Forensic Applications of Infrared Spectral Imaging

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A thesis submitted for the degree of Doctor of Philosophy (Science)

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Certificate of Authorship and Originality

I certify that the work in this thesis has not previously been submitted for a degree

nor has it been submitted as part of requirements for a degree except as fully

acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in

my research work and the preparation of the thesis itself has been acknowledged. In

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Katherine Bojko (nee Flynn)

21st February 2008

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List of Publications

Types of Publication	Number	Reference
Papers Published in Refereed Journals	3	[1,2,3]
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- 1. Flynn, K., O'Leary, R., Lennard, C., Roux, C., Reedy, B. J. "Forensic Applications of Infrared Chemical Imaging: Multi-Layered Paint Chips" Journal of Forensic Sciences 2005;50(4):832-41.
- 2. Flynn, K., O'Leary, R., Roux, C., Reedy, B. J. "Forensic Analysis of Bicomponent Fibers Using Infrared Chemical Imaging" Journal of Forensic Sciences 2006;51(3):586-596.
- 3. Bojko, K., Roux, C., Reedy, B. J. "An Examination of the Sequence of Intersecting Lines using ATR-FTIR Spectral Imaging" Accepted for publication in Journal of Forensic Sciences, 2008.
- 4. Flynn, K., Reedy, B. J., Roux, C., Tahtouh, M., O'Leary, R., Lennard, C. "Forensic Applications of Infrared Chemical Imaging" Presented at the 17th International Symposium on the Forensic Sciences, Australian and New Zealand Forensic Science Society, Wellington, NZ March 2004

- 5. Flynn, K., Reedy, B. J., Roux, C. "Determining the Sequence of Intersecting Lines Using Infrared Chemical Imaging" Presented at the 17th Meeting of the International Association of Forensic Sciences, Hong Kong, China August 2005.
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- 7. Reedy, B. J., Flynn, K., Tahtouh, M., Burger, F., Rutlidge, H., Kalman, J., Doble, P., Roux, C. "Forensic Applications of Infrared Chemical Imaging" Presented at the 6th Australian Conference on Vibrational Spectroscopy, Sydney, Australia September 2005.
- 8. Flynn, K., Roux, C., Reedy, B.J. "Further Forensic Applications of Infrared Spectral Imaging" Presented at the 18th International Symposium on the Forensic Sciences, Australia and New Zealand Forensic Science Society, Fremantle, WA, Australia April, 2006.
- 9. Flynn, K., Reedy, B. J., Roux, C., Lennard, C. "Applications of Infrared Chemical Imaging to Questioned Document Examinations" Presented at the 17th International Symposium on the Forensic Sciences, Australian and New Zealand Forensic Science Society, Wellington, NZ March 2004.

- 10. Flynn, K., Reedy, B. J., Roux, C., Lennard, C. "Examination of Line Crossings by Infrared Chemical Imaging". Presented at the 57th Annual Meeting of the American Academy of Forensic Sciences, New Orleans, LA, USA February 2005.
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- 13. Flynn, K., Reedy, B. J., Roux, C. "Infrared Chemical Imaging of Bicomponent Fibers" Presented at the 6th Australian Conference on Vibrational Spectroscopy, Sydney, Australia September 2005.
- 14. Tahtouh, M., Flynn, K., Walker, S., Roux, C., Reedy, B. J. "FTIR spectral imaging applications in trace evidence" Presented at the National Institute of Justice (NIJ)/Federal Bureau of Investigation (FBI) Trace Evidence Symposium, Clearwater Beach, Florida, USA August 2007.

Abstract

Fourier transform infrared (FTIR) spectral imaging is emerging as an exciting new tool in forensic analysis. This technique is capable of simultaneously collecting thousands of infrared spectra using an array detector, thus yielding both spectral and spatial information with extremely fast collection times. The aims of this research were to examine potential forensic applications of FTIR spectral imaging, in particular in the physical evidence area.

Infrared spectral images of multilayered paint chips have been successfully obtained, with the chief advantage over conventional infrared analysis being that thousands of infrared spectra are collected in a few minutes across the whole paint sample. As with conventional infrared spectroscopy, chemical species can be identified from their spectra, but there are also a number of different ways to make multi-component spectral (and hence chemical) comparisons between two samples easy to visualise and understand. Infrared spectral images of two paint chips being compared side-by-side can be viewed as a "movie", in which each frame is an intensity map of the two samples at a given wavenumber (frequency) value. In another approach, the spectra in the image files are classified into chemically similar groups, resulting in a "cluster" image that makes it possible to simultaneously compare all of the layers in two paint chips.

Bicomponent fibres are a special class of fibres that comprise two polymers of different chemical and/or physical properties. In over 50% of the bicomponent fibre

samples analysed, infrared spectral imaging was able to spatially resolve two spectroscopically distinct regions when the fibres were examined side-on. The technique provided characteristic infrared spectra of each component and images which clearly illustrated the side-by-side and sheath-core configuration of these components in the fibre. It was possible to prepare and image a cross-section of one of the fibres, but in general the preparation and analysis of fibre cross-sections proved very difficult. A number of infrared sampling techniques were investigated and spectral imaging results were compared with those obtained using conventional fibre microscopy techniques.

Attenuated total reflectance (ATR) FTIR spectral imaging was shown to be successful for determining the sequence of heterogeneous line intersections produced using ballpoint pens and laser printers. By imaging at the particular frequencies corresponding to the functional groups specific to the ballpoint pen ink and toner materials, it was possible to form spectral images showing their spatial distribution. It was possible to determine whether the ink was above or below the toner, by examining whether there was a gap present in the ink spectral image at the point of intersection with the toner. Blind tests were performed and the results obtained using ATR-FTIR spectral imaging were directly compared to those obtained by experienced forensic document examiners using methods regularly employed in casework. ATR-FTIR spectral imaging was shown to achieve a 100% success rate in the blind tests, whereas some incorrect sequence determinations were made by the

unable to image ink-jet printing, gel pens, roller ball pens and felt-tip pens, and was also unable to determine the sequence of intersecting ballpoint pen lines.

Overall, infrared spectral imaging was shown to be a successful technique for analysing multi-layered paint chips, bicomponent fibres and determining the sequence of intersecting ballpoint pen and toner lines. In the past five years, there has been a significant increase in the number of reported forensic applications of infrared spectral imaging. It is anticipated that this technique will continue to grow in importance as a tool for forensic scientists over the next decade, and that infrared spectral imaging will find a regular place in forensic laboratories.