

Analysis of Latent Fingerprint Deposits by Infrared Microspectroscopy*

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We report the use of infrared (IR) microspectroscopy for the analysis of fingerprint residues. The advantage of using an IR microscope lies in the ability to visualize and obtain spectra of individual particles and droplets that make up fingerprint ridge deposits at a spatial resolution of approximately 10 μm . Our initial results suggest that infrared microspectroscopy in reflection-absorption mode provides reproducible spectral analysis of fingerprint residue. Since infrared microspectroscopy is nondestructive to the sample, we will be able to study the changes in fingerprint ridge deposits as a function of time. The method holds promise for probing the difference between latent fingerprints of adults and children.

Index Headings: Infrared microspectroscopy; Latent fingerprints; Forensic science.

INTRODUCTION

The examination of latent fingerprints is an important aspect of crime scene investigations, but fingerprints are not always recoverable or clear. In child abduction cases, children's prints are often not obtained. Therefore, there is interest in the law enforcement community in finding new methods of developing latent fingerprints. To solve this problem, a better understanding of the chemical composition of fingerprint residue is crucial.

The chemical composition and mechanisms of skin secretions from children and adults have been studied by diverse research groups using a variety of chromatographic methods.¹⁻³ Early work on the differences in chemical composition of human skin surface lipids from birth to puberty was performed by Ramasastry and co-workers using thin-layer chromatography.¹ Alexiou and co-workers measured the excretion of amino acids, ammonia, and proteins in the sweat of children using ion exchange chromatography.² The study of skin surface lipids in children performed by Stewart and Downing involved the use of gas chromatography.³ For law enforcement purposes, research has been performed by Buchanan, Asano, and Bohanon to study the chemical differences in children's and adults' fingerprint secretions.⁴ Their experiments were performed by analyzing the residue in fingerprint ridges by gas chromatography-mass

spectrometry (GC/MS), and they concluded that the chain lengths are longer in the fatty acid esters in the fingerprint residue of adults. Since the use of GC/MS involved sample extraction, evaporation, and reconstitution, we have developed a method to analyze specific chemical components in fingerprint residue without any additional sample preparation after collection.

We report the use of infrared (IR) microspectroscopy, frequently referred to as microscopical infrared spectroscopy in the forensics community, for the analysis of fingerprint residue. The advantage of using an IR microscope lies in the ability to image individual particles and droplets that make up fingerprint ridge deposits at a spatial resolution of approximately 10 μm . Infrared microspectroscopy is nondestructive to the sample, which allows for the study of variations in fingerprint ridge deposits over time.

Research has been reported on the use of synchrotron-source infrared microspectroscopy for the study of latent human fingerprints.⁵ However, we have found that conventional glowbar-source infrared microspectroscopy has demonstrated sufficient sensitivity and spatial resolution to obtain spectra with adequate signal-to-noise ratios. The benefit of the glowbar-source technique is the potential of using a portable Fourier transform infrared (FT-IR) spectrometer in the field, which is impossible with current synchrotron-based technology.

EXPERIMENTAL

Reflection mode was chosen for experimentation due to the ease of sample collection and sample storage. For reflection-absorption experiments, the samples were obtained by having research volunteers deposit fingerprints on aluminum-coated slides. One fingerprint was obtained prior to washing of hands, one print was obtained after hands were washed and rinsed for approximately five minutes with water, and a third print was obtained after washing, rinsing, and rubbing the forefinger across the forehead. Since the hands do not contain sebaceous glands, the skin surface residue on the hands comes from eccrine glands in the epidermis.⁶ Therefore, the print obtained from washed hands should be free of sebaceous material. The print obtained after touching the forehead would contain sebaceous material since there is a high density of sebaceous glands in the forehead region.⁶

The fingerprint deposits were observed using either a 15 \times or 32 \times objective on the microscope. Under the microscope, there were two distinct types of residue observed: droplets and solid particles. Typically, a single droplet or particle was selected and the aperture was set according to the size of the droplet or particle. Spectra were collected at 4 cm^{-1} resolution and averaged for 128

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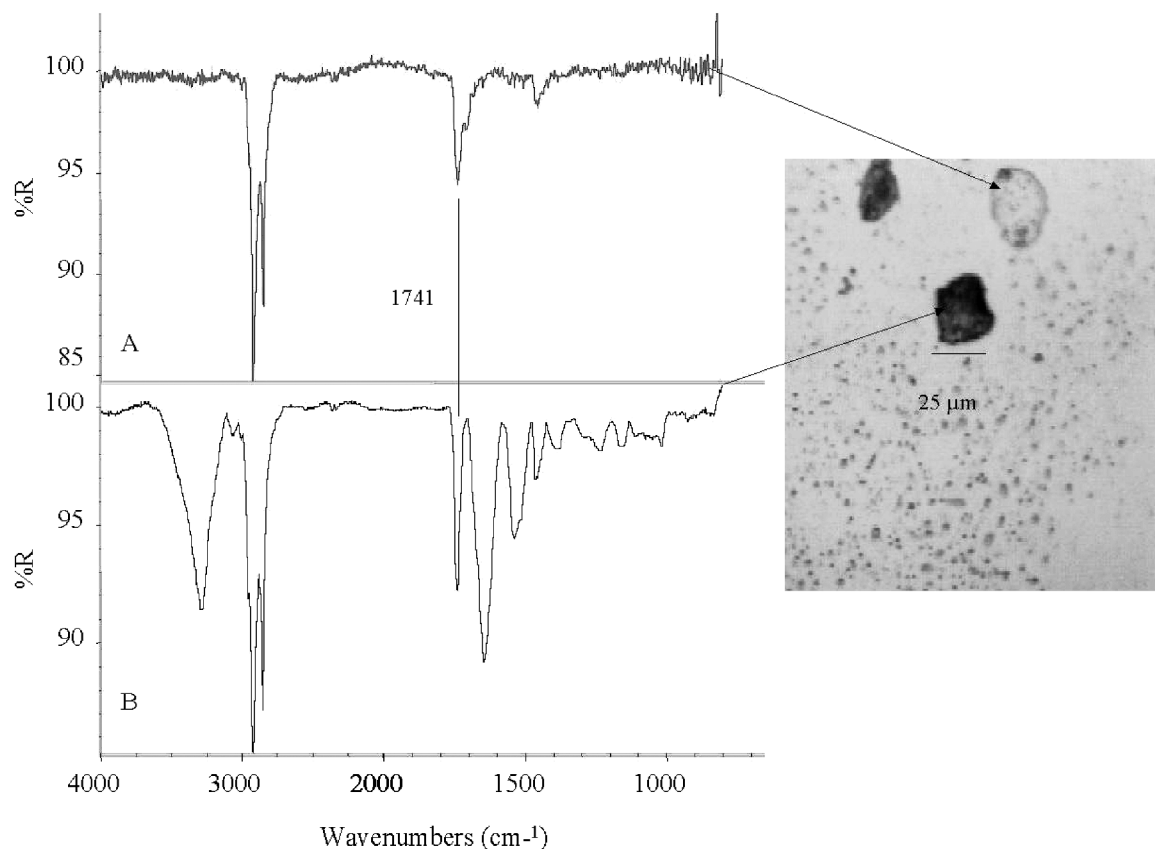


FIG. 1. Micrograph and corresponding spectra of an eccrine fingerprint deposit obtained from an adult male.

scans. A liquid-nitrogen-cooled MCT-High D* detector with a response range of 4000–800 cm^{-1} was used.

For attenuated total reflection (ATR) mode experiments, the sample collection was identical to that for reflection-absorption mode, and analysis was performed using a Thermo Nicolet Corporation Infinity Series[™] Diamond ATR objective.

RESULTS AND DISCUSSION

Optimization of Instrument Parameters. To determine the optimum conditions for obtaining spectra using microscopic FT-IR, experiments were performed in reflection-absorption and ATR modes. The results indicate that reflection-absorption mode is the preferred method for obtaining spectra of fingerprint residue because no appreciable signal was detected in ATR mode. The lack of results using the ATR mode probably results from the fact that fingerprint ridges are not deposited as continuous films but as individual droplets and particles.

A visual comparison of skin surface residue deposits suggests that very little residue is deposited in eccrine prints when the hands are washed before collection. However, even with a small amount of material, we were able to limit the analysis to individual droplets within the fingerprint ridge and record spectra. To determine the optimum conditions for obtaining these spectra, both the 15 \times and 32 \times microscope objectives were used. The results indicate that the use of the 32 \times microscope is preferable due to the ability to visualize the smaller particles without significant loss of signal. The typical aperture size used with the 32 \times objective was 20 \times 20 μm , al-

though the aperture was changed to adapt to the size of the droplet/particles under study.

Sebaceous prints contain greater amounts of material than eccrine prints, although the diameters of the solid particles do not vary significantly from those found in eccrine prints. Therefore, it was determined that for all of our experiments involving fingerprints, the 32 \times objective would be used.

The data revealed that 128 scans were sufficient to produce spectra with peak-to-peak signal-to-noise ratios of more than 100 to 1 for most prints studied. For eccrine prints with very little material deposited, 1000 scans were sometimes required to enhance the signal-to-noise ratio.

Eccrine Analysis. Figure 1 shows a representative photomicrograph and corresponding spectra of fingerprint res-

TABLE I. Characteristic frequencies and vibrational modes obtained from a particle in the eccrine fingerprint deposit of an adult male.

Frequency (cm^{-1})	Vibration
3281	N-H stretch (secondary amide)
1741	C=O stretch (saturated ester)
1655	C=O stretch (secondary amide)
1546	Major: N-H in-plane bend (secondary amide) Minor: C-N stretch
1463	CH ₃ asymmetric bend CH ₂ symmetric bend
1379	CH ₃ symmetric bend
1233	C-N stretch (secondary amide)
1160	C-C-O stretch (saturated ester)
1113	O-C-C stretch (saturated ester)

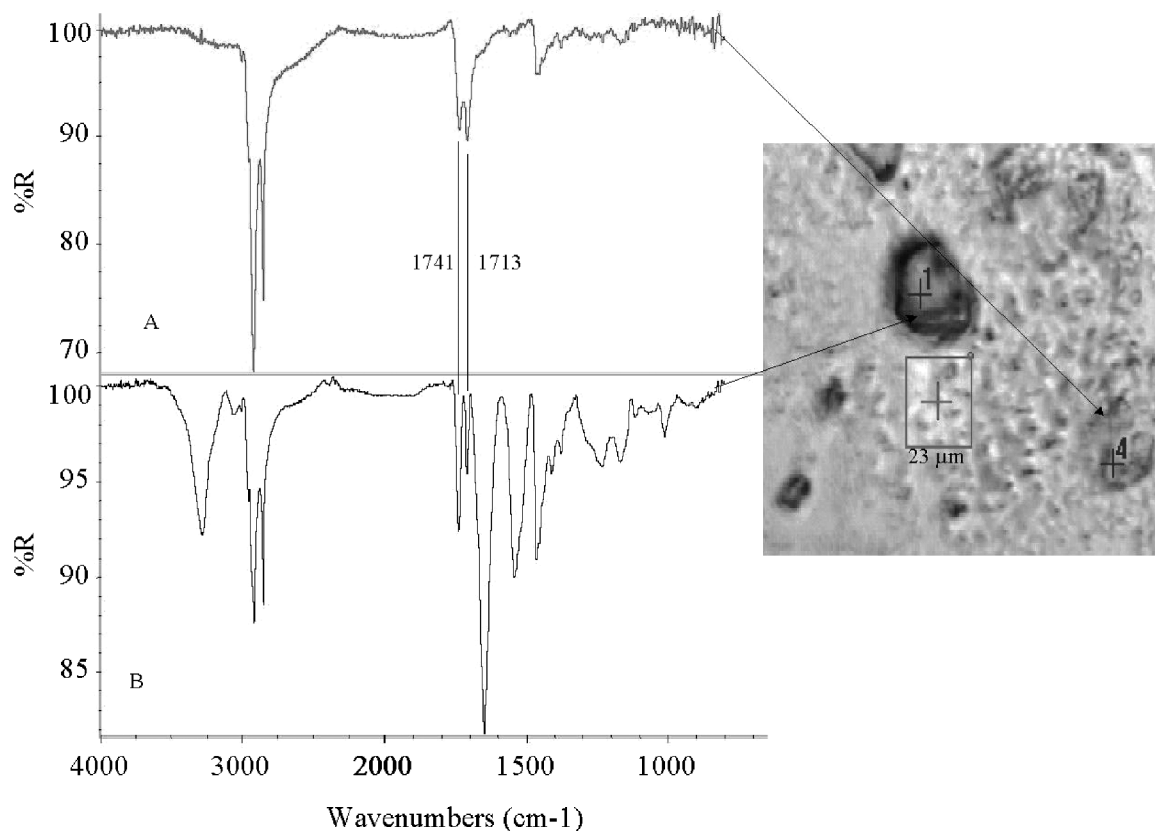


FIG. 2. Micrograph and corresponding spectra of a sebaceous fingerprint deposit obtained from an adult male.

idue that was obtained from an adult male after the hands were washed. The spectrum labeled A is characteristic of spectra that were obtained of eccrine secretions of adults. To determine the chemical composition of the droplet, the position and intensity of the peaks were compared to library spectra of biological compounds. Since a match was not found, the peak positions and intensities were analyzed to determine the functional groups present in the droplet.

The most notable feature in the spectrum is the C–H stretching vibration just below 3000 cm^{-1} . At 1741 cm^{-1} , a peak corresponding to a carbonyl stretching vibration is apparent and contains a shoulder at 1713 cm^{-1} , which is likely due to the presence of a second carbonyl stretching mode. At 1463 cm^{-1} , there is a peak corresponding to a methyl asymmetric bend. The peak assignments suggest that the chemical composition of the droplet represented in spectrum A is an ester of a dicarboxylic acid, and this result is consistent with results obtained by Buchanan, Asano, and Bohanon, who detected the presence of acid esters in adult fingerprint residue using GC/MS.⁴

The spectrum labeled B is characteristic of the dark particles deposited in eccrine fingerprints. To determine the chemical composition of the dark particle shown in Fig. 1, peak assignments were made and are shown in Table I. The peak assignments shown in Table I suggest the presence of a secondary amide, which would be characteristic of protein-containing skin cells. Eberhardt⁷ presumed that solid particles visually observed in microscopic studies of skin surface residue were remainders of cell walls from oil-secreting glands and these spectral results support the presumption. Additional peaks in the spectrum suggest the presence of saturated esters.

Sebaceous Analysis. Figure 2 shows a representative photomicrograph and corresponding spectra of fingerprint residue that was obtained from an adult male when the forehead was touched after the hands were washed. The droplet shown in Fig. 2A (point 4) is chemically similar to the droplet shown in Fig. 1A. The major difference in the two spectra labeled A is the intensity of the peaks, which is a function of the amount of material deposited.

The composition of the solid particle (point 1) is chemically similar to the particle that was present in the eccrine fingerprint shown in Fig. 1B. The major difference between spectrum B of the eccrine material and spectrum B of the sebaceous material, shown in Fig. 2, is the presence of a peak at 1713 cm^{-1} . The presence of this peak is attributed to the carbonyl stretching vibration of an acid ester.

It has been reported that squalene is the major component in skin surface residue in fingerprints of adults,⁴ but our results indicate that pure squalene is not the major component. Squalene is an acyclic triterpene and will undergo oxidation in the presence of bacteria to form a dicarboxylic acid.⁸ These preliminary spectral results suggest that squalene oxidation products are a likely component in adult fingerprint residue since an acid ester can be produced from esterification of a dicarboxylic acid.⁹

CONCLUSION AND FUTURE WORK

The capability of using infrared microspectroscopy to study fingerprint ridge deposits has been demonstrated. The reproducibility of the method has been tested and the random variation in the analytical signal was less than

10%. Relative to GC/MS, there are several inherent benefits of using infrared microspectroscopy to study the composition of residue in fingerprints, but the major benefit is the ability to retain the fingerprint for time studies.

Now that the ability to analyze fingerprint residue by microscopic FT-IR has been demonstrated, current work is focused on using the technique to study differences in children's fingerprint residue. It has been indicated that latent fingerprints of children disappear more quickly than those of adults⁴ and as a result, there is significant interest in the forensic community to understand how the chemical composition of children's fingerprints may change with time so that new methods of processing children's fingerprints may be developed.

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