Detection of Cocaine and its Impurities in Human Fingernails using Palm-sized Near-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[1]and Sulaf Assi[1]
[1]Liverpool John Moores University L3 3AF, UK.
[2]Agilent Technologies, Field Detection Group, OX11 0RA, UK.
[3]Faculty of Science, Lebanese University, Beirut, Lebanon.
m.wilson3@2019.ljmu.ac.uk

Introduction

Fingernails represent a matrix for detection of drugs, which they accumulate over long periods of times (Capelle *et al.,* 2015).

Near-infrared (NIR) spectroscopy offers non-destructive, rapid and portable technique for variety of pharmaceutical and forensic applications. The weak absorption of NIR spectroscopy allows it to be used for assessing the physiochemical properties of samples (Scotter, 2005).

Aim and Objectives

The aim of this research was to evaluate the feasibility of palm-sized NIR spectroscopy and machine learning analytics (MLAs) for detection of drugs/impurities in fingernails. The objectives were:

- Explore the spectroscopic activity of a range of fingernails, their endogenous compounds and drugs.
- Interpret NIR spectra of drugs and fingernails.
- Evaluate the potential of NIR combined with MLAs for detecting drugs in fingernails.

Methodology

- Participants were recruited via LJMU's community site and provided a set of fingernail clippings (7-10). Ethical approval was provided from LJMU (PBS/2021-22/04).
- Fingernails were measured 'as received' using the palm-sized NIR spectrometer (Figure 1). Fingernails were then spiked with cocaine or its impurities (Table 1).
- Fingernails were measured instantly after being spiked and up to six-weeks from spiking date.
- Spectral pre-treatment was made using multivariate scatter correlation (MSC) and Savitzky-Golay first derivative (D1).
- Spectral visualisation, interpretation and MLAs were applied using Matlab 2019a.

Figure 1. Palm-sized NIR spectrometer.

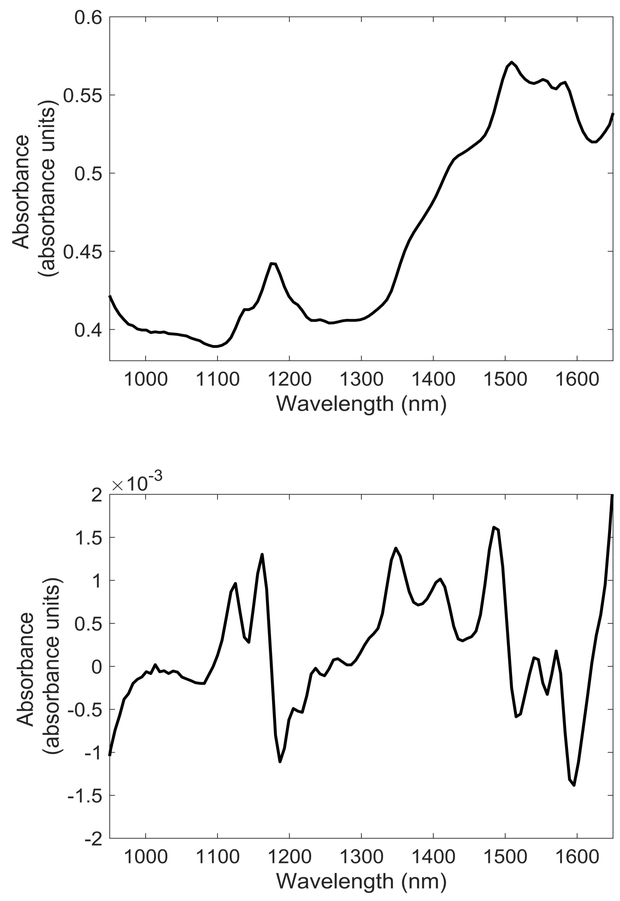

Figure 2. Raw (top) and MSC-D1 NIR spectra (bottom) of a fingernail.

Results and Discussion

NIR spectroscopy was successful in characterising endogenous constituents in fingernails with key bands related to aliphatic C-H, aromatic/alkene C-H, amine N-H and O-H (Correia *et al.,* 2015). After being spiked with drugs, NIR spectra of fingernails showed bands corresponding to each drug (Table 1; Figure 3).

Table 1. Functional groups of fingernails that have been spiked with the following drugs: benzocaine (BEN); cocaine (COCN); diltiazem (DIL); levamisole (LEV); lidocaine (LID) and procaine (PRO).

Drug	Band (nm)	Functional Group
BEN	1043 1143	2nd overtone of N-H of a primary amine 2nd overtone C-H stretching related to aromatic structure
COCN	1143 1180	2nd overtone C-H stretching related to aromatic structure 2nd overtone C-H stretching related to CH_3 group
DIL	1680-1900 1200-1350	1st overtone C-H stretching 2nd overtone S-H stretching
LEV	1143 1180	2nd overtone C-H stretching related to aromatic structure 2nd overtone C-H stretching related to CH_3 group
LID	1143 1180	2nd overtone C-H stretching related to aromatic structure 2nd overtone C-H stretching related to CH_3 group
PRO	1143 1180	2nd overtone C-H stretching related to aromatic structure 2nd overtone C-H stretching related to CH_3 group

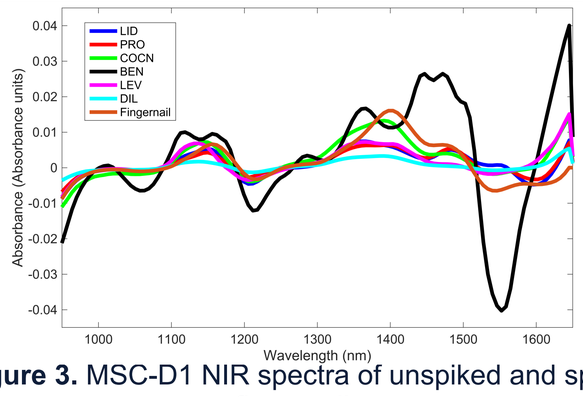

Figure 3. MSC-D1 NIR spectra of unspiked and spiked fingernails.

Fingernails Characterisation

Despite the presence of overlapping bands attributed to weak NIR signal corresponding overtones and combination bands (Jee, 2022); MLAs applied to NIR spectra were able to classify spiked fingernails into clusters. Thus, PCA showed distinct cluster for each fingernail set depending on the drug that it had been spiked with. There was no overlap between clusters; however, adjacent clusters were seen for lidocaine and procaine spiked fingernails and that attributed to similarity in chemical structure of both drugs. Hence, both drugs had benzene and amide groups.

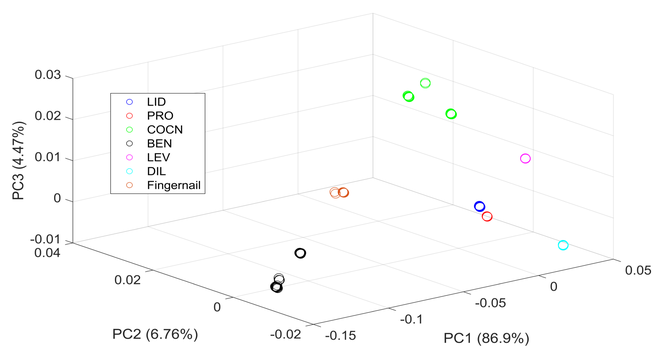

Figure 4. PC scores of fingernails spiked with the six drugs.

Classification of Spiked Fingernails

SOM offered an additional unsupervised clustering approach to PCA. Neurons in (Figure 5) as purple hexagons and were connected to each other via the red lines (distance between neurons). Smaller densities had higher densities and larger distances had lower distances. The clusters highlighted in yellow correspond to unspiked fingernails and showed that users of different drugs can be differentiated.

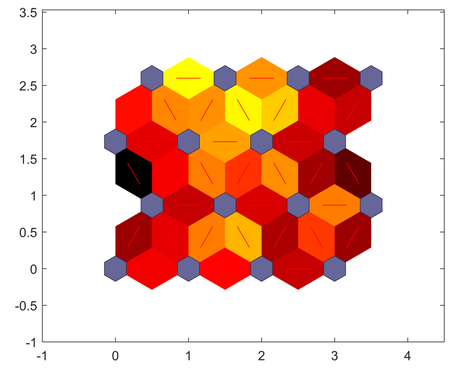

Figure 5. U-Matrix for the spectra of unspiked and spiked fingernails.

Deposition of Drugs in Fingernail

The algorithm grouped the unspiked and spiked fingernails into 16 groups. Group two (n = 30) was comprised of unspiked fingernails. Hence, NIR and MLAs showed ability to differentiate unspiked and spiked fingernails. The spiked fingernails were grouped into 15 separate groups and this was attributed to variation of drug deposition into fingernails.

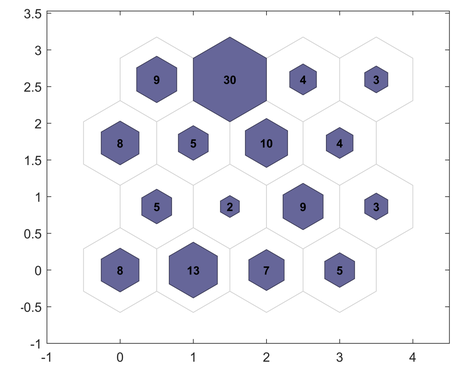

Figure 6. SOM sample hit map for spectra of un-spiked and spiked fingernails.

Weight planes showed that PC1 and PC2 shared similar characteristics relating to drugs' C-H groups. The fingernails' proteins and constituents consisted of amine N-H and O-H groups at 1400 - 1550 nm, which corresponded to overlap between keratin and water. Thus, an overlap can be observed between PC1 and PC2 (Figure 7).

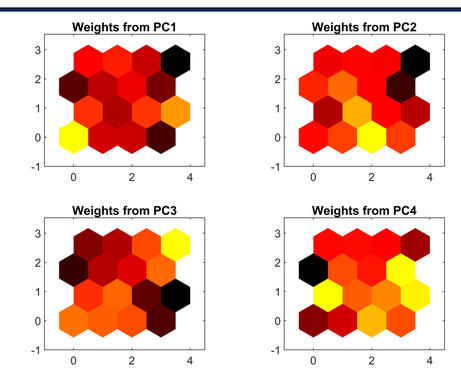

Figure 7. Weight planes of unspiked and spiked fingernails.

Conclusion

The present work proposed a novel method for the identification of drugs in fingernails by spectral visualization and classification algorithms. PCA showed detailed information corresponding to the samples' physical characteristic and findings were confirmed through SOM. Hence, SOM showed to be a powerful analytic and was able to predict spectra without previously knowing classes or the spectral membership. Future work will look at deep learning with several layers of neurons.

Correia, R., Domingos, E., Tosato, F., dos Santos, N., Leite, J., da Silva, M., Marcelo, M., Ortiz, R., Filgueiras, P. and Romão, W. (2018) Portable near infrared spectroscopy applied to abuse drugs and medicine analyses. *Analytical Methods*, 10 pp.593-603 DOI: 10.1039/c7ay02998e [Accessed 1st December 2022].

[NIR Spectroscopy]. [RD Jee]. In: Moffat AC, Osselton MD, Elliott SP (eds). *Clarke's Analysis of Drugs and Poisons*, [online]. London: Pharmaceutical Press. **http://www.medicinescomplete.com/** [Accessed 1st December 2022].

Scotter, C. (2005) *Encyclopaedia of Analytical Science*. 2nd ed. Amsterdam: Elsevier.