K18 The Evaluation of Mono-, Di-, and Trivalent Cations for the Optimized Surface-Enhanced Raman Spectroscopy (SERS) Enhancement to Detect Synthetic Cannabinoids in Biological Samples

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After attending this presentation, attendees will understand: (1) the principles of SERS; (2) how the use of mono-, di-, and trivalent cations as aggregating agents with gold nanoparticles can affect SERS enhancement and detection of synthetic cannabinoids; (3) how SERS can be used to create a low limit of detection for synthetic cannabinoids; and, (4) how SERS can be a fast and easy analysis for drug detection in toxicological samples.

This presentation will impact the forensic science community by demonstrating the application of SERS as a useful procedure for detecting trace levels of various JWH and PINACA compounds and their metabolites in solution that is rapid, sensitive, and applicable to a variety of biological matrices.

The use and abuse of synthetic cannabinoids has become a global issue due to their easy access and growing popularity in young adults. This popularity has led to an increase in emergency room visits due to synthetic cannabinoid intoxication in recent years. As more of these drugs become illegal, new synthetic legal versions of these compounds are made, which presents problems for the forensic scientist as standard methods may not detect the target drug.

The most common method of screening for drugs of abuse in biological samples is the immunoassay. However, this method presents some disadvantages, particularly for newly synthesized compounds which may not respond to the test. Other problems include cross-reactivity between different synthetic cannabinoids, hook effects, and high cut-off values for determining if the drug is present. More advanced methods, such as GC/MS, have also been used; however, these procedures involve complex sample preparation and long run times. A potential solution to this issue is surface enhanced Raman spectroscopy.

Raman spectroscopy is an under-utilized technique for the detection and identification of drugs due to its perceived low sensitivity. However, when Raman spectroscopy is performed in the presence of metallic nanoparticles, the signal can be enhanced by several orders of magnitude due to localized metallic plasmon field effects. This process is known as Surface Enhanced Raman Spectroscopy (SERS). The addition of aggregating agents, generally ionic salts, further increases this signal due to the creation of hot-spots resulting from nanoparticle interactions. This method has recently been confirmed to work for the toxicological detection of benzodiazepines with limits of detection ranging from 1ng/mL - 200ng/mL.

In this project, gold nanoparticles were prepared using a sodium citrate reduction with mono, di, or trivalent cation aggregating agents. The concentration, absorbance, size, and zeta potential of the nanoparticles was analyzed before and after the addition of the aggregating agents (KCl, NaCl, $MgCl_2$, $CaCl_2$, $AlCl_3$, and $RuCl_3$) to assess the effect on the SERS enhancement. It was experimentally determined that the SERS enhancement for mono and divalent cations was due to the chloride anion interaction with the nanoparticle. However, the trivalent cations produced SERS enhancement via the cations interaction with the surface of the nanoparticle to cause aggregation.

Experiments were performed using a variety of synthetic cannabinoids including JWH-018, JWH-073, JWH-081, JWH-122, APINACA (AKB48), AB-PINACA, ADB-PINACA, AB-CHMINACA, and several of their metabolites. The six different chloride aggregating agents were examined at 0.0167M. From this analysis, 0.017M of $MgCl_2$ was determined to be the optimal aggregating agent. Then, varying concentrations of $MgCl_2$ were examined to optimize sensitivity of detection for a bench top and portable Raman system. While 0.017M $MgCl_2$ was the optimal concentration for the bench top Raman, a portable Raman system required a 2-fold increase in concentration of $MgCl_2$ for optimal detection. Using this SERS method, synthetic cannabinoids could be detected at concentrations as low as 18ng/mL. Spiked urine samples at physiological concentrations were next screened using a supported liquid extraction involving an ammonium acetate buffer followed by dichloromethane solvent system.

These results demonstrate that SERS can be a useful and more comprehensive alternative to immunoassays in the screening of synthetic cannabinoids in urine.

SERS, Synthetic Cannabinoids, Toxicology