Selective by Design: Development of SERS-MIP Substrates for Field Detection of Illicit Substances

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ABSTRACT

This study outlines the initial stage in developing field-portable sensors for detecting seized drugs with high selectivity and sensitivity. The final form of the desired sensors must include a substrate that meets the requirements of both a SERS substrate and a MIP. To this end, a three-phase substrate selection reduced prospective substrates from twelve to two. Both SERS fiberglass and SERS nylon swabs successfully detected crystal violet. However, challenges with nanoparticle size and distribution caused poor reproducibility in detecting target analytes and therefore requires further studies.

INTRODUCTION

The 2022 NFLIS report identified methamphetamine and cocaine as the two most frequently reported seized drugs by crime labs[1]. Current detection methods, such as colorimetric tests[2], are not confirmatory, can yield false reports, and are reliant on human interpretation.

Portable instrumentation, such as Raman spectrometers, lacks the sensitivity and specificity required for the analysis of samples in mixtures or complex matrices. Surface-Enhanced Raman Spectroscopy (SERS) enhances sensitivity but provides no additional specificity.

Molecularly Imprinted Polymers (MIPs) are substrates engineered with nano cavities complementary to the analyte(s) they aim to target, making them highly specific, but not increasing sensitivity. The combination of SERS and MIPs will allow for the sensitive and specific identification of illicit materials in the field.

MATERIALS & METHODS

Gold nanoparticle synthesis: Gold nanoparticles (AuNPs) synthesis followed a modified Turkevich[3] method, using sodium hydroxide as a capping agent and sodium borohydride as a reducing agent agent.

Deposition of AuNPs onto substrates: Once synthesized, deposited onto substrates via pipetting or submersion during synthesis.

Table 1. Substrates assessed in phases one and two 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 Polydimethlysiloxane Polycaprolactone	
Cellulose Canvas	Sol-gel tetramethoxyortho silicate/ CarboWax (PEG) 20M/ Aminopropyl triethoxysilane	
Nylon	Proprietary	

Substrates: Substrate chemical properties and images are shown in **Table 1**.

Instrumentation: All Raman spectra were collected using a Renishaw inVia™ InSpect confocal Raman microscope using a 20x or 100x objective, 532 nm or 785 nm laser, and a spectral range of 100-3200 cm^{-1}. Parameters varied depending on the substrate and analyte being tested.

Data Processing: The spectra were baseline corrected, normalized to the highest peak and smoothed using SpectraGryph 1.2 software.

Substrate assessment: Substrates were assessed in three phases to ensure their suitability for both SERS and MIP requirements.

Phase 1 - Physical properties and ability to integrate nanoparticles: This phase assessed the physical properties of the twelve substrates and their interaction with the aqueous AuNP solution.

Phase 2 - Crystal violet (CV) SERS: 2.5- 10 µL of 10^{-3} M crystal violet solution depending on the study was pipetted onto the 9 substrates selected for Phase 2 to determine their SERS enhancement and potential interferences from the substrates.

Phase 3 - Analysis of illicit drugs: 5 µL of methamphetamine (0.0067 M in methanol) and 5 µL of cocaine (0.1 M in methanol) were pipetted onto two SERS Copan swabs.

RESULTS & DISCUSSION

Phase 1: Physical properties and ability to integrate nanoparticles

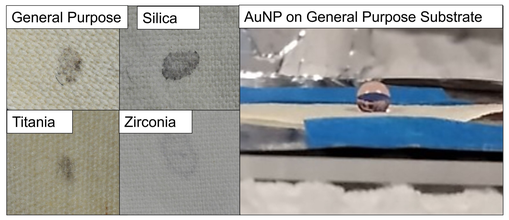

Figure 1. Substrates exhibiting intrinsic hydrophobic behavior: Fabric Phase Sorptive Extraction (FPSE) Membrane (General Purpose)| Silica | Titania | Zirconia

- Four substrates exhibited intrinsic hydrophobic behavior (general purpose, titania, zirconia, and silica)
- This behavior was evidenced by the high contact angles observed when water-based AuNP solutions were pipetted onto their surfaces in **Figure 1**
- The contact angle greater than 90° observed indicated poor wetting and limited interaction between the aqueous AuNP solution and the substrates

Phase 2: Crystal violet SERS studies

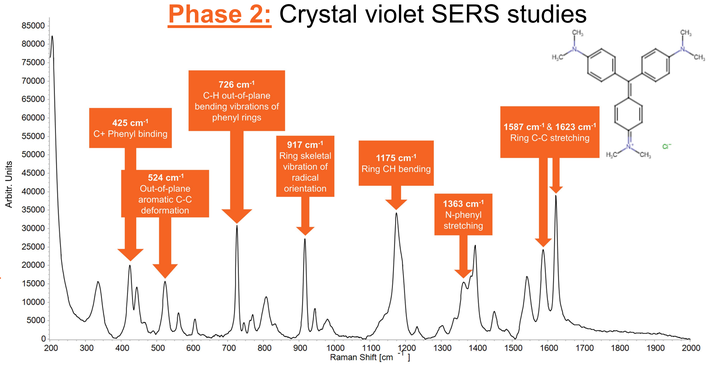

Figure 2. Raman spectrum of crystal violet on aluminum foil with characteristic peaks indicated for C+ phenyl binding, out-of-plane aromatic C-C deformation, C-H out-of-plane bending vibrations of phenyl rings, ring skeletal vibration of radical orientation, ring CH bending, N-phenyl stretching, and ring C-C stretching

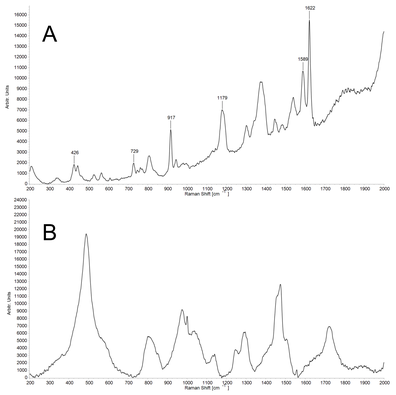

Figure 5. CV on SERS fiberglass with characteristic peaks indicated (**A**) and plain SERS Fiberglass (**B**)

Figure 2 highlights characteristic peaks of CV including C+ Phenyl binding, ring skeletal vibration of radical orientation, ring CH bending, and ring C-C stretching

All four cotton type substrates (**Figure 3**) were excluded in Phase 2 as their Raman spectra exhibited bands in locations similar to those of CV and the illicit substances investigated in this study

Cellulose based substrates did not allow for the enhancement of characteristic bands for CV

Identification of CV using SERS nylon swabs and SERS fiberglass is shown in **Figure 4A** and **Figure 5A** respectively

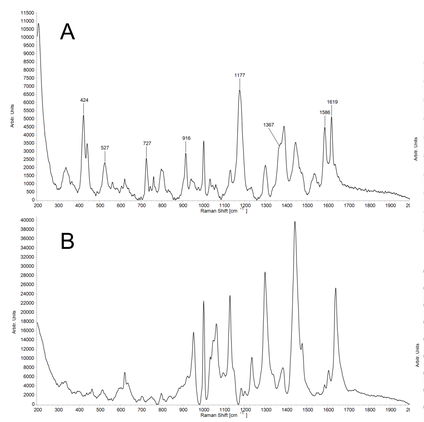

Figure 4. CV on SERS nylon swab with characteristic peaks indicated (**A**) and plain SERS nylon swab (**B**)

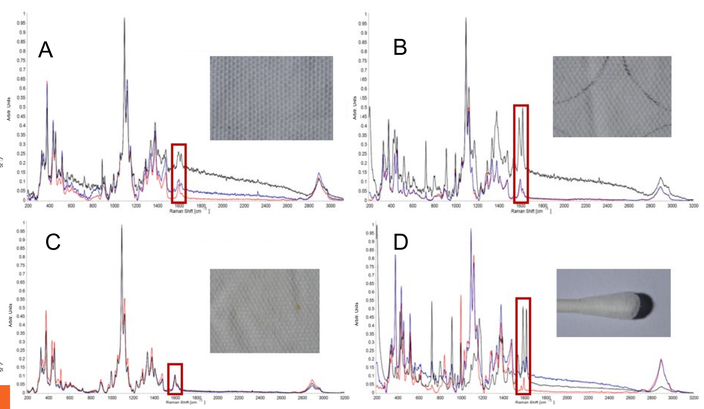

Figure 3. CV on cotton canvas (**A, B,** and **C**) and bud (**D**). **Red spectra-** Blank non-SERS substrate **Blue spectra-** Non-SERS substrate and CV solution in methanol **Black spectra-** Non-SERS substrate and CV solution in water.

Phase 3: Analysis of illicit drugs

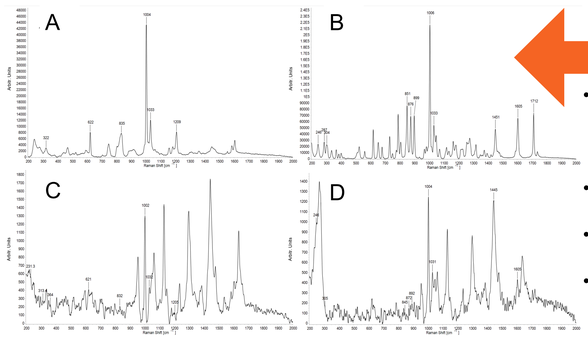

Figure 6. Methamphetamine on aluminum foil (**A**), Cocaine on aluminum foil (**B**), Methamphetamine on SERS nylon swab (**C**) and Cocaine on SERS nylon swab (**D**)

- As seen in **Figures 6C and D**, characteristic bands for methamphetamine and cocaine could not be identified on the SERS nylon substrates, which could be due to their low concentrations used in the study
- The same results were observed for methamphetamine using the SERS fiberglass
- CV exhibits a greater scattering efficiency than methamphetamine and cocaine
- This higher efficiency can be attributed to its molecular structure, which includes a larger conjugated system and stronger chromophoric properties, in contrast to the comparatively smaller and less conjugated molecular frameworks of the illicit substances

CONCLUSIONS

- Characteristic peaks of CV were successfully identified using both SERS fiberglass and SERS nylon swabs, which were selected for Phase 3
- Characteristic peaks for both methamphetamine and cocaine were not enhanced as anticipated using either SERS substrates
- Reproducibility challenges were observed, which could be attributed to the non-uniform distribution of nanomaterials and analytes across the SERS substrates
- Inability to detect target analytes could be due to low concentration and uneven distribution of nanoparticles across the substrate surface
- Further studies using SERS nylon swabs and SERS fiberglass and greater concentrations of the illicit substances are currently being conducted

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