

Identification of recently handled materials by analysis of latent human fingerprints using infrared spectromicroscopy

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Abstract

Analysis of fingerprints has predominantly focused on matching the pattern of ridges to a specific person as a form of identification. The present work focuses on identifying extrinsic materials that are left within a person's fingerprint after recent handling of such materials. Specifically, we employed infrared spectromicroscopy to locate and positively identify microscopic particles from a mixture of common materials in the latent human fingerprints of volunteer subjects. We were able to find and correctly identify all test substances based on their unique infrared spectral signatures. Spectral imaging is demonstrated as a method for automating recognition of specific substances in a fingerprint. We also demonstrate the use of Attenuated Total Reflectance (ATR) and synchrotron-based infrared spectromicroscopy for obtaining high-quality spectra from particles that were too thick or too small, respectively, for reflection/absorption measurements. We believe the application of this rapid, non-destructive analytical technique to the forensic study of latent human fingerprints has the potential to add a new layer of information available to investigators. Using fingerprints to not only identify who was present at a crime scene, but also to link who was handling key materials will be a powerful investigative tool.

Introduction

Early research on the chemistry of latent fingerprints used chromatography to study the differences in chemical composition in the lipids of surface skin cells between children and teenagers.¹ Additional research has been done using chromatography to measure the excretions of amino acids, ammonia and proteins in sweat.² Thin-layer chromatography has aided in research on human skin surface lipids.³ In addition, the gas chromatography/mass spectroscopy (GC/MS) combination method has shown that the

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chemical compositions of adult fingerprints are very different from children's.⁴ More recently, use of infrared spectromicroscopy in analyzing fingerprint residue was found to be an effective way to study chemical differences in the ridges of latent fingerprints with eccrine and sebaceous materials.⁵ Use of synchrotron-based infrared spectromicroscopy has also been demonstrated for fingerprints⁶ and forensic studies in general.⁷ In the present study we explore a different aspect of fingerprint analysis, the feasibility of identifying trace residual substances left in the fingerprint of a subject who had recently been handling those substances.

For many years infrared spectroscopy has been used to identify a wide variety of samples or to determine something's authenticity. One such case was in 1989 when the technique was used to determine the authenticity of a winning lottery ticket.⁷ Infrared has also been extensively used in the identification of fibers from crime scenes.⁸ It is only in more recent years that spectroscopy has been used to study and identify microscopic particles.⁹ In the present study, we demonstrate the potential of infrared spectromicroscopy as an effective way to identify microscopic particles deposited within latent fingerprints. These particles are present from residual amounts of materials left on a person's fingers after handling such materials. The application of this technique in investigations would, for example, aid in identifying a suspect accused of building bombs by finding bomb-making substances in the person's latent fingerprints. In a case where the accused person has used a gun, investigators would be able show who was holding the gun when it was fired by finding gunpowder deposits in their fingerprints. This could also aid in the positive identification of drug dealers and users by finding the illicit drug(s) in the latent fingerprints of the accused individual.

In our experiment, we had volunteers handle a mixture of common materials before giving fingerprints. We were able to find and positively identify microscopic particles of these materials within the fingerprints using infrared spectromicroscopy. This demonstration experiment shows that IR spectromicroscopy is a rapid, powerful, and non-destructive tool for accurately identifying substances left in a person's latent fingerprints. This potentially could have a significant impact on forensic science and could dramatically enhance the amount of information that can be obtained from the study of fingerprints.

Experimental

This experiment was conducted in accordance to University of California and Lawrence Berkeley National Laboratory Committees for the Protection of Human Subjects (C.P.H.S. #2004-12-80, expires 2/17/2006). Gold plated glass microscope slides were used as the substrate for the fingerprints under study. Collection of the samples was done by asking volunteers to touch a well-mixed powder mixture containing Ibuprofen, Vitamin C, Non-Dairy Creamer, and Sweet'N Low®. They were asked to wipe off any excess powder using their hands and then two fingerprints were obtained from each subject on a gold coated slide. Since the volunteers wiped off any excess material from their fingers, no powder was noticeable on their fingers without the aid of a microscope. This procedure simulates a typical amount of residual powder left on someone's fingers that could then be deposited within a latent fingerprint. Each subject's fingerprints were assigned a random 6-digit number; when analysis of an individual fingerprint is discussed below it is labeled by that number.

The infrared spectral analysis of the samples was primarily done using a Thermo Electron Corporation Continuum infrared microscope coupled with a Thermo Electron Corporation Nexus 870 FTIR bench equipped with an EverGlo Globar IR source and an extended range KBr beamsplitter. Particles within the fingerprints were visually located by using 4X and 10X objectives with 10X eyepieces, then a 15X all-reflecting infrared objective was used to obtain the IR spectrum of each particle. Exhaustive studies of each fingerprint were not done; instead we performed a random sampling of areas within the fingerprints where particles were visually observed in the microscope. The samples were measured in reflection/absorption geometry and referenced to a clean gold slide. The reflex aperture which defines the region from which infrared spectra are collected was set to match the size of the particle found, and gold reference spectra were collected through the same aperture settings for proper spectral normalization. For collection of the data, a liquid-nitrogen cooled MCT-A* detector was used, the number of scans co-added was typically 64, and data were obtained with a spectral resolution of 4 cm⁻¹.

A spectral library search compared the intensity and position of the peaks in the spectrum of the sample to spectra in the large commercial FTIR libraries using the built-

in search functions of the Thermo-Electron OMNIC data acquisition and analysis software. The library search showed the top matches for each spectrum and ranked the matches according to a percent match. The IR spectra of each of the four test compounds used in this study were also verified by measuring each by the KBr pellet transmission method.¹⁰ The measured Ibuprofen spectrum was identified through the search as Ibuprofen from the Georgia State Forensic Drugs Library. The Sweet'N Low® spectrum was identified as Sweet'N Low® 2nd formulation in saccharin, casio4 dextrose, cream tarter from the same library. The vitamin C spectrum was identified as ascorbic acid from the FDM FTIR Spectra of Organic Compounds library. The Non-Dairy Creamer spectrum was identified as starch from the Coatings Technology library. Non-Dairy Creamer has an abundant amount of starch in it, so the spectra obtained from this substance were always identified in a spectral library search as starch. Library searches are only useful if the compound of interest is in the library, and identification of well-mixed substances can be more difficult, although there are many well-established IR spectral interpretation methods that can be followed in such cases.¹⁰

Some larger particles yielded spectra with saturated absorbances making their unique identification more difficult. For these particles, IR spectra were also collected using attenuated total reflectance (ATR) using a Thermo Nicolet Corporation Infinity Series Diamond ATR objective and the same Continuum IR microscope. In this case the reflex aperture was kept at $100 \times 100 \mu\text{m}$ for all the particles regardless of their size. A contact alert pressure sensor system by Thermo Nicolet was used to ensure that the pressure applied was the same for each sample. ATR only probes a thin known depth of a sample in contact with the crystal, and so is a useful technique for thicker samples.

The synchrotron beamline 1.4.3 at the Advanced Light Source, Berkeley, was used for identifying the smallest particles that were otherwise almost undetectable using a thermal globar IR source. This beamline is equipped with a Nicolet Nic-Plan IR microscope with an MCT-A* detector and a Nicolet Magna 760 FTIR bench with a KBr beamsplitter. The synchrotron has a significant brightness advantage over thermal sources because the synchrotron source is diffraction limited.¹¹ This means that the focused spot in the IR microscope is approximately the size of one wavelength, and particles with diameters between a few and 10 microns could be readily measured.

Identification of individual particles

When looking at the fingerprints under a visual light microscope, it was impossible to see which particles were one substance and which were another. However by using FTIR spectromicroscopy, vibrational spectra of individual particles were obtained and identified using the spectral library search. Nominally, the numbers of particles of each of the four test substances found in the fingerprints corresponded to the initial powder mixture ratios. For example, more non-dairy creamer particles were found than vitamin C or ibuprofen. Our random sampling found particles of all four compounds in most fingerprints, but in a few fingerprints particles of one or two different substances in the mixture were not found, though as stated before, we did not perform exhaustive searches.

In this study we found 22 particles that matched to ibuprofen with an average match value of 70.68%. For vitamin C, we found 18 particles that matched with an average match value of 74.34%. We found 65 particles that matched to non-dairy creamer with an average match value of 81.16%. A total of 54 particles of Sweet'N Low® were found to match with an average match value of 78.21%. Table I summarizes the number of particles with excellent (E), good (G) and satisfactory (S) matches. In all cases the top match was the substance identified, and probably the lower match scores were obtained when the particle measured contained more than one substance (either one of the other three test substances or something else on the subject's hands).

Figure 1 shows examples of IR spectra obtained from particles within the fingerprints of volunteers and the corresponding library reference spectrum for each substance. As the match values indicate, and as can be readily seen by comparing the spectra by eye in Figure 1, each substance can be identified with a high degree of certainty.

Identification by infrared imaging

In order to identify more particles, spectral maps were obtained of an area within a fingerprint to see if it was possible to identify the differences between the different substances in the powder mixture. The maps were taken using a global source with a fixed square reflex aperture of $60 \times 60 \mu\text{m}$, x and y step sizes of $30 \mu\text{m}$, a resolution of 4 cm^{-1} and 64 scans for each point. With FTIR spectromicroscopy systems now offering array detector technologies, this method of infrared imaging will allow investigating and identifying particles from complete fingerprints in a relatively rapid manner.

An important application of obtaining large area maps of a fingerprint is to correctly identify if specific substances are present. We made use of the spectral library search engine to help automate this task. After a map was taken, all of the individual spectra from the map were placed into a new “library” (this library consists of only spectra from the acquired fingerprint map). Now we could use one known spectrum, such as ibuprofen from the Georgia State Forensic Drug library, and then search only the new fingerprint “library” for matches to this spectrum. When the search is done, it shows the top matches, and if that substance is present, then the match percentage will be reasonable. Using this type of correlation technique, a spectral map of the whole fingerprint can be rapidly analyzed for matches to a predetermined set of substances. Most spectral imaging software can readily perform a correlation analysis between every point on the map and a known spectrum. By automating this correlation imaging for a suite of reference spectra from substances of interest, one could generate an overlay to the visual microscope image of the fingerprint which highlights in different colors the locations and identifications of various particles.

Figure 2 shows the results of an infrared imaging identification run on a portion of a subject’s fingerprint. The left panel shows the visible microscope image and the right panel shows the locations and color-coded identifications of three test compounds found in this region. All larger particles were identified using this technique, but some smaller ones were not. However this technique shows great promise for automating the spectral analysis to correctly recognize substances of interest within fingerprints.

Additionally it would be possible to use infrared imaging even in the case of not having good reference library spectra. Using principle components analysis (or other spectral sorting tools), one can automatically determine the primary spectral components within the large group of spectra from an infrared image. These spectral components can then be matched to library spectra when available, or subjected to further standard IR interpretation techniques.¹⁰

Advanced IR techniques for identification of more difficult particles

Although the facile reflection/absorption technique seemed to work well for many particles found in the test fingerprints, there were some particles in which the spectra showed the saturated absorbances (reflectivity going essentially to zero). In this situation, micro-ATR is a useful alternative. This technique works well for large particles ($>60 \times 60 \mu\text{m}$), which tend to be thicker.

Figure 3 shows an example of data collected from the same thick particle using reflection/absorption (lower curve in red) and using the diamond ATR objective (upper curve in blue). There is a significant improvement in the data with the ATR technique when compared to the data taken using the usual reflection/absorption technique. Because the absorption peaks are much better defined (not saturated) with the ATR measurement, the spectral library match scores are also much higher, as indicated.

Although the benefit of using ATR is that it enables particles to be identified more accurately, the drawbacks include the fact that the ATR crystal must touch the sample directly. When the ATR objective is retracted, typically the particle(s) sticks to the lens. Therefore, the original sample is destroyed and the lens must be cleaned after every sample is taken. Another drawback that was encountered was the fact that when pressure is applied to the diamond, it changes the diamond spectra. To solve this problem, the same amount of pressure must be applied to both the background and the sample scans, otherwise diamond absorption peaks will always occur in the data. Pressure application and/or measurement tools are therefore important accessories to ATR systems.

ATR works well for large ($>60 \times 60 \mu\text{m}$), thick particles, while reflection/absorption works for average sized particles ($\sim 30 \times 30 \mu\text{m}$ to $60 \times 60 \mu\text{m}$).

Smaller particles are possible to analyze using the global source, but only with significantly greater averaging times (number of sample scans) because the only way to further reduce the global's focused spot size is to reduce the apertures sizes, significantly impacting the amount of light on the sample. For small particles ($< 40\ \mu\text{m}$), we found that a synchrotron infrared source works the best due to its ability to have a focused spot size in the IR microscope of approximately one wavelength (diffraction limited).¹¹ This allows excellent signal to noise spectra still with only 64 or 128 scans.

Figure 4 shows spectra from the same point on a small particle within a fingerprint using a global source (shown with the thin line in black) and the synchrotron source (shown with thick line in blue). In both cases, 128 scans were co-added at $4\ \text{cm}^{-1}$ resolution. Although most of the peaks can be just seen in the spectrum from the global source, it is much noisier, details are lost, and the measured spot was still ~ 16 times larger than the focused synchrotron spot. The synchrotron source is an ideal way to accurately identify these smaller particles. While a synchrotron source would not be routinely used for forensic science, these user facilities exist around the world and could be employed in the case of a highly important and difficult to analyze sample.

Conclusions and Future Outlook

This study has shown that infrared spectromicroscopy is able to locate and positively identify microscopic particles from a mixture of common materials in latent human fingerprints in ideal laboratory conditions. These positive results demonstrate that IR spectromicroscopy is a rapid, powerful, and non-destructive tool for accurately identifying substances left in a person's latent fingerprints. We used spectral imaging to demonstrate automated recognition of specific substances of interest within a fingerprint. We also described successful methods for obtaining high-quality spectra from residual particles that did not easily lend themselves to straightforward reflection/absorption analysis.

It is important to note that we only looked for materials in fingerprints left on gold coated surfaces which are ideal for infrared reflection analysis whereas real-world forensics will find fingerprints on a variety of surface materials and geometries which can

render them more or less difficult to analyze. Other metallic surfaces should be relatively straightforward for analysis similar to our descriptions above. However surfaces such as glass, plastic, wood, paper, cloth, etc. will all have their own (sometimes strong) infrared absorptions. These IR absorptions of the underlying surface will effectively mask away some parts of the spectrum rendering these regions unusable for spectral identifications. The effectiveness of finding foreign materials within latent fingerprints in these cases will be dependent on having enough identifying spectral features outside of these blocked spectral regions. A good follow-up to our study would be to determine which types of forensically-relevant materials can be spectrally identified on which types of surfaces.

We believe the application of this technique to forensic studies has the potential to significantly enhance the amount of information that can be obtained from the study of fingerprints. Being able to identify not only who was present at a crime scene, but also being able to link specific people to specific acts via what is left in their fingerprints will be a powerful investigative tool.

Acknowledgements

We would like to thank Dale L. Perry and Wayne R. McKinney for help with our early forensic and fingerprint investigations. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 at Lawrence Berkeley National Laboratory.

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Table I. Summary of the library match scores for particles found in each of 8 subject's fingerprints. Most fingerprints had numerous readily identifiable particles of the four test compounds with excellent spectral match scores.

Fingerprint # Item Found	102483	102494	102504	102540	102567	102584	102595	102809
Sweet'N Low®	4 E 8 G	1 E 6 G	4 E 5 G	5 E 1 G	4 G 1 S	1 E 3 G	6 E 2 G 1 S	1 E 1 G
Non-Dairy Creamer (Starch)	4 E 9 G	7 E 11 G	10 E 1 G 1 S	7 E	3 E 1 G	5 E 1 G	1 E 2 G	2 E
Ibuprofen	1 E 4 G 2 S	1 G 1 S	4 G 2 S	3 S	0	1 E 2 G	0	1 S
Vitamin C (Ascorbic Acid)	1 G 1 S	3 E 1 G 1 S	2 G 1 S	2 G 2 S	0	1G 1 S	2 G	0

E=Excellent match to library spectra (>80%)

G=Good match to library spectra (70%-79%)

S=Satisfactory match to library spectra (55%-69%)

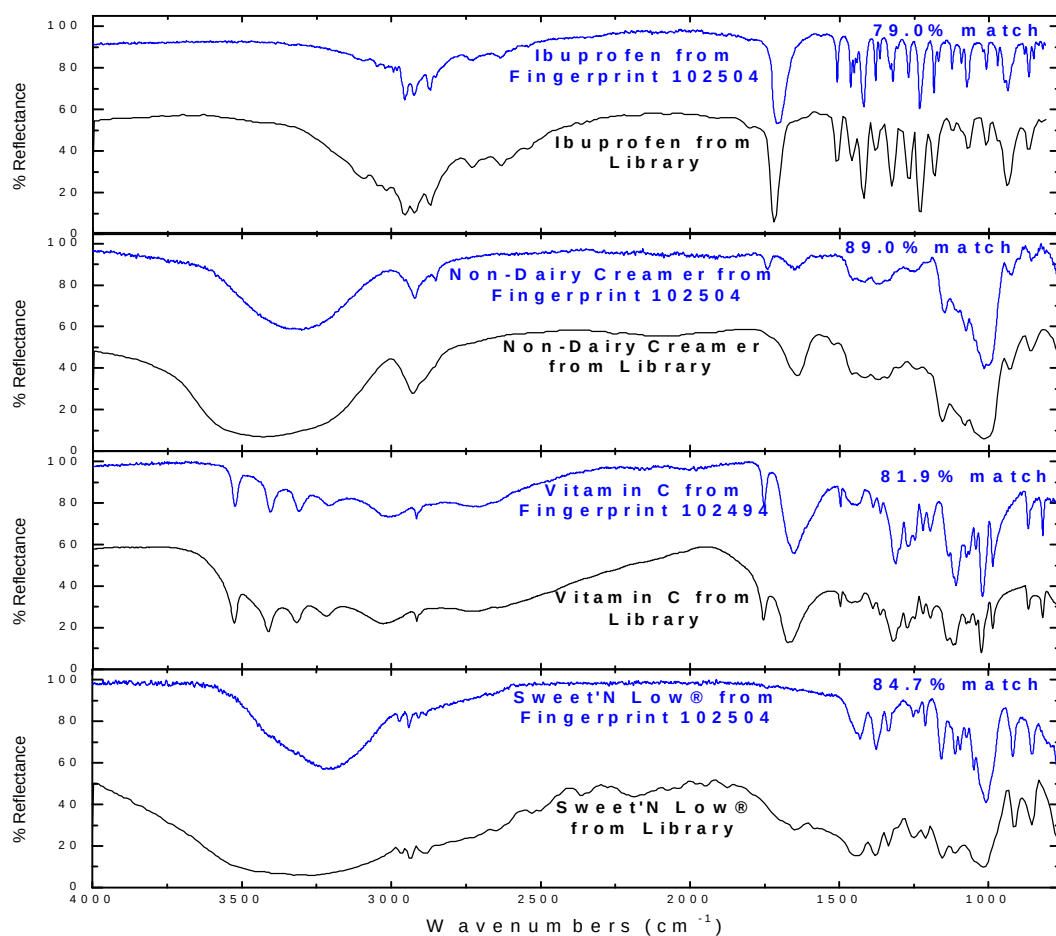


Figure 1. Example spectra obtained from particles found in the studied fingerprints (upper and in blue), and the corresponding library spectrum for each identified substance (lower and in black, scaled for visual clarity by 1.7). The spectra obtained are very distinct and can be well matched to the library spectra yielding an excellent identification.

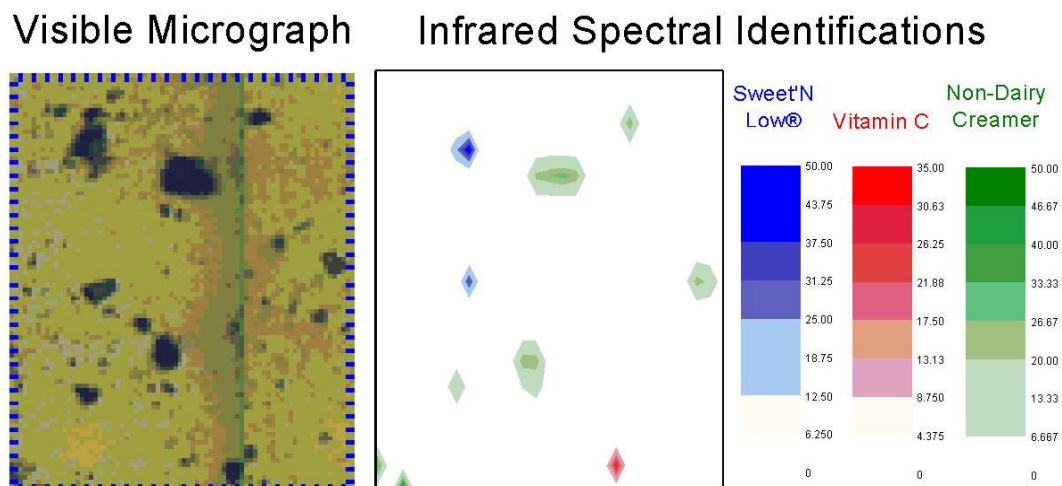


Figure 2. Results of identifying particles using infrared imaging (right) and the visible image from the microscope (left) are shown. The tick marks on the micrograph are 30 microns apart. All of the larger particles, which are color coded according to substance, were identified using this technique.

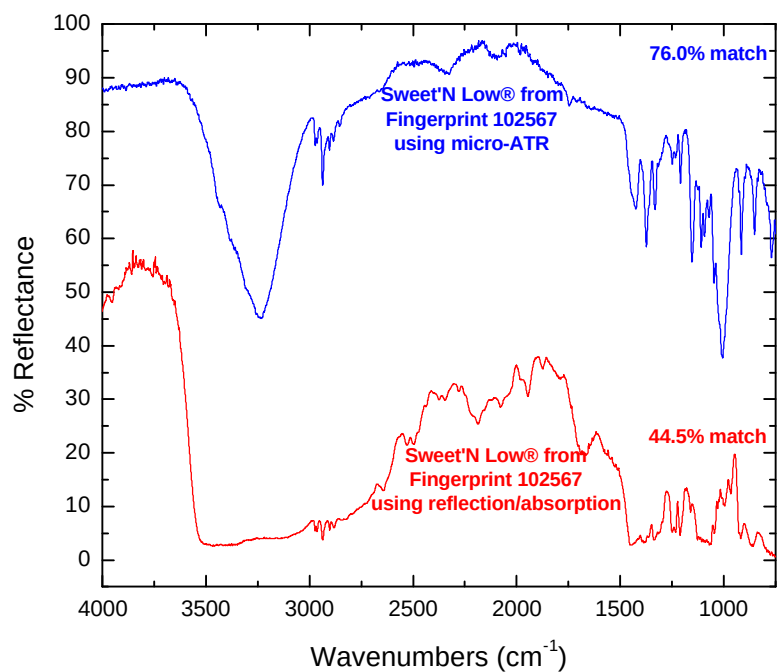


Figure 3. Data collected from the same particle using reflection/absorption (bottom in red) versus ATR (top in blue). For thicker particles, the ATR technique gives a more defined spectrum, no saturated peaks, and higher quality spectral matches.

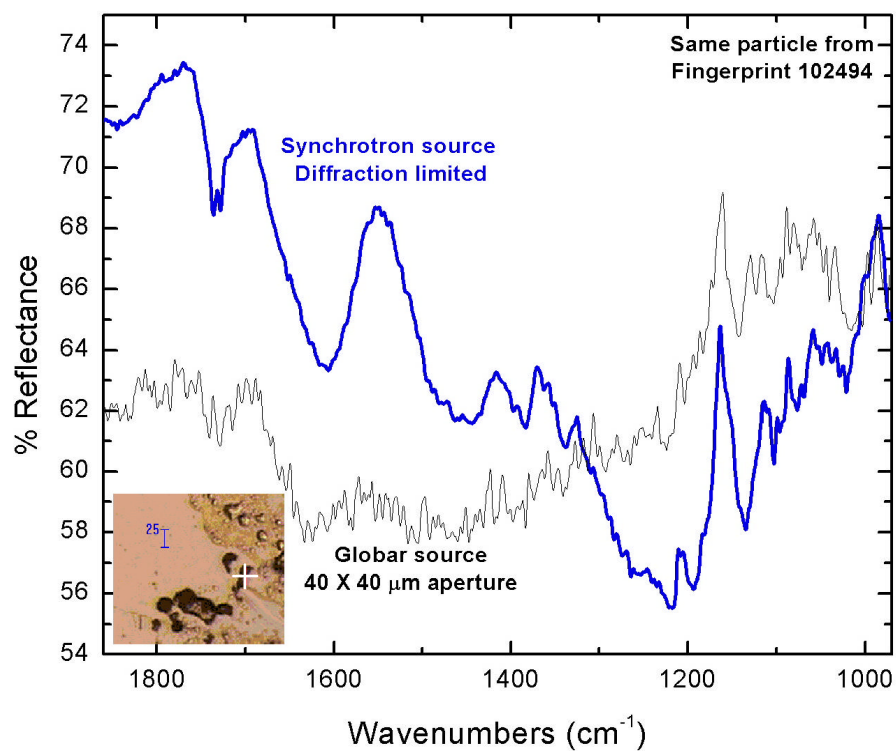


Figure 4. Data collected from the same point (shown by the white cross in the inset micrograph) on the same fingerprint using the synchrotron source (in blue with thick line) and global source (in black with thin line). A 25 micron scale bar is located in the inset micrograph. The synchrotron source works well for small particles (< 40 μm) whereas a global source would require very long averaging times to obtain a reasonable signal-to-noise ratio.