Field Detection of Cocaine and its Impurities in Human Fingernails Using Portable Attenuated Total-Reflectance Fourier Transform Infrared Spectroscopy and Machine Learning Analytics

Megan Wilson[1], Leung Tang[2], Ismail Abbas[3], Jason Birkett[1], Iftikhar Khan[1], Dhiya Al-Jumeily OBE[4] and Sulaf Assi[1]
[1]School of Pharmacy and Biomolecular Sciences, Liverpool John Moores University, L3 3AF, UK.
[2]Agilent Technologies, Field Detection Group, OX11 0RA, UK.
[3]Faculty of Science, Lebanese University, Beirut, Lebanon.
[4]School of Computer Science and Mathematics, Liverpool John Moores University, L3 3AF, UK.
m.wilson3@2019.ljmu.ac.uk

LIVERPOOL JOHN MOORES UNIVERSITY

Introduction

- In recent year, fingernails have become an interest in forensic toxicology as a useful matrix for the detection of endogenous compounds, drugs and impurities. This is attributed to nails accumulating substances over a long period of time and acting as drug depots (Shu *et al.,* 2015). Substances are incorporated into fingernails through the blood's simple diffusion, which deposits the substances into the nail bed and into the germinal matrix.
- Fingernails are comprised of a laminated keratinised structure of alpha keratin, which possess sulphur-rich amino acids, cysteine and cystine.
- Attenuated total reflectance Fourier transform-infrared (ATR-FTIR) spectroscopy is a spectral fingerprinting technique that offers characteristic signatures relating to the analyte's chemical properties (Meyers, 2000). Moreover, ATR-FTIR spectroscopy non-destructive nature make it convenient for characterising fingernails.

Objectives

The aim of this study was to utilise portable ATR-FTIR spectroscopy combined with machine learning analytic (MLAs) for detection of cocaine and its impurities in fingernails. This study also looked at the deposition of drugs into fingernails over a six-week spiking period, with the aim of differentiating acute versus chronic drug exposure.

Methodology

- Ethical approval was obtained via LJMU (PBS/2021-22/04). Participants, recruited via LJMU, donated approximately 7-10 fingernail clippings.
- Fingernails were measured 'as received' prior to spiking. ATR-FTIR spectra of cocaine and its impurities (benzocaine, diltiazem HCl, levamisole HCl, lidocaine HCl and procaine HCl) were collected using the portable Agilent 4500 ATR-FTIR spectrometer (Figure 1).
- A measurement was taken at start (week 0) and once a week for six weeks to monitor drug deposition. Spectra were imported into Matlab 2019a for spectral visualisation and the application of MLAs. Two MLAs were used (unsupervised): principal component analysis (PCA) and artificial neural networks self-organising maps (SOM) in order understand patterns among the measured fingernail samples.

Figure 1. Agilent 4500a ATR-FTIR spectrometer.

Results and Discussion

Spectral Interpretation: Figure 2 demonstrates the deposition of cocaine into fingernails and was featured in spiked fingers with key bands observed at 2500 cm^{-1} (N-H stretching), 1728 cm^{-1} (carbonyl group stretching), 1105 cm^{-1} (C-O stretching) and 1071 cm^{-1} (monosubstituted benzene stretching) (Silvia *et al.*, 2018) (Figure 2).

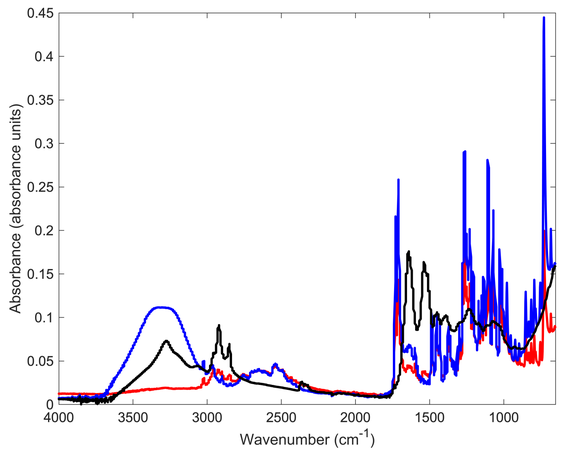
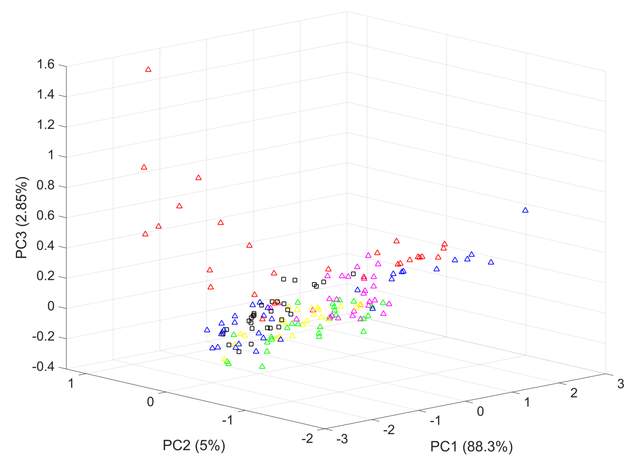


Figure 2. ATR-FTIR spectra of cocaine HCl (blue), fingernail spiked with cocaine (red) and unspiked fingernail (black.

PCA: PCA outcomes confirmed that cocaine showed the highest affinity for fingernails and was deposited to a higher level in comparison to its impurities. Therefore, fingernails spiked with cocaine were clustered separately from the other sets of spiked fingernails (Figure 3). This can be attributed to cocaine's OH group, which binds to the fingernail's keratin. The deposition of cocaine in fingernails is influenced by duration. Exposure taking place over a longer period of time meant that a greater number of drug-protein interaction occurred. Hence, a higher level of cocaine was detected after the six-week spiking period.

Figure 3. PC scores plot of the ATR-FTIR spectra of spiked fingernails including fingernails spiked with cocaine (red).



SOM: A 3 x 3 map was chosen to account for the three expected variations among the data, including: (1) the fingernail's physical properties, fingernail's water content and the deposition of cocaine into the nail. In this respect, SOM confirmed PCA findings and identified nine groups. Two key groups were identified, those being (1) fingernails spiked with cocaine (n = 27) and (2) un-spiked fingernails (n = 31). Due to the poor uptake of impurities, overlap was observed with un-spiked fingernails.

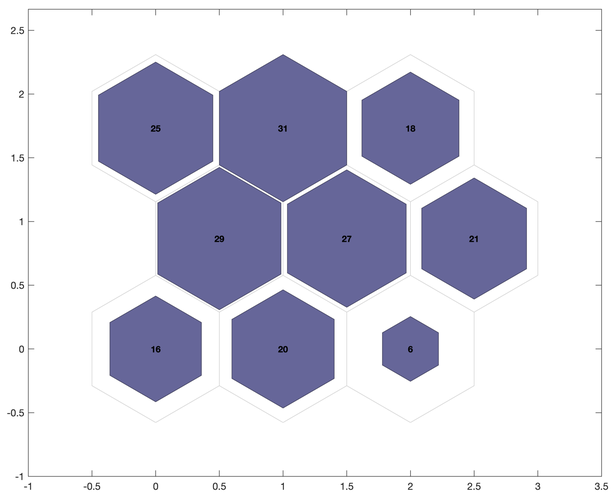


Figure 4. SOM sample hits of the ATR-FTIR spectra of un-spiked and spiked fingernails.

Conclusions

ATR-FTIR spectroscopy could accurately detect cocaine in fingernails. However, impurities showed minimum affinity to fingernails and were not deposited to the same extent as cocaine. The combination of ATR-FTIR spectroscopy and MLAs showed potential for differentiating acute versus chronic drug exposure, a key finding for court proceedings in relation to possession with intent to supply. Future work will explore spiking fingernails over longer time intervals/environmental conditions in order to understand challenges occurring in different settings.

References

Silvia, A., Grobério, T., Zacca, J., Maldaner, A. and Braga, J. (2018) Cocaine and adulterants analysis in seized drug samples by infrared spectroscopy and MCR-ALS. *Forensic Science International*, 290 pp.169-177.

Shu, I., Jones, J., Jones, M., Lewis, D. and Negrusz, A. (2015) Detection of Drugs in Nails: Three Year Experience. *Journal of Analytical Toxicology*, 39 pp.624-628 DOI: 10.1093/jat/bkv067 [Accessed 30th October 2022].

Meyers, R. (2000). *Encyclopaedia of Analytical Chemistry*. 1st ed. Chichester: John Wiley and Sons Ltd.