Reagents for infrared chemical imaging of fingerprints on difficult surfaces

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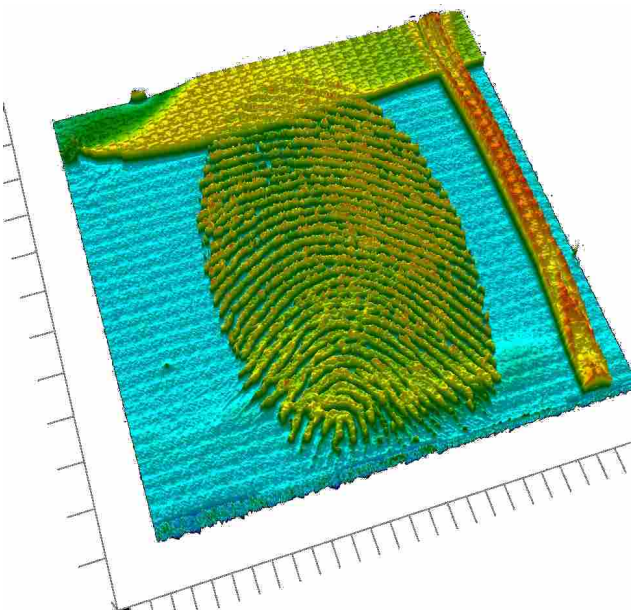

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In light of knowledge attained, the happy achievement seems almost a matter of course, and any intelligent student can grasp it without too much trouble. But the years of anxious searching in the dark, with their intense longing, their alterations of confidence and exhaustion and the final emergence into the light – only those who have experienced it can understand it.

Albert Einstein, 1933

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 the 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 addition, I certify that all the information sources and literature used are indicated in the thesis.

Mark Tahtouh

08/12/2008

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Abbreviations

A/CAA	anthracene / 2-cyanoacrylic acid adduct
A/CAA-K	anthracene / 2-cyanoacylic acid potassium salt adduct
A/CAC	anthracene / 2-cyanoacyloyl chloride adduct
A/1-CECA	anthracene / 1-cyanoethyl 2-cyanoacylate adduct
A/2-CECA	anthracene / 2-cyanoethyl 2-cyanoacylate adduct
A/ECA	anthracene / ethyl 2-cyanoacylate adduct
A/ECA-d_5	anthracene / pentadeuteroethyl 2-cyanoacylate adduct
A/MA	anthracene / maleic anhydride adduct
A/MCA	anthracene / methyl 2-cyanoacylate adduct
A/MCA-d_3	anthracene / trideuteromethyl 2-cyanoacylate adduct
ATR	attenuated total reflection
3-BPN	3-bromopropionitrile
1-CECA	1-cyanoethyl 2-cyanoacrylate
2-CECA	2-cyanoethyl 2-cyanoacrylate
2-CECAc	2-cyanoethyl cyanoacetate
DAB	diaminobenzidine
DBU	1,8-diazobicyclo[5,4,0]undec-7-ene
DFO	1,8-diazafluorene-9-one
DMAC	dimethylaminocinnamaldehyde
DMF	*N,N*-dimethylformamide
DMSO	dimethylsulfoxide
DTA	differential thermal analysis
ECA	ethyl 2-cyanoacrylate (superglue)
ECA-d_5	pentadeuteroethyl 2-cyanoacylate
FPA	focal plane array
FTIR	Fourier transform infrared
GS-MS	gas chromatography – mass spectrometry
HSAB	hard soft acid base
HMPA	hexamethylphosphoramide
3-HPN	3-hydroxypropionitrile
2-HPN	2-hydroxypropionitrile
IR	infrared

MCA-d_3	trideuteromethyl 2-cyanoacrylate
MMD	multi-metal deposition
MNF	minimal noise fraction
MS	mass spectrometry
NMR	nuclear magnetic resonance
NWSD	non-water-soluble deposit
oligo-2-CECA	oligo-2-cyanoethyl 2-cyanoacrylate
OsO_4	osmium tetroxide
PD	physical developer
PC	principal component
P_2O_5	phosphorus pentoxide
poly-1-CECA	1-cyanoethyl 2-cyanoacylate polymer
poly-2-CECA	2-cyanoethyl 2-cyanoacylate polymer
poly-ECA-d_5	pentadeuteroethyl 2-cyanoacylate polymer
poly-MCA-d_3	trideuteromethyl 2-cyanoacylate polymer
RTX	ruthenium tetroxide
SO_2	sulfur dioxide
$SOCl_2$	thionyl chloride
SPR	small particle reagent
TGA	thermogravimetric analysis
VMD	vacuum metal deposition
WSD	water-soluble deposit

Note: as a supplement to the above list of abbreviations, a fold out page at the back of this thesis contains structures, names and abbreviations for the majority of the compounds discussed.

Abstract

Fingerprints continue to be an important form of forensic evidence for individual identification. A number of techniques are currently available for the detection and enhancement of invisible or latent fingerprints. While these techniques perform well on many surfaces, there are a number of surfaces that pose problems. On such surfaces, Fourier transform infrared (FTIR) chemical imaging can provide superior results. FTIR chemical imaging involves the simultaneous collection of thousands of mid-infrared spectra across a sample using a focal plane array (FPA) detector. This allows for the collection of chemically specific spectral data while maintaining spatial information. Images can then be generated based on spectral / chemical contrast between components within a sample. A key aim of this project was to further investigate the use of FTIR chemical imaging for the detection and enhancement of latent (untreated) and developed (treated) fingerprints on a number of *'difficult'* surfaces.

During the initial development of an infrared chemical imaging technique for fingerprints, an un-optimised set of image collection parameters was used. Using these settings, the collection of an entire fingerprint image was time consuming (often several hours or days). A systematic method for the optimisation of the image collection parameters has been developed. This method allows the optimisation of parameters such as spectral resolution, number of co-added scans, spectral range, pixel aggregation and image formation parameters in order to minimise image collection time and file size while maintaining the quality of the fingerprint image produced.

A commonly-used fingerprint detection technique for latent fingerprints on non-porous or semi-porous surfaces involves fuming samples with monomeric ethyl 2-cyanoacrylate (superglue). This reagent leaves a white residue (polymeric cyanoacrylate) on the ridges of latent fingerprints, rendering them visible under white light. On some surfaces, such as polymer banknotes, however, the contrast between cyanoacrylate-developed fingerprints and the background is poor. FTIR chemical imaging of cyanoacrylate fumed fingerprints on polymer banknotes and other difficult surfaces has been shown to provide better results than optical techniques alone. During this project, further investigations into the use of FTIR chemical imaging for latent fingerprints treated with commercial cyanoacrylate monomer on a range of difficult surfaces were conducted. While excellent results were obtained on many

samples, the need for novel cyanoacrylates containing infrared absorbance in specific parts of the spectrum was identified.

A major focus of this project has been the identification, synthesis and characterisation of modified cyanoacrylates which may be used as reagents for FTIR chemical imaging of fingerprints. Monomers that contained particular functional groups that show vibrational modes in the range from 2500 – 1800 cm^{-1} were sought. This region typically contains very few vibrational bands and therefore a reagent that could be used to give fingerprints absorptions in this range is desirable. This would provide the necessary contrast between the ridge details of the treated fingerprint and the background on which it may be located.

In total four novel cyanoacrylates were prepared. These included 2-cyanoethyl 2-cyanoacrylate (2-CECA), 1-cyanoethyl 2-cyanoacrylate (1-CECA), trideuteromethyl 2-cyanoacrylate (MCA-d_3) and pentadeuteroethyl 2-cyanoacrylate (ECA-d_5).

Each of the four novel monomers was tested a reagent for the detection and enhancement of latent fingerprints on a number of surfaces via FTIR chemical imaging. The 2-CECA monomer was found to be less volatile than conventional cyanoacrylate and thermally decomposed at the temperatures required to vaporise it. Treating latent fingerprints with this monomer at a reduced pressure yielded better results on reflective surfaces. On less reflective surfaces, such as polymer banknotes, however, the nitrile band of 2-CECA was almost undetectable and therefore could not be used for imaging the treated prints.

Fingerprints treated with the deuterated monomers (MCA-d_3 and ECA-d_5) showed characteristic bands in the region from 2300 – 1900 cm^{-1} owing to C–D stretching vibrations. Once again, however, the relatively low intensity of these bands meant that they were only detected from prints on reflective surfaces.

The monomer that produced the best results was 1-CECA. Surprisingly the contrast between the ridge detail and the background, was not generated by the nitrile band at 2250 cm^{-1} as anticipated. Instead it appears that the absorption band for the carbonyl group in poly-1-CECA is sufficiently resolved from any absorption within this region from the background surface (such as polymer banknotes) to provide good contrast images of the treated fingerprint. High quality fingerprint images were obtained of prints treated with 1-CECA on

all difficult surfaces tested including white opaque acrylic sheets, fluorescent acrylic sheets and all areas of polymer banknotes including areas containing raised intaglio printing.