



DETECTION AND IDENTIFICATION OF CONTAMINANTS IN FINGERPRINTS USING INFRARED CHEMICAL IMAGING



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Abstract: Infrared chemical imaging has been a powerful tool in the study of digital trace evidence, especially in the detection and identification of contaminants present in those traces. After obtaining optimal conditions for collecting images and spectra, in transmission mode and in a barium fluoride window four known substances — phenobarbital, mirtazepine, caffeine and benzoic acid — were tested and detected as contaminants of fingerprints. The results were satisfactory in all cases. Mirtazepine and phenobarbital, which have a potential forensic interest, were used in a study of fingerprint blind samples in 27 volunteers. No false positives were found. The results confirm that infrared chemical imaging is an efficient technique in the detection and identification of contaminants in digital trace evidence.

INTRODUCTION

Criminal and forensic sciences have increasingly played an essential role in the justice system by providing scientific information for criminal investigation. The use of vibration spectroscopy techniques, namely the development of infrared chemical imaging, has provided a more detailed study of fingerprints. Infrared chemical imaging aims to create a greater contrast between ridges and grooves which make up the digital fingerprint and the matrix where it is located (Tahtouh et al. 2005).

The formation of digital traces results from the interaction between two surfaces. Therefore, the composition of digital trace evidence on surfaces results from a complex mixture of secretions from secretor glands and environmental contaminants (Ramotowski 2001; Walker et al. 2009).

AIM OF THE STUDY

This study aims to assess the potential of infrared chemical imaging in the detection and identification of contaminants manipulated by individuals and contaminants present in their fingers, allowing us to obtain more information from a fingerprint.

INSTRUMENTATION

The emergence of infrared chemical imaging has widely increased the applications of infrared spectroscopy, extending them to many areas such as forensic science (Williams et al. 2004). It allows us to obtain spectral and space information of complex and heterogeneous samples, making it a powerful tool for the study of forensic samples which are limited, and for the study of which



non-destructive techniques are always preferred (Koening et al. 2001).

Infrared chemical imaging involves spectra collection of a high number of sampling points that are usually collected in individual or group pixels of a multi-channel detector. The obtained data can be seen as a data cube and are able to allow the formation of three-dimensional pictures if the radiation used enters the sample sufficiently. For mapping of the surface, the data cube includes a three-dimensional data block with two dimensions and a third one that corresponds to the wavelength (Cullen et al. 2012). Each wavelength produces a picture and a spectrum can be obtained from each pixel that makes up the picture. A Nicolet IN MX spectrometer was used in the digital trace evidence analysis carried out in this study. The integrated architecture of this system eliminates the need for an external spectrometer and provides an exceptional experience of optical microscopy, allowing for fast results and a high space resolution (Nicolet).

METHODOLOGY AND RESULTS

OPTIMISATION OF PARAMETERS

During the initial development of a study by infrared chemical imaging it is necessary to optimise several image collection parameters to minimise the collection time and to ensure the necessary quality (Tahtouh et al. 2007).

In order to optimise the spectral resolution, the number of scans, the step size, the image size and the image formation parameters, we used the following methodology: digital traces were deposited after hands had been washed and dried; the right index finger was passed on the forehead and put in contact with a barium fluoride window; infrared chemical images were processed using a Nicolet IN10 MX spectrometer and a multi-channel detector. All images and spectra were collected and processed using OMNIC Picta software (version 9.1). With a size of 3mm x 3mm, all images were obtained

using the transmission mode. The parameters mentioned above were changed and optimised. Table 1 summarises the optimised values of the parameters for the collection of images.

Table 1 — Summary of the optimised parameters for the collection of images

Parameter	Optimised settings
Spectral Resolution	32 cm ⁻¹
Number of scans	4
Step size	25 µm
Image size	3 mm x 3 mm
Image formation parameters	Frequency slice within the range 2850 — 2980 cm ⁻¹ from the second derivative data

PRELIMINARY STUDY OF DETECTION AND IDENTIFICATION OF CONTAMINANTS IN DIGITAL TRACE EVIDENCE

Compounds with different proprieties and different functional groups, such as phenobarbital, caffeine, benzoic acid and mirtazapine, were chosen with the objective of being familiar with detection and identification of contaminants in digital trace evidence. The experimental spectra were compared with existing ones in the libraries made available by the equipment supplier or created by the operator. The correspondence percentage indicated by the software (> 80 % Excellent; 70-79 % Good; 65-69 % Satisfactory) was taken into account, and was determinant for additional recognition (Mou & Rabalais 2009).

All pictures were obtained using the transmission mode, at 32 cm⁻¹ resolution and four scans. The spectra of the compounds were collected at 4 cm⁻¹ resolution and 256 scans. Figure 1 shows an infrared chemical image from a section of a contaminated digital fingerprint with phenobarbital particles and Figure 2 the respective infrared spectrum.



Figure 1 — Infrared chemical images from a section of contaminated fingerprint with phenobarbital, on the left an image formed at 2800 cm⁻¹, on the right an image formed at 1700 cm⁻¹, second derivative, barium fluoride window, transmission.

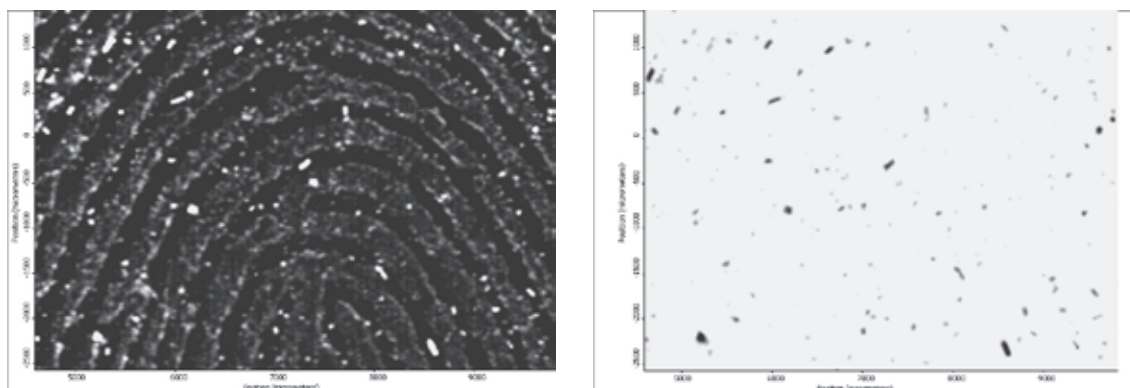
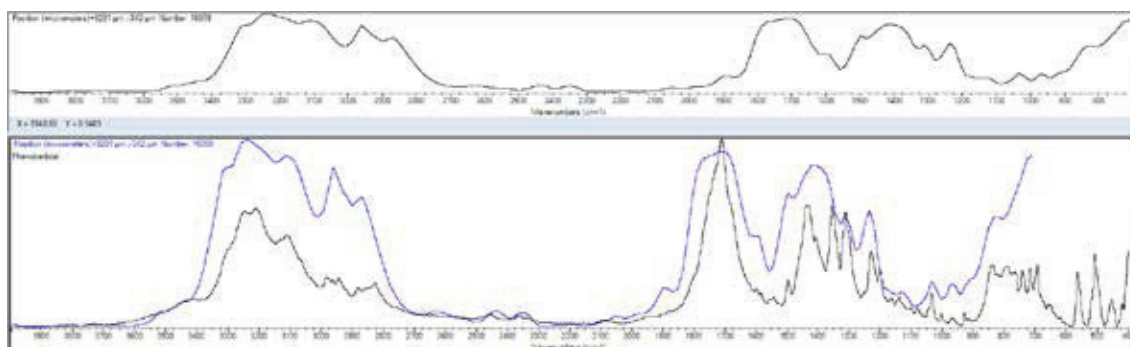


Figure 2 — Infrared spectrum of phenobarbital in the digital trace evidence from Figure 1 (above) and infrared spectrum reference (below, in black), comparability 67 %.



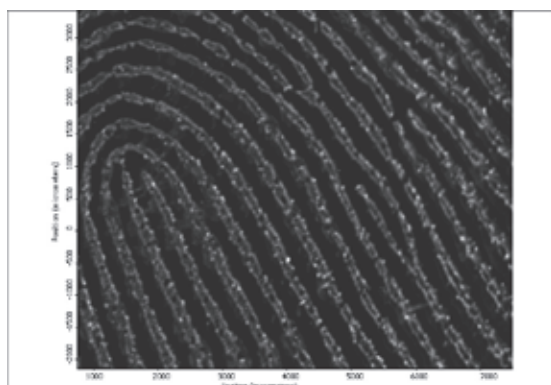
IDENTIFICATION TESTS OF CONTAMINANT SUBSTANCES ON DIGITAL TRACE EVIDENCE

Subsequently, we carried out the identification of contaminant compounds in digital traces, resulting from the previous manipulation of substances by the provider. We aimed, in this way, to detect and correctly identify the compounds without knowing if the volunteer had manipulated them. The two contaminant substances used were phenobarbital and mirtazapine. 27 different trials were used. 27 volunteers were requested to choose one of the following options: not to manipulate any of the compounds, manipulate mirtazapine, manipulate phenobarbital or manipulate both compounds. Thereafter, each volunteer put the right index finger in a barium fluoride window, resulting in infrared chemical images of digital trace evidence.

All the chemical images were processed using OMNIC Picta software (version 9.1). The identification of the spectra of the compounds was performed using OMNIC Spectra software through comparison with the spectra of the following spectral libraries: HR Georgia State Forensic Drugs (for phenobarbital identification) and Project (library created for the mirtazapine study). Figure 3 shows the infrared chemical image of a digital fingerprint section of a volunteer who didn't manipulate any of the compounds, with no contaminant particles visible.



Figure 3 — Infrared chemical image of a digital fingerprint section, without manipulation of compounds, $\nu=2930\text{ cm}^{-1}$.



Notable in this figure is the contrast obtained between ridges and grooves as well as the same typical characteristics of a digital fingerprint. Figure 4 shows the infrared chemical image of a digital fingerprint section of a volunteer that chose only to manipulate the phenobarbital.

Figure 4 — Infrared chemical image of a digital fingerprint section of a volunteer that chose only to manipulate the phenobarbital; above an image formed at 2928 cm^{-1} , below an image formed at 1700 cm^{-1} .

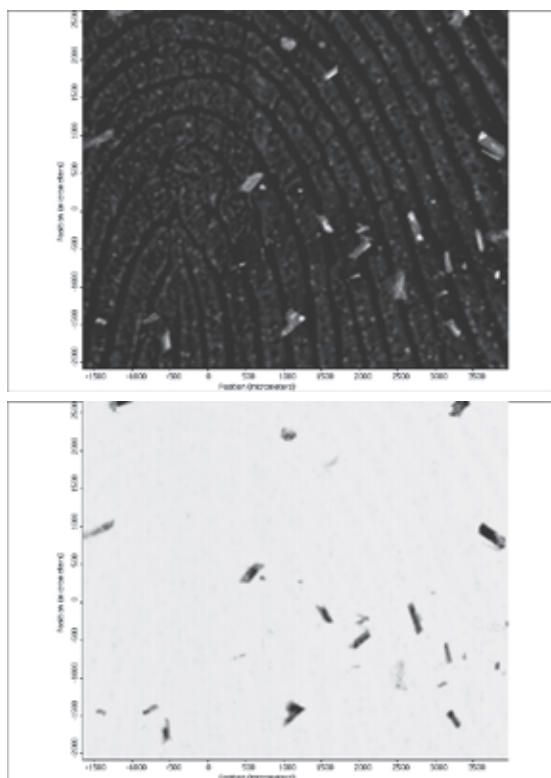


Figure 5 shows the respective infrared spectrum and, Figure 6, the reference spectrum of phenobarbital. In the chemical image of Figure 4 the contrast between ridges and grooves of the digital fingerprint is visible, allowing us to observe the contaminant particles in the sample. The chemical image on the right shows the space distribution of the particles.

Figure 5 — Infrared spectrum obtained from the phenobarbital particle.

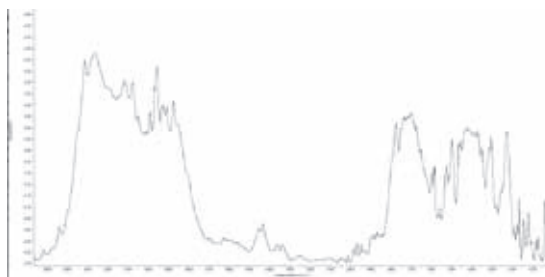
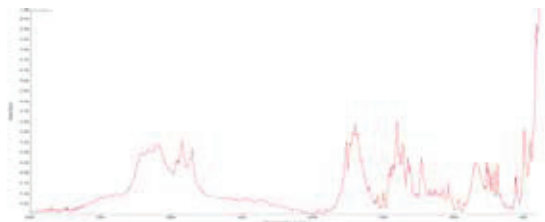


Figure 6 — Reference infrared spectrum of phenobarbital.



The infrared chemical image of a digital fingerprint section of a volunteer that only manipulated mirtazepine is displayed in Figure 7. Figure 8 shows, as an example, the infrared spectrum of contaminant particles. The reference infrared spectrum of mirtazepine is shown in Figure 9. It is possible to observe, in the chemical image in Figure 7, the ridges and grooves of the digital fingerprint and also the presence of some contaminant particles in which the space distribution is clearly visible on the right figure.



Figure 7 — Infrared chemical image of a digital fingerprint section of a volunteer that chose only to manipulate mirtazepine; above an image formed at 2919 cm^{-1} , below an image formed at 1400 cm^{-1} .

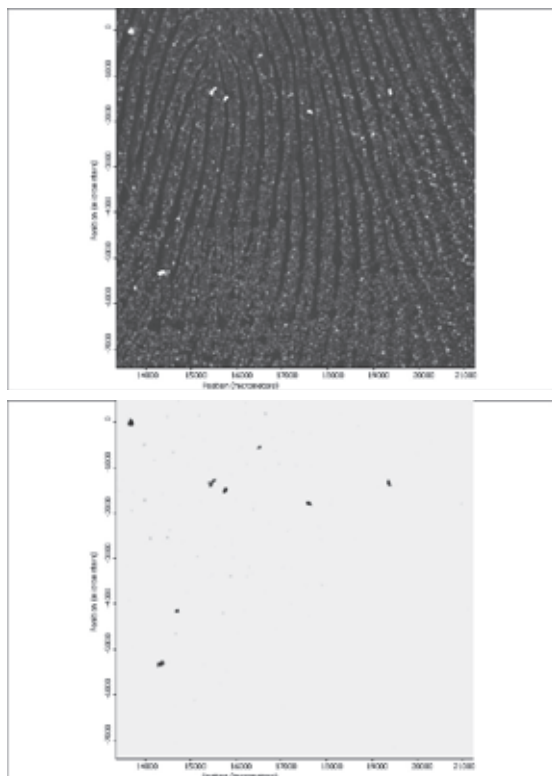


Figure 8 — Infrared spectrum obtained from the mirtazepine particle.

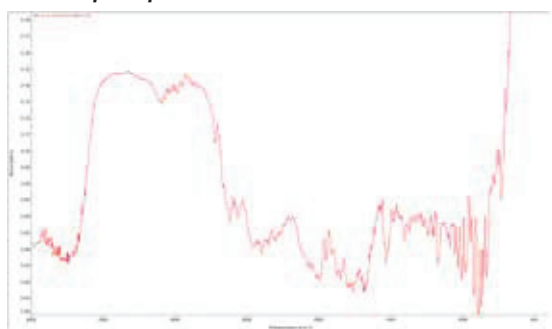


Figure 9 — Reference infrared spectrum of mirtazepine.



The results obtained from the digital trace evidence from the volunteer who decided to manipulate both compounds are displayed in Figures 10 and 11. The identification of the two contaminants was obtained as a first comparability in comparison with the spectral database used.

Figure 10 — Infrared chemical image of a digital fingerprint section of a volunteer who manipulated both compounds; above an image formed at 2915 cm^{-1} , below an image formed at 1400 cm^{-1} .

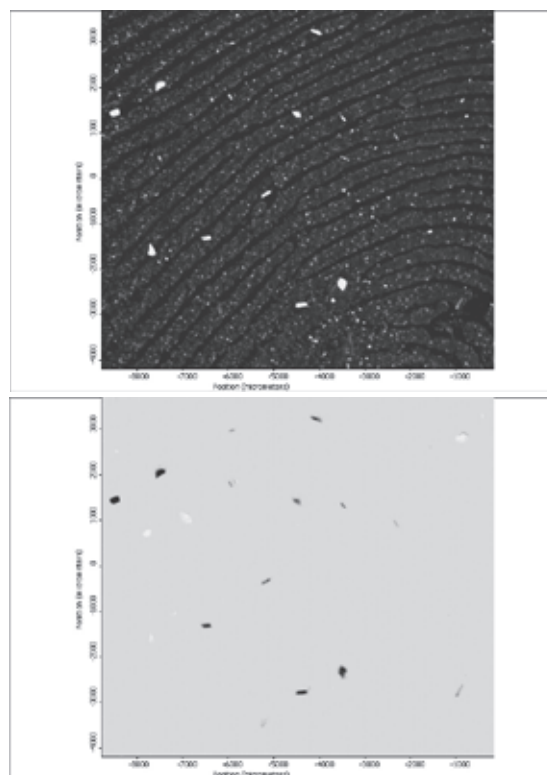
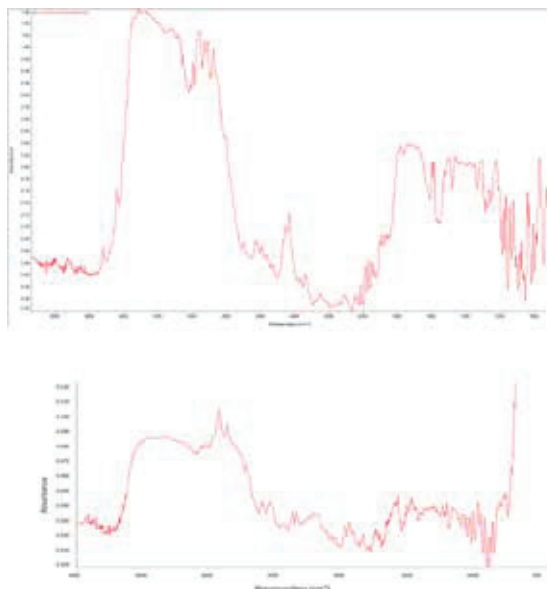




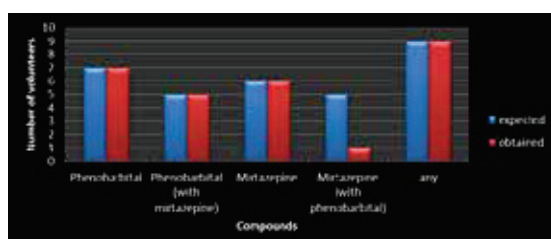
Figure 11 — Infrared spectra recorded for the contaminants of the digital traces of the volunteer who manipulated both compounds, comparability of 45 % for mirtazepine and 74 % for phenobarbital.



GLOBAL ANALYSIS OF THE RESULTS

A general perspective of the results obtained is summarised in Figure 12.

Figure 12 — Global perspective of the results obtained from the sample study of digital fingerprint with phenobarbital and / or mirtazepine by infrared chemical imaging.



From the 27 volunteers that participated in this study, 7 manipulated phenobarbital only, 6 manipulated mirtazepine only, 9 didn't have any contact with any of the compounds and 5 manipulated both of them. There was no evidence of false positives and in all the trials the compound identification fits the first choice in the research in spectral libraries. The mirtazepine detection when manipulated with phenobarbital

appeared to be more problematic, with the 4 false negatives recorded. The mirtazepine adherence seems to be more difficult due to the presence of another compound, since no false negative was recorded as a unique contaminant. It will require a higher number of samples to confirm this conclusion.

CONCLUSION

During the study of the contaminant substances, infrared chemical imaging shows that it is a potential technique. In a preliminary study, using a barium fluoride window, as a matrix, in transmission mode, four substances were collected with different chemical functions, two of them with potential forensic interest. The identification of these compounds was successfully performed. In order that the contaminant substances may be correctly identified it is obviously necessary that the infrared spectrum is included in the existing database. The highest percentage values of correspondence obtained in the mirtazepine identification (in which the spectrum inserted in the database was obtained in this study) suggests that the creation of a database with the compounds spectra collected in the same conditions as the contaminant under research will be an advantage for the investigation of interesting compounds.

This database should be used with others that already exist. From the blind study of digital fingerprints of the 27 volunteers, who were requested to manipulate (or not) two known substances, mirtazepine and phenobarbital, the absence of any false positive is highlighted. Phenobarbital was identified in all the samples where it was present, separately or together with mirtazepine. This last compound was identified when it was manipulated separately. False negatives were obtained for mirtazepine as a result of the manipulation, by volunteers, of the two substances. It will be desirable, in a future study, to increase the number of samples assessed to develop the statistical consistency of the results. The infrared chemical imaging showed, undoubtedly, a technique with great potential in the investigation of fingerprints in the forensic area.



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