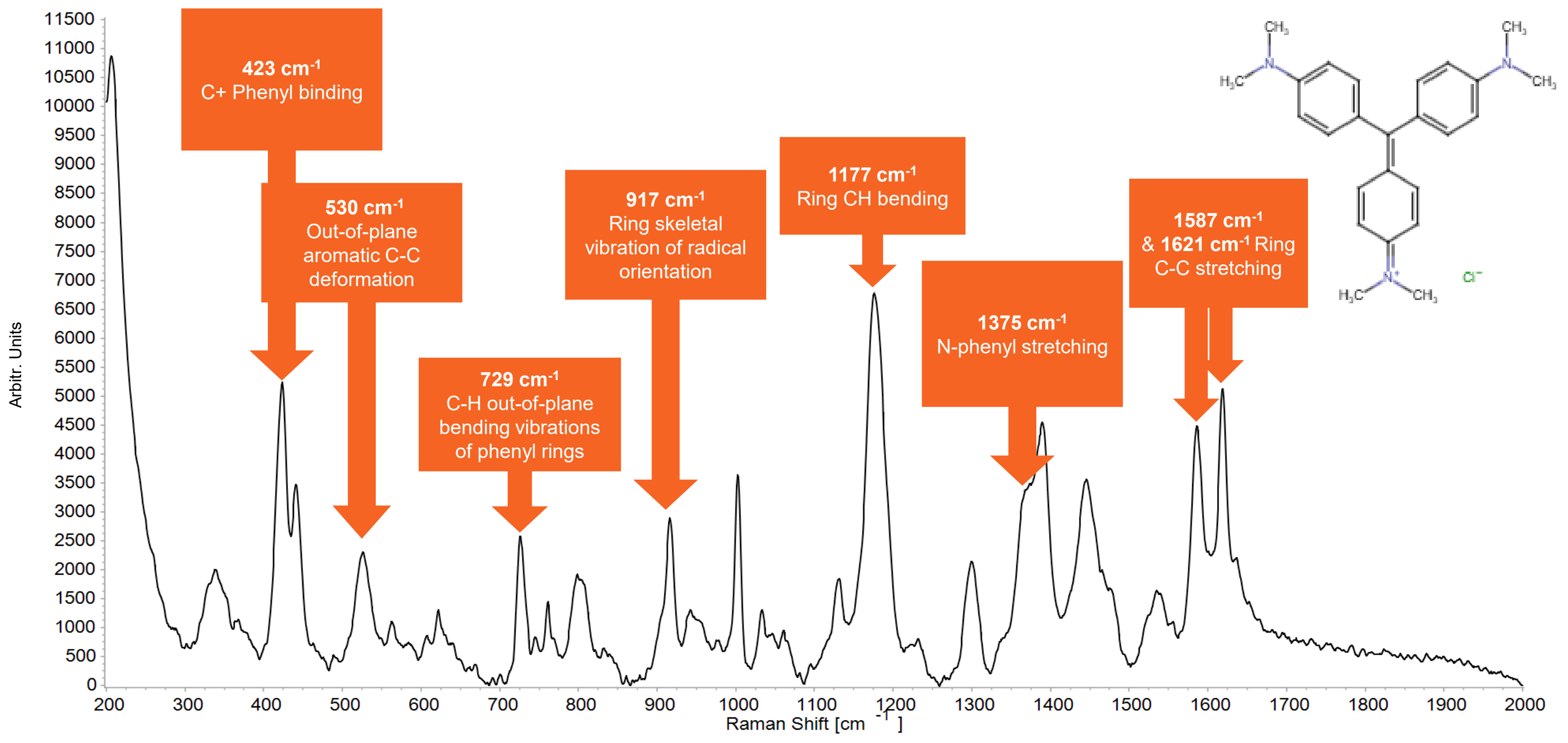


Figure 4 Raman spectrum of crystal violet on aluminum foil with characteristic peaks indicated for C+ phenyl binding, out-of-plane aromatic C-C deformation, C-H out-of-plane bending vibrations of phenyl rings, ring skeletal vibration of radical orientation, ring CH bending, N-phenyl stretching, and ring C-C stretching

- **Figure 4** shows the characteristic Raman bands for CV on an aluminum foil covered microscope slide and the vibrational modes associated
- All cotton and cellulose substrates were excluded following phase two as they did not allow the identification of CV
- Successful identification of CV is shown in **Figures 5** and **6** for both SERS nylon swabs (**Fig. 5A**) and SERS fiberglass (**Fig. 6A**)

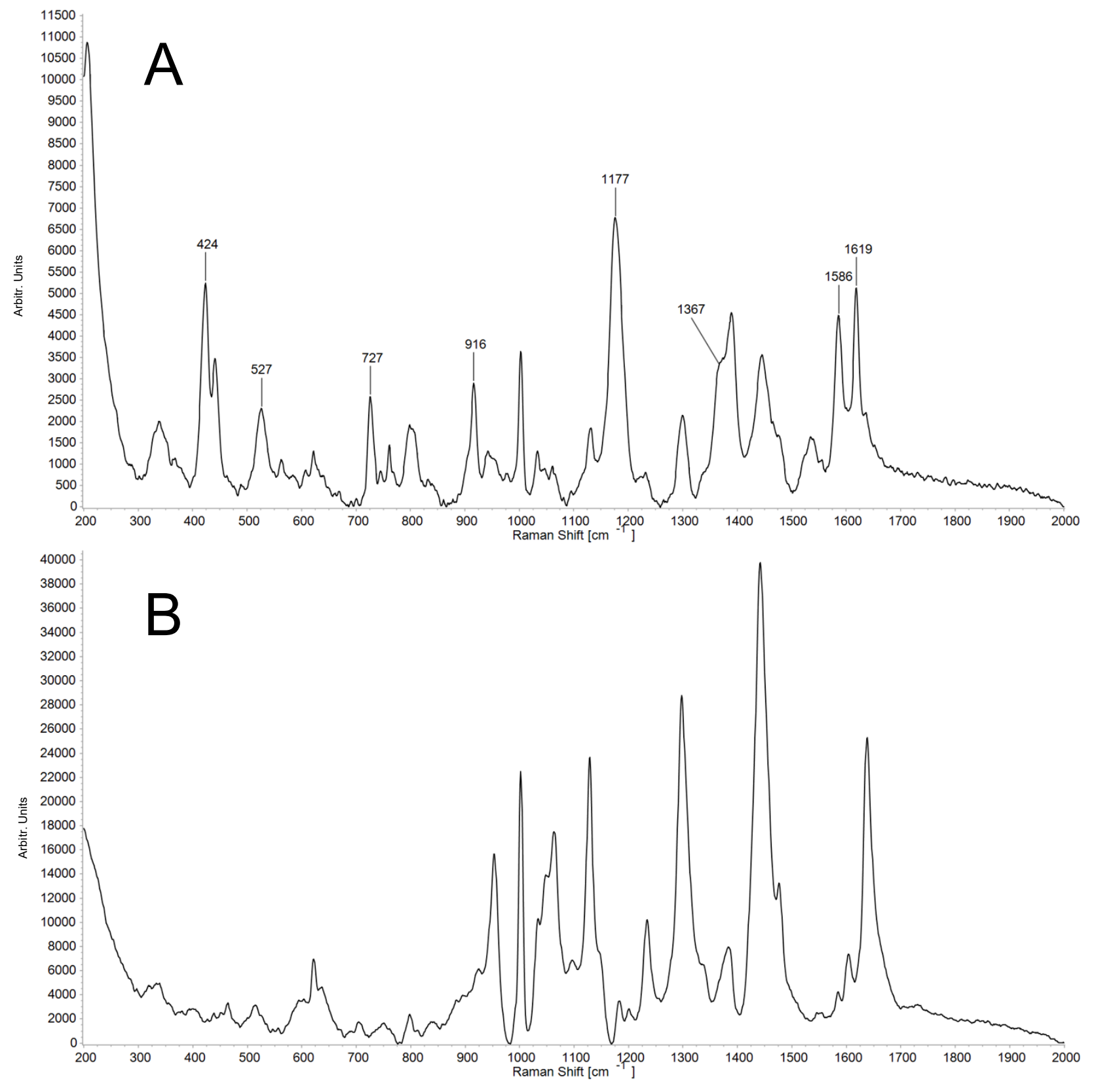


Figure 5. CV on SERS nylon swab with characteristic peaks indicated (**A**) and plain SERS nylon swab (**B**)

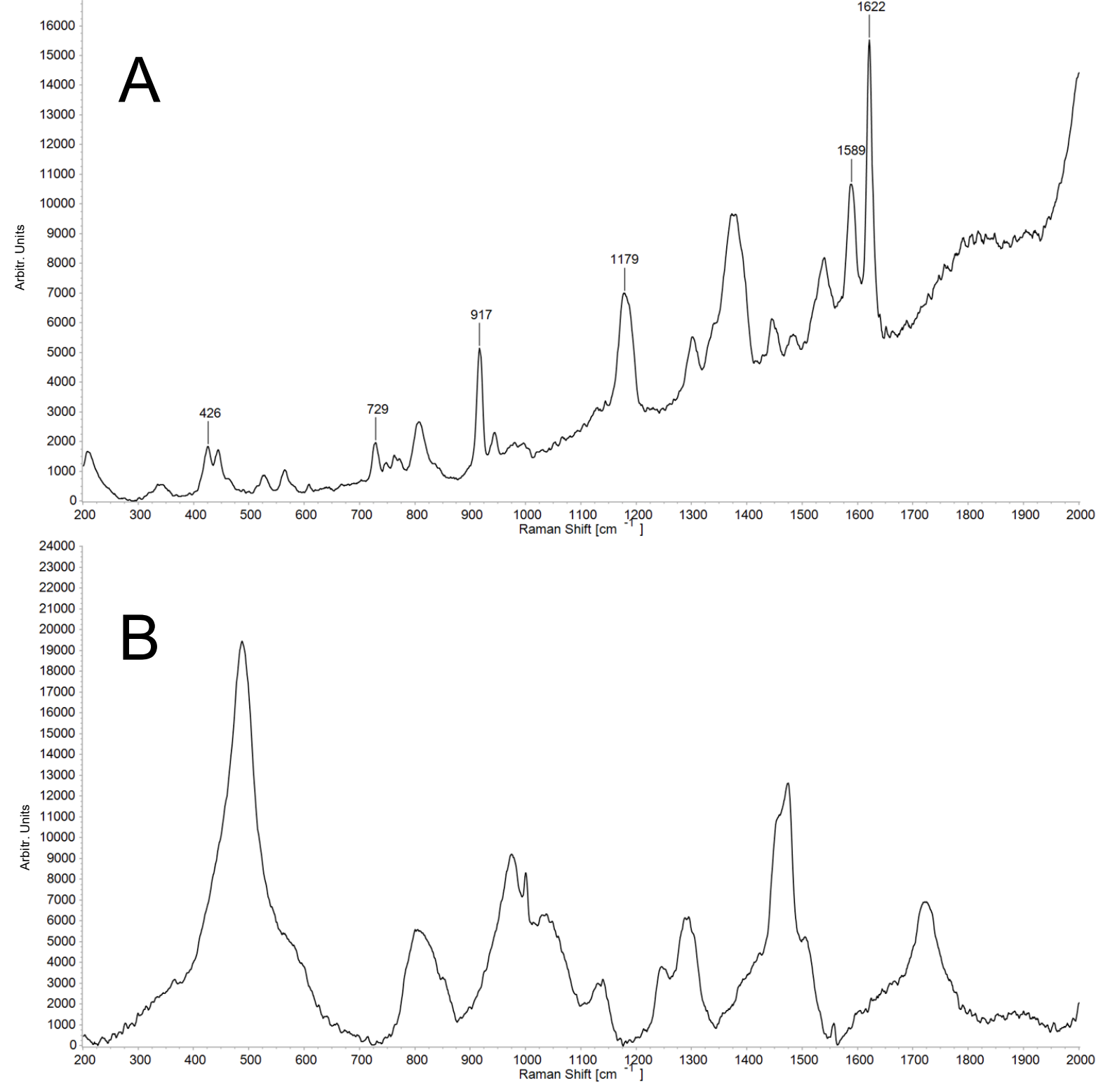


Figure 6. CV on SERS fiberglass with characteristic peaks indicated (**A**) and plain SERS Fiberglass (**B**)

Phase 3: Analysis of illicit drugs and cutting agents

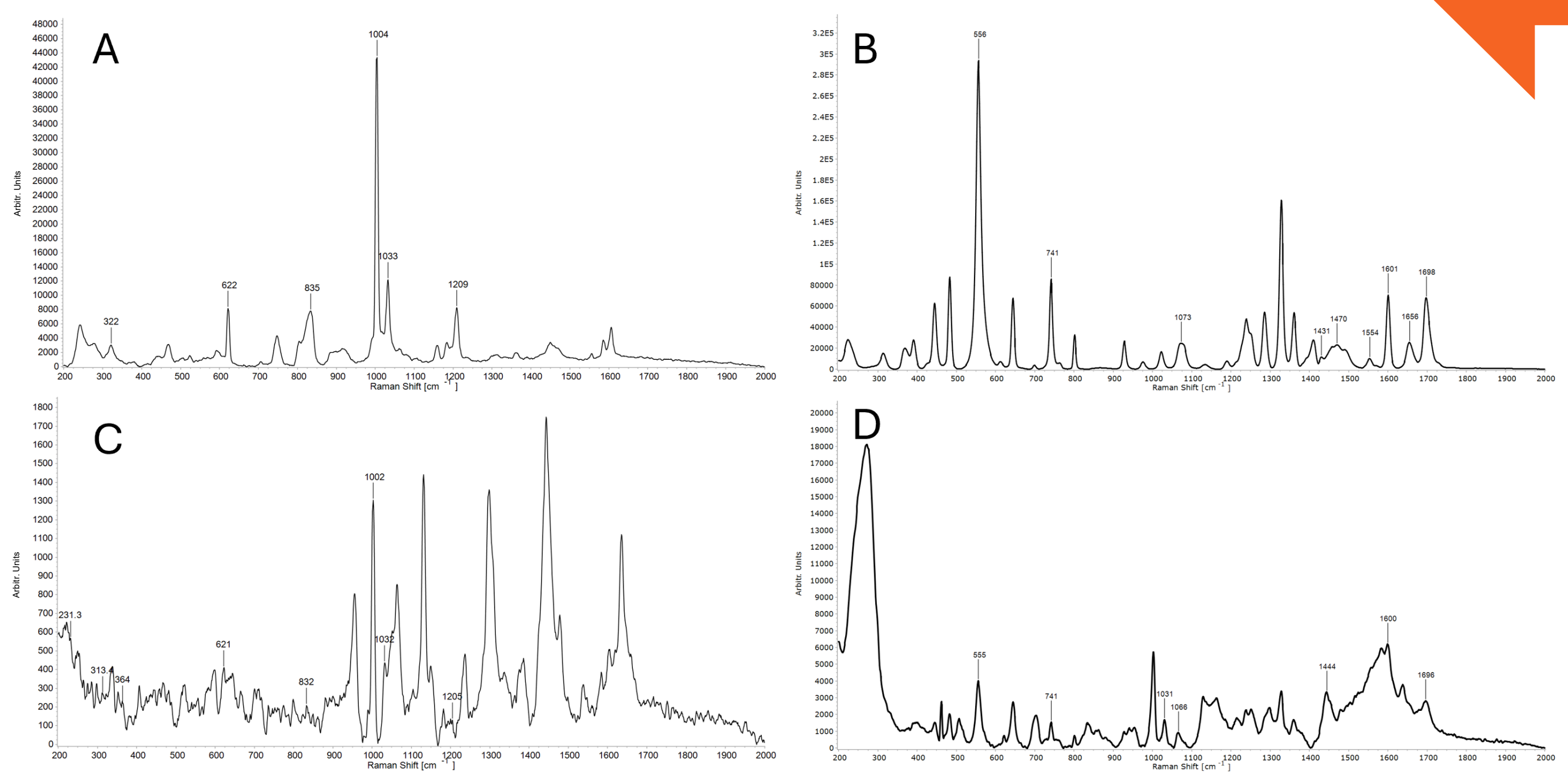


Figure 7. Methamphetamine on aluminum foil (**A**), caffeine on aluminum foil (**B**), Methamphetamine on SERS nylon swab (**C**) and caffeine on SERS nylon swab (**D**)

- As seen in **Figure 7C**, characteristic bands for methamphetamine were not reproducibly identified on the SERS nylon substrates, which could be due to their low volumes used in the study and the need to optimize the size and distribution of AuNPs
- The labeled Raman bands in **Figure 7C** can be attributed to the Raman spectra of a SERS nylon swab (**Figure 6B**) or are not of a high enough signal to noise ratio to be considered for identification
- **Figure 7B** and **7D** demonstrate the successful identification of caffeine using the SERS nylon swabs, with characteristic caffeine bands observed in both the aluminum foil–covered slide and the SERS nylon swab spectra
- Both caffeine and CV exhibit a greater scattering efficiency than methamphetamine due to their molecular structures being large and more conjugated
- Although SERS fiberglass was identified for phase three testing, it failed to retain structural integrity under magnetic stirring conditions; therefore, agitation of the caffeine solution in contact with the substrate was performed using a rocker
- Powdered caffeine-imprinted polymer was evaluated using a caffeine solution to assess its capacity to remove caffeine from the solution
- Absorbance results shown in **Table 2** demonstrate a higher absorbance from the caffeine solution after the exposure to the MIP polymer

Table 2 Absorbance data from UV-Vis spectrophotometer of caffeine in chloroform solution both with and without MIP powder imprinted for caffeine.

Caffeine in chloroform replicates 1-7		
Replicates	**Wavelength (nm)**	**Absorbance**
1	272	1.101
2	272	1.16
3	272	1.195
4	272	1.237
5	272	1.295
6	272	1.294
7	272	1.335
Average absorbance: 1.231		
MIP w/ Caffeine in chloroform replicates 1-7		
Replicates	**Wavelength (nm)**	**Absorbance**
1	274	0.353
2	275	0.353
3	269	0.354
4	269	0.361
5	269	0.369
6	275	0.373
7	275	0.385
Average absorbance: 0.364		
MIP + Caffeine solution/Caffeine solution 0.364/1.231 = 0.296		

CONCLUSIONS

- SERS fiberglass and SERS nylon swabs allowed for detection of CV and were therefore selected for phase three
- Caffeine was identified using the SERS nylon swab
- Methamphetamine was not successfully identified using the SERS nylon swab
- Reproducibility issues observed were likely due to the inhomogeneity of the size and distribution of the AuNPs. Future work intends to optimize the nanomaterials used in the SERS substrates
- Magnetic stir bars proved detrimental to the integrity of the SERS fiberglass material causing a rocker to be used for further absorbance studies
- An absorbance study demonstrates the ability of the powdered MIP polymer imprinted for caffeine to remove caffeine from solution upon exposure

REFERENCES

[1] https://www.cbp.gov/newsroom/stats/drug-seizure-statistics

[2] J. Turkevich, P.C. Stevenson, J. Hillier, A study of the nucleation and growth processes in the synthesis of colloidal gold, Discuss. Faraday Soc. 11 (1951) 55. https://doi.org/10.1039/df9511100055.

ACKNOWLEDGEMENTS

This work was supported by the Center for Advanced Research in Forensic Science (CARFS) Phase II, a National Science Foundation (NSF) and National Institute of Justice (NIJ) co-funded Industry-University Cooperative Research Center (IUCRC) [Award No. 2310951]. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.

Department of Forensic Science
College of Criminal Justice
forensics.shsu.edu

CARFS ForensicResearch.org
Center for Advanced Research in Forensic Science

INSTITUTE FOR FORENSIC RESEARCH TRAINING AND INNOVATION