K30 Electrochemical Detection of Fentanyl Using Screen-Printed Carbon Electrodes With Confirmatory Analysis of Fentanyl and Its Analogs in Oral Fluid Using Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS)

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Learning Overview: After attending this presentation, attendees will be able to explain the theory behind the use of electrochemical techniques such as Square-Wave Voltammetry (SWV) for the analysis of fentanyl and illicit substances in forensic science and will understand the importance of these techniques as screening tools.

Impact on the Forensic Science Community: This presentation will impact the forensic science community by providing new methods of screening illicit substances both at the crime scene and within the lab that are fast, reliable, and provide both qualitative and quasi-quantitative data. This work may aid in speeding up and improving the seized drug workflow on cases, helping to reduce backlog and increase the speed of investigations.

Due to the growing number of cases involving fentanyl and fentanyl analogs, opioid abuse poses a significant threat to the United States. Opioid-related overdose deaths have increased over the past several years leading to a public health emergency declared by the Department of Health and Human Services. New Psychoactive Substances (NPS) have compounded the issue due to having similar or increased potency. NPS are synthetic analogs to known controlled substances designed by making modifications to the core chemical structure in most cases, and include fentanyl-analogs and synthetic cannabinoids, among others. Electrochemistry can provide a rapid, sensitive, and selective screening technique to overcome the limitations faced by other methods in the field. Electrochemistry offers a versatile platform that is sensitive, portable, and low cost, which can be modified to suit a variety of needs and detection requirements.

Utilizing Screen-Printed Carbon Electrodes (SPCEs), a fast, simple, and sensitive approach toward the detection, identification, and quasi-quantitation of fentanyl, was achieved both in an electrochemical cell and as a drop on the electrode surface. Electrooxidation of fentanyl at the electrode was demonstrated using SWV between -0.5V and +1.6V with 100mM Tris-HCl buffer at pH 8.5 as supporting electrolyte. Parameter optimization was conducted. Voltammograms demonstrated the presence of two oxidation peaks at 750mV (peak I) and 880mV (peak II) versus pseudo Ag/AgCl. Fentanyl oxidation was observed at concentrations of ~76ng/mL in cell and ~300ng/mL in a 100µL drop.

Reproducibility between electrodes, assessed as the average Relative Standard Deviation (RSD), for peak I and peak II in cell was 12% and 18%, respectively. RSD in drop was 13% and 15% for peaks I and II. Accuracy of the detection method was determined in cell by analyzing single-blind samples prepared in lab and demonstrated better accuracy in lower concentrations of fentanyl versus higher concentrations. The assessment of the effects of interfering compounds, including cocaine, methamphetamine, quinine, and acetaminophen, was performed. Analysis of various ratios of fentanyl to interferent were analyzed and demonstrated the ability of the method to detect fentanyl while present in these mixtures. The mechanism of the electrooxidation of fentanyl in the system is proposed herein.

A confirmatory Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS) method for the analysis of fentanyl and fentanyl analogs in oral fluid using dynamic Multiple Reaction Monitoring (dMRM) was developed and validated. A total of 13 fentanyl/fentanyl analogs with 7 internal standards were analyzed. The limit of detection of the majority of drugs was determined to be 0.01ng/mL with the limit of quantitation at the lowest calibrator of 0.1ng/mL with coefficients of determination between 0.9992 and 0.9999. Solid Phase Extraction (SPE) was used in the assessment of bias, precision, matrix effects, recovery, and process efficiency, which were deemed acceptable based on validation guidelines. Selectivity was demonstrated through the analysis of 12 additional illicit substances commonly encountered in the forensic laboratory. Processed sample stability and freeze/thaw stability were also assessed.

Electrochemistry, Fentanyl, LC/MS/MS