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Editorial: Luminescence and electrochemical methods: Analysis of physical evidence

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Editorial on the Research Topic
Luminescence and electrochemical methods: Analysis of physical evidence

In this inspiring issue, three interesting and diverse peer-reviewed articles were published: two full research articles and one review article. The topics of these articles covered luminescence and electrochemical methods for the analysis of physical evidence. The three articles discussed the detection of fentanyl and its analogs *via in situ* electrochemical-surface enhanced Raman spectroscopy (EC-SERS), the utilization of electrochemistry to probe the degradation and time since deposition of blood and, finally, the role of fluorescence spectroscopy in the analysis of blood. These articles highlighted some of the main challenges currently facing forensic practitioners working with different types of physical evidence and provided suggestions for some of the fundamental unanswered questions. Can we rapidly differentiate between fentanyl and its analogs? Can we predict the degradation behavior of bloodstains at different temperatures using electrochemistry? How can fluorescence spectroscopy be beneficial for blood analysis?

Due to the increase in casework related to fentanyl and its analogs, there is a genuine need for simple, rapid and sensitive methods for their identification and differentiation. In this respect, the *in situ* electrochemical-surface enhanced Raman spectroscopy (EC-SERS) method was developed by Ott et al. for the rapid detection of fentanyl and six of its analogs. In this detailed study, the authors initially optimized the experimental conditions for the SERS substrate and amperometric detection. The synthesis and roughening of the SERS substrate (Ag nanoparticles) were performed *in situ* utilizing cyclic voltammetry (CV) and multipulse amperometric detection (MPD). Consequently, MPD parameters were optimized to obtain the maximum response and improved enhancement due to SERS hot spot generation. Major functional groups in fentanyl were identified, and acetyl fentanyl, methoxyacetyl fentanyl, furanyl fentanyl, acryl fentanyl, valeryl fentanyl and despropionyl fentanyl (4-ANPP) analogs were successfully analyzed due to their difference in the amide portion. This is significant for crime laboratories when minor differences in the drug molecule structure can make identification challenging. Sensitivity was evaluated by determining the limit of detection of each drug by measuring the signal

at the major Raman shift for fentanyl (1,004 cm^{-1}), and concentrations in the low-to-mid ppb range were obtained. Analysis of mixtures of fentanyl with heroin (1:4), methamphetamine (1:4), and caffeine (1:20) to simulate seized drugs showed that EC-SERS produced a great signal for fentanyl despite its low concentration in the samples. The application of *in situ* EC-SERS for fentanyl and its analogs shows huge promise as a highly rapid and sensitive approach with great discrimination power.

In the other two articles, by Tiessen et al. and Weber (Weber and Lednev), analysis of blood evidence was described. Blood is one of the most important types of evidence; it is a rich source of DNA, it can be used to understand the circumstances of the crime through bloodstain patterns, and it is a common matrix for toxicological analysis. Tiessen et al. expanded the use of electrochemical methods to probe changes in hemoglobin (Hb) as the primary analyte in degrading blood samples. A total of three oxidation peaks were observed for Hb using differential pulse voltammetry (DPV). Then, in neutral pH solution, fresh blood, 2-week-old liquid blood kept in the refrigerator and a 3-day-old dried bloodstain were analyzed. The fresh blood analysis indicated that degradation of blood formed mainly water and hydrogen, whereas aged samples produced hydrogen peroxide; hydrogen peroxide was obtained when blood was studied in basic pH solution. In the time since deposition (TSD) investigation, a decrease in the reduction peak was observed, and an increase in the magnitude of the oxidation peak was noticeable, which was expected due to environmental oxidative damage. Parameters such as different donors and environmental factors (Sun exposure, humidity and temperature) can highly influence TSD determination. The use of an electrochemical approach provided insights into the oxidation/reduction behavior of blood on the surface of the electrode, and further investigation is required to develop a universal method for determining the TSD of blood evidence.

The interaction of light with matter can provide a wealth of information regarding the matter under investigation. Scientists have utilized the different sources of radiation to their advantage and have determined the molecular signature of a variety of biomolecules. Weber and Lednev focused on TSD of blood using fluorescence spectroscopy due to its high sensitivity. Fluorescence spectroscopy takes advantage of the fluorescent molecules in blood, mainly tryptophan (Trp, present in albumin and γ-globulin), nicotinamide adenine dinucleotide (NADH) and flavin adenine dinucleotide (FAD). Steady state fluorescence, fluorescence lifetime and phenotype research were the main approaches covered. The results depicted changes over time in the detected signal of the biochemical species; for example, for peripheral blood, the Trp signal decreased over the first 24 h of sample deposition, while the signal from NADH increased during that time. Despite the limited specificity of fluorescence, it has shown excellent proof-of-concept results for TSD and blood analysis.

Articles in this Research Topic approached important topics in forensic analysis of physical evidence, and the results presented can be further utilized to expand the preliminary findings. In future articles, we hope to see the continuation of the current work to establish new means and methods for answering investigative questions in forensic science.

Author contributions

EA-H wrote and edited the editorial.

Conflict of interest

The author declares that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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