The Identification of Controlled Substances by TLC-SERS

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Theory

Thin layer chromatography (TLC) combined with surface-enhanced Raman spectroscopy (SERS) proved to be an ideal method for separating and identifying controlled substances and mixtures. This combined method adheres to the standards set forth by the Scientific Working Group for the Analysis of Seized Drugs (SWGDRUG) and is a rapid, reliable, and repeatable method of drug analysis.

TLC is a separation method used as a screening test in forensic laboratories. This technique involves depositing sample onto a planar stationary phase then using a liquid mobile phase that travels up the stationary phase by capillary action. The ending result is a plate of spots that are the separated components of the mixture.

Raman spectroscopy is an identification method that examines the frequency change of a light source due to its interaction with the sample. The major limitations to Raman spectroscopy are low sensitivity and fluorescence interference.

SERS enhances the scattering procedure of Raman spectroscopy and corrects the disadvantages of normal Raman spectroscopy. The procedure mirrors that of normal Raman—the main difference being the addition of a silver nanoparticle colloid.

TLC-SERS is completed on a TLC plate by adding a metallic colloid to a separated TLC spot, and then directly analyzing the spot using Raman spectroscopy.

Methods and Materials

This research analyzed the illicit drugs cocaine, codeine, methamphetamine, and 3,4-methylenedioxy-N-methylamphetamine (MDMA). The drugs were mixed with caffeine for the drug mixture analysis. The same procedure was carried out on all of the above drugs. A sample of 0.100g was weighted out and placed in a glass vial. From the 0.100g of sample, 0.0100g was combined with 2.5mL of methanol to make a liquid solution.

To confirm that the dispersive Raman spectrometer equipped with a 780 nm frequency-stabilized single mode diode laser was working properly, a polystyrene reference standard was analyzed daily. Substrate tests were also conducted using aluminum plates and silica gel on glass TLC plates. The solid samples and dried residues from the liquid solutions were tested using normal Raman spectroscopy and SERS using the following collection parameters: auto exposure with the signal to noise ratio set to 500 and a maximum collection time of 3 minutes. The normal Raman and SERS spectra were used as comparisons for the TLC-SERS spectra of the drugs and mixtures. To analyze using TLC-SERS, the liquid solution was spotted on a TLC plate, then separated using a 9:1 chloroform to methanol TLC bath. The spots were found using a short wave UV light. The sample spots were analyzed using normal Raman spectroscopy. To perform the SERS analysis, a drop of silver colloid was placed directly onto the TLC plate spot then analyzed with the Raman spectrometer. This procedure was conducted for all four drugs and for the separated drug mixtures.

Results

The illicit drugs were not detectable on the TLC plates using normal Raman spectroscopy. When the TLC spots of the drugs were analyzed with SERS, the spectrum was enhanced thus enabling direct drug identification.
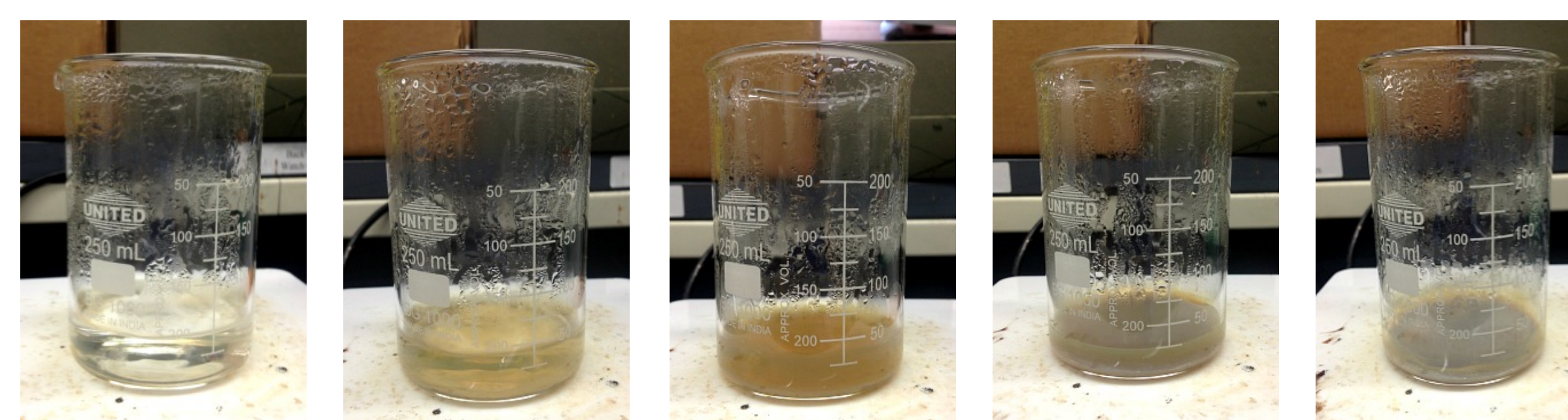
Silver Colloid Preparation

Figure 1 shows the silver colloid being prepared. The pictures were taken in 10 minute increments. The colloid is composed of two solutions: the first being 0.170g silver nitrate and 1.00L deionized water and the second being 1.00g sodium citrate and 0.100L deionized water. 50.0mL of the silver nitrate solution was heated to a boil, and then 1.00mL of sodium citrate solution was added. The solution was heated for one hour.

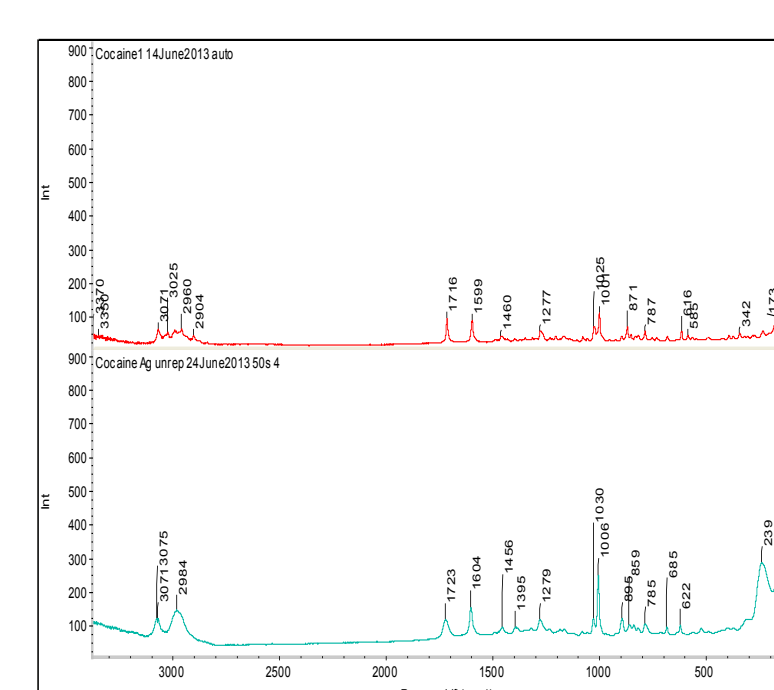### Cocaine: normal Raman vs. SERS

Figure 2 shows two spectra for the analysis of cocaine. The top is the normal Raman spectrum of cocaine while the bottom is the SERS spectrum of cocaine.

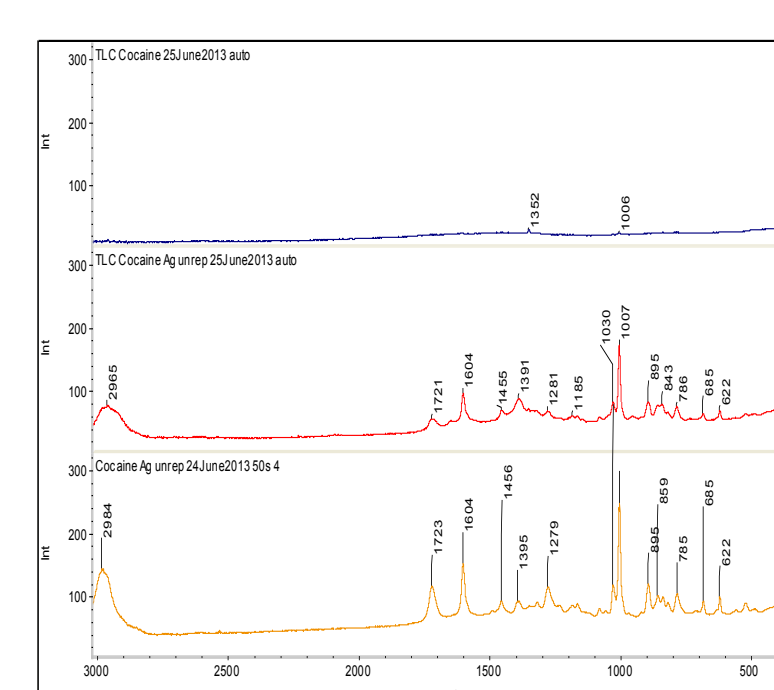### Cocaine: TLC-normal Raman vs. TLC-SERS vs. SERS

Figure 3 shows three spectra for the analysis of cocaine. The top is a normal Raman spectrum of a cocaine spot on a separated TLC plate. The middle is a SERS spectrum of a cocaine spot on a separated TLC plate. The bottom is a SERS spectrum of cocaine on an aluminum slide.

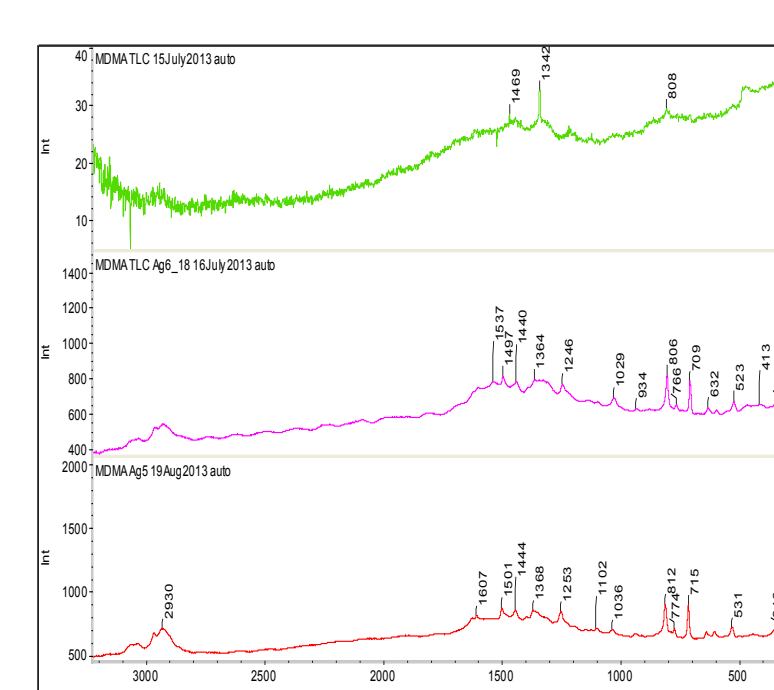### MDMA: TLC-normal Raman vs. TLC-SERS vs. SERS

Figure 4 shows three spectra for the analysis of MDMA. The top is a normal Raman spectrum of a MDMA spot on a separated TLC plate. The middle is a SERS spectrum of a MDMA spot on a separated TLC plate. The bottom is a SERS spectrum of MDMA on an aluminum slide.

Conclusions

TLC-SERS proved to be a successful method for the separation and identification of controlled substances and controlled substance mixtures. This combined technique has the potential to greatly benefit the forensic science community because it requires less sample, time, and money when compared to other methods of illicit drug analysis and conforms to the currently accepted standards of drug identification set forth by SWGDRUG.

Future Work

Additional research experiments will be conducted using different illicit drugs and drug mixtures. An investigation into the use of gold colloids, rather than silver colloids, for SERS enhancement will be explored. Also, the authors will evaluate the limits of detection for this technique. Last, research focusing on the detection of illicit drugs in body fluids using both normal Raman and SERS spectroscopy will be explored.

References

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Acknowledgements