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Detection and Identification of Explosive Particles in Fingerprints Using Attenuated Total Reflection-Fourier Transform Infrared Spectromicroscopy

ABSTRACT: The application of attenuated total reflection (ATR)-Fourier transform infrared (FTIR) spectromicroscopy for detection of explosive particles in fingerprints is described. The combined functions of ATR-FTIR spectromicroscopy are visual searching of particles in fingerprints and measuring the FTIR spectra of the particles. These functions make it possible to directly identify whether a suspect has handled explosives from the fingerprints alone. Particles in explosive contaminated fingerprints are either ingredients of the explosives, finger residues, or other foreign materials. These cannot normally be discriminated by their morphology alone. ATR-FTIR spectra can provide both particle morphology and composition. Fingerprints analyzed by ATR-FTIR can be used for further analysis and identification because of its non-destructive character. Fingerprints contaminated with three different types of explosives, or potential explosives, have been analyzed herein. An infrared spectral library was searched in order to identify the explosive residues. The acquired spectra are compared to those of finger residue alone, in order to differentiate such residue from explosive residue.

KEYWORDS: forensic science, attenuated total reflectance, Fourier transform infrared spectroscopy, fingerprints, nondestructive, detection, identification of explosives

Various situations exist in detection and identification of explosives in real forensic cases. These may include improvised explosive devices, explosive residues at crime scenes, suspect shipments, and screening of hidden explosives carried by travelers on airlines (1,2). Techniques such as gas chromatography-mass spectrometry, high performance liquid chromatography, capillary electrophoresis, ion mobility spectrometry, and infrared spectroscopy have been reviewed for their application in the detection of explosives (3–5). However, all of these techniques are destructive. Nondestructive techniques are required in certain situations, such as detecting and identifying explosives in fingerprints. The main purpose of fingerprint investigation is to compare questioned and known friction skin ridge impressions from fingers in order to determine if the impressions match those of the suspects. This requires that the ridge patterns of the fingerprint are not disturbed by the detection procedure.

Nondestructive techniques such as Raman spectroscopy and infrared microspectroscopy have been used to analyze finger deposits and extrinsic materials in fingerprints (6–13). For example, Williams et al. analyzed fingerprint residues using infrared microspectroscopy (7). The detection of drugs of abuse in latent and cyanoacrylate-fumed fingerprints using Raman spectroscopy was reported by Day et al. (8,9). Grant et al. identified individuals handling key materials by analyzing extrinsic trace residual substances left in fingerprints (10). Chemical images of latent finger marks were collected by Ricci et al. using infrared spectroscopic imaging (11). Cheng et al. obtained Raman spectra and Raman band images of plastic explosive particles using Raman microscopy (12).

Traditional Fourier transform infrared (FTIR) spectroscopy has been successfully utilized to detect explosives (14,15), but it is destructive and requires special sample treatments. For example, Janni et al. obtained the FTIR spectra of vapors of explosive molecules (14). This requires that the explosives be heated in order to vaporize or decompose them prior to detection. However, the attenuated total reflection (ATR) microscope, used in conjunction with FTIR spectroscopy, enables samples to be examined directly in the solid state without any further preparation. The ATR-FTIR spectromicroscope provides multiple applications by switching between the visual and measurement modes. In the visual mode, the sample can be observed by an optical microscope and thus moved to a specific position to allow the detector to be focused onto a small area or a minute (microscopic) particle. Particles with diameter as small as 20 μm can be investigated. The FTIR spectra of such small particles are then obtained by switching the system to the spectrum measurement mode. Because of its nondestructive character and the simple sample preparation, which is significant in forensic analysis, ATR-FTIR spectromicroscopy has become an attractive analytical technique for obtaining chemical information from physical evidence.

In this work, we have examined the fingerprints obtained from handling three different types of explosives, or potential explosives. The substrate used for the fingerprints is stainless steel. The ATR microscope is used to search for particles in the fingerprints and then the FTIR spectra of these particles are measured.

Methods and Materials

Trinitrotoluene (TNT) with purity of 99%, and white–yellow in color, was purchased from Chem. Service, Inc. (West Chester, PA). Trinitrobenzene (TNB) with purity of 99.9%, and ammonium nitrate (AN) with purity of 99% (colorless) were purchased from Sigma-Aldrich, Inc. (St. Louis, MO). All chemicals were used as

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received without further purification. TNT and TNB are well known high explosives. AN is commonly used as fertilizer, and thus is readily available in bulk. As a strong oxidizing agent, AN forms an explosive mixture when combined with hydrocarbons, such as diesel fuel and kerosene. In terrorist acts such as the Oklahoma City bombing in 1995, AN and fuel oil mixtures were used for improvised bombs. Herein, AN is analyzed as potential explosive.

In order to eliminate any possibility of contamination, the hands of two volunteers were cleaned with ordinary soap, rinsed in water, and dried and aged in air for 30 min before touching the chemicals. The thumbs and index fingers were contaminated by pressing them on the explosive powders that were spread on clean glass slides. Excessive powder was rubbed off by another hand until no powder was visible on the fingers by the naked eye. The contaminated thumbs and index fingers were pressed onto clean stainless steel in order to prepare doped fingerprints. Stainless steel was chosen as the substrate because it is transparent in the infrared region, making it ideal for the analysis. In order to simulate realistic cases and to investigate the possibility of interferences on the detection process, an AN contaminated fingerprint on a metal lid from a jar was also investigated.

The infrared spectral measurements of the particles in the fingerprints were made on a Tensor 27 FTIR spectrometer coupled with a Hyperion 1000 ATR microscope accessory, both of which are from Bruker Optics, Inc. (Billerica, MA). The particles present in the latent fingerprints were visualized by using the 20 \times ATR objective of a germanium crystal with 10 \times eyepieces. Images of the particles before and after detection were taken by a digital camera coupled to the ATR microscope. Infrared spectra of the particles were obtained using the spectrometer measurement mode over the range of 4000–600 cm^{-1} with a resolution of 4 cm^{-1} , typically after 32 scans. The spectrum of clean stainless steel was used as a reference. The typical diameters of the particles examined ranged from 20 to 100 μm . An Omano OM9949T stereomicroscope equipped with an Omano CAM 500 digital camera (both from The Microscope Store, L.L.C., Wirtz, VA) was used to take pictures of the fingerprint on the metal lid before and after the measurements.

In order to compare the intensities and positions of the peaks in the spectra of the particles and thereby identify the particles, the spectrum of each particle was searched in an infrared spectral library that included the infrared spectrum databases from Fiveash Data Management, Inc. (Madison, WI), and the OPUS infrared spectrum library from Bruker Optics, Inc. The search results showed the matching spectra ranking in terms of match percent.

Results and Discussion

A fingerprint is a reproduction of the friction ridges in the fingers. When a finger touches any surface, the natural skin secretions from the eccrine glands present in the friction ridge skin, and other materials present on the finger, such as skin residue and sebum, are deposited on the contact surface. An impression of the friction ridges is thereby transferred from the finger to the contact surface. The secretions of the eccrine glands on the finger consists of *c.* 99% water and 1% solid matter including inorganic salts and organic materials such as urea, amino acids, proteins, lactic acid, and glucose (16). The fingerprints are often invisible to the naked eye and are thus referred as latent fingerprints. The latent fingerprints become visible by shining oblique light on them (8). There are many techniques available for developing and visualizing the latent fingerprints. For example, powder dusting, iodine fuming, ninhydrin spraying, super glue fuming, and laser lighting are often

used (2,16). Among these techniques, laser lighting can visualize the latent fingerprints without the aid of any chemicals or powders and does not interfere with subsequent procedures (2,16). Therefore, this technique can be used as a preliminary test to locate latent fingerprints for other types of evidence examination such as DNA analysis and detection of explosives. In this work, the latent fingerprints are located by oblique lighting without being treated with any chemicals or powders.

There were no visible differences between our clean and explosive contaminated fingerprints. This is because the explosive particles were comparable in size to the finger residues. Continuous ridge patterns were present when observing the fingerprints by the naked eyes. When viewed using the 200 \times microscope, the fingerprints appeared fragmented and only irregular shaped small sections were present. These can be either explosive particles or finger residues. Examples of particles found in the fingerprints before and after infrared detection and their infrared spectra are shown in Figs. 1 and 2. In both figures, (a) is the image of a particle before detection, (b) is the image after detection, and (c) is the infrared spectrum of the particle. The particles can not be discriminated from their morphology in Figs. 1a and 2a, because they have irregular shapes and the morphology does not provide any information about the nature of the material. However, their infrared spectra are different. The particles were identified from their infrared spectra as AN (Fig. 1) and finger residue (Fig. 2). Both of the particles are in an AN contaminated fingerprint. The spectra of particles in clean fingerprints are identical to those of finger residue particles in the AN contaminated fingerprints and the spectra of finger residues in clean fingerprints from two volunteers are also identical. Because the particles are pressed by the ATR probe, they appear larger than before detection. The diameter of the tip of the ATR crystal that touches the particle is only about 6 μm and the penetration depth of the infrared radiation is <1 μm . This means that, theoretically, a particle with a diameter as small as 6 μm can be analyzed by ATR-FTIR spectromicroscopy as long as the probe is located directly on the particle. The diameters of particles in Figs. 1 and 2 are *c.* 25 μm . Particles smaller than 20 μm were not analyzed in our experiments. This is due to the following. First, the particles smaller than 20 μm are not clearly observed because of the limited magnification of our microscope. Second, it is difficult to precisely

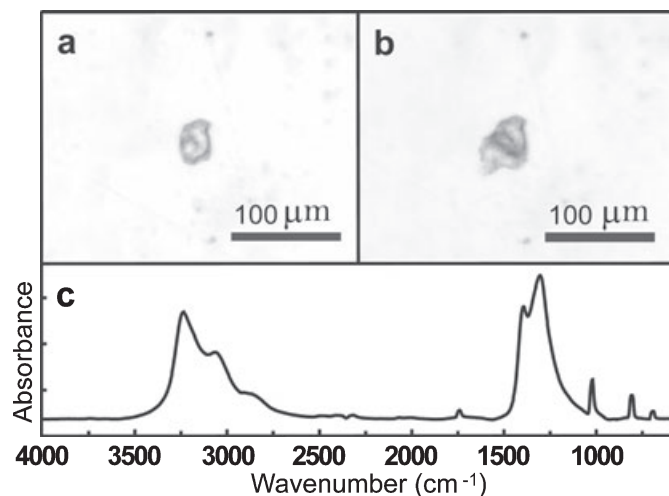


FIG. 1—(a) The image of an ammonium nitrate (AN) particle in a fingerprint before infrared detection, (b) the image of this AN particle after infrared detection, and (c) the infrared spectrum of this AN particle.

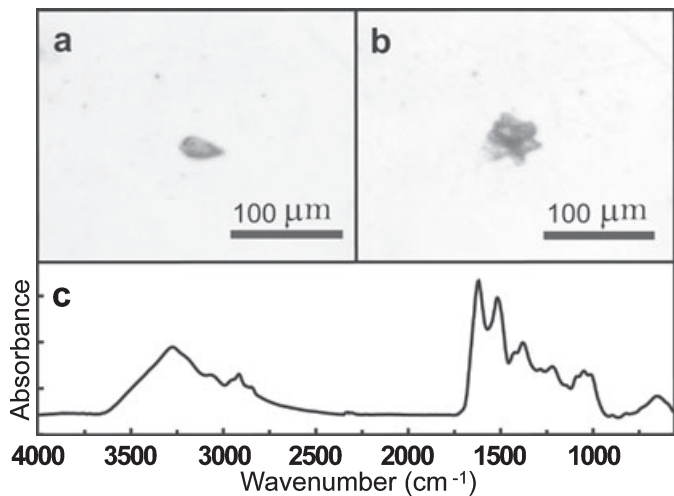


FIG. 2—(a) The image of a finger residue particle before infrared detection, (b) the image after infrared detection, and (c) the infrared spectrum of this finger residue particle.

locate the probe on such small particles. Third, there are many significantly larger particles in the contaminated fingerprints that can be easily observed.

Even though the particles after detection are pressed and larger than before, the ridge patterns in the fingerprints are not affected by the detection because the 6 μm diameter of the ATR crystal is much less than the width of the fingerprint line and the inter-line spacing. For an AN-contaminated fingerprint on a metal lid as shown in Fig. 3, the average width of the fingerprint ridges is *c.* 400 μm and the average spacing between the lines is about 100 μm . No visual interference was observed when comparing the images of fingerprints before and after the detection of explosives. Therefore the infrared detection process does not disturb the fingerprint for further identification, which depends on the ridge patterns within the fingerprint. Therefore, the ATR-FTIR spectromicroscopy can be regarded as a nondestructive technique when detecting explosive particles in fingerprints on a hard surface. This nondestructive capability is especially significant in forensic science because there is little or even no control over the quantity and quality of the specimens in real cases. The result of ATR-FTIR analysis of fingerprints on the lid is identical to that on stainless steel, as shown in Fig. 4.

An infrared spectral library was used to identify the particles in the fingerprints from their spectra. The particle spectrum is searched in the library and the best matches for each spectrum are shown and ranked in order of matching percent. Among the three types of explosives, only one explosive, AN is found in the library because of the limitations of our library. Both the spectra we obtained (Fig. 4a) and that from the library (Fig. 4b) are shown. For the explosives TNB and TNT, perfectly matched spectra were not found in our library, but the spectrum of 1,3-dinitrobenzene (DNB) in the library matches these two spectra very closely. Therefore, even though there is no perfect matching spectrum for the unknown explosive, the closely matching spectrum can provide information about the unknown constituent. The three spectra, TNB, TNT, and DNB are shown in Fig. 5. The spectrum of finger residue shown in Fig. 6a was also searched in our library. The highly ranked spectrum shown in Fig. 6b is that of zein, a prolamine protein derived from corn. This is not surprising because the constituents of finger residues include proteins. It was reported that the concentration of proteins in eccrine sweat (secretion of the eccrine gland present on fingers) is *c.* 150–250 mg/L (16).

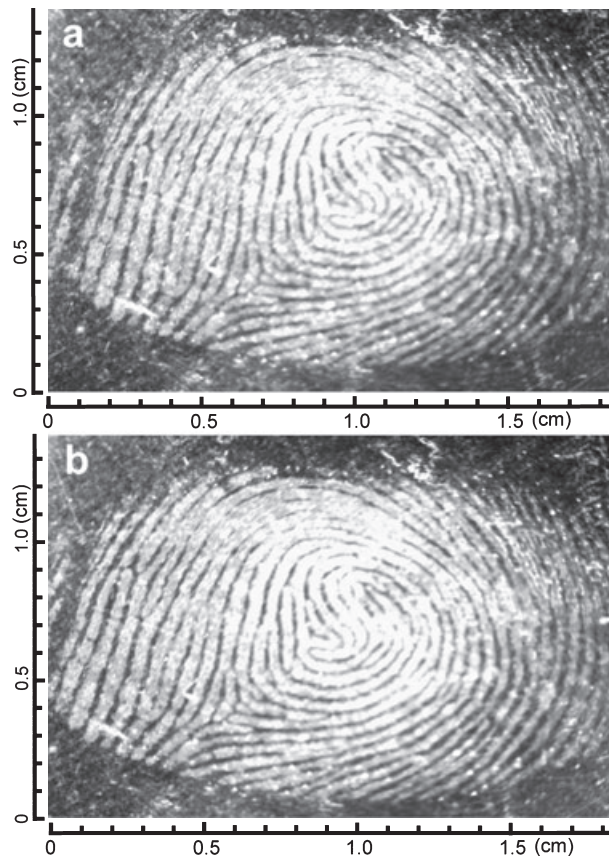


FIG. 3—The images of a fingerprint on a metal lid (a) before and (b) after detection.

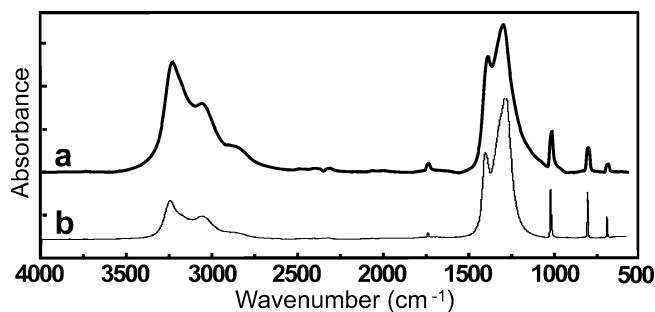


FIG. 4—(a) The infrared spectrum of AN obtained from an AN particle in a fingerprint and (b) the infrared spectrum of AN from the infrared spectral library.

All of the spectra of the explosive particles obtained from fingerprints are compared to those spectra from bulk explosives. No difference is found between them except that the intensity of explosives in the fingerprint is lower than those in the bulk because the amount of explosives in the fingerprint is minute.

The spectra of explosive particles obtained from fingerprints can contain additional spectra from finger residues. The spectra in Fig. 7 were obtained while detecting particles in AN contaminated fingerprints. Figure 7a is the spectrum of an AN particle, Figs. 7b and 7c are the spectra of a mixture of AN and finger residue, and Fig. 7d is the spectrum of a finger residue alone. In Figs. 7b and 7c, the peaks in the range of 1470–1160 cm^{-1} can be ascribed to AN and the two sharp peaks near 1645 and 1538 cm^{-1} are ascribed to finger residue. The relative infrared intensities of AN and finger residue depend on their ratio in the mixture. For example, in

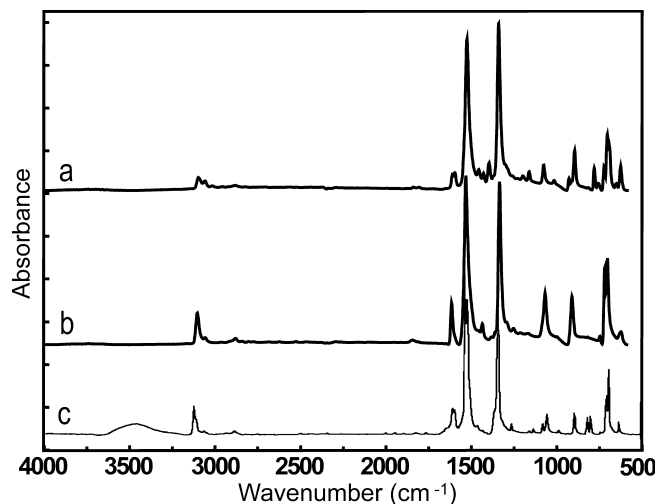


FIG. 5—(a) The infrared spectrum of trinitrotoluene (TNT) obtained from a TNT particle in a fingerprint, (b) the infrared spectrum of trinitrobenzene (TNB) obtained from a TNB particle in a fingerprint, and (c) the infrared spectrum of 1,3-dinitrobenzene (DNB) obtained from the infrared spectral library.

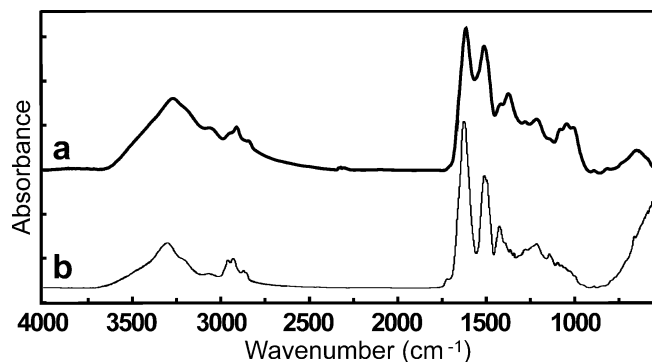


FIG. 6—(a) The infrared spectrum of finger residue in a fingerprint and (b) the infrared spectrum of zein obtained from the infrared spectral library.

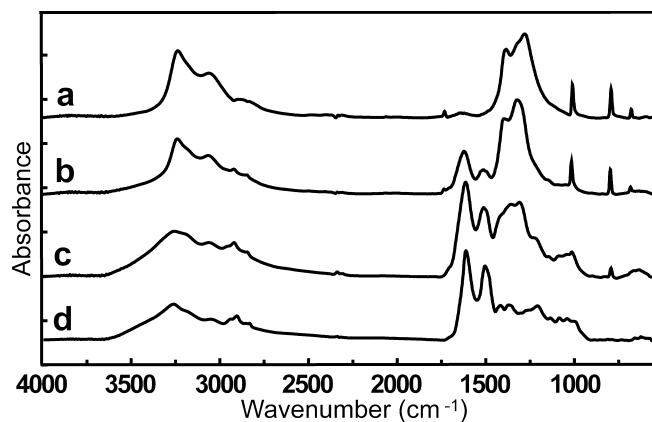


FIG. 7—(a) The infrared spectrum of an AN particle in a fingerprint, (b) the infrared spectrum of a mixture of AN (high concentration) and finger residue, (c) the infrared spectrum of a mixture of AN (low concentration) and finger residue, and (d) the infrared spectrum of finger residue alone.

Figs. 7a–d, the intensities of the sharp peak near 716 cm^{-1} decrease as the ratio of AN decreases. The interference of finger residue must be considered when identifying the unknown

explosive particles in fingerprints. The spectrum of the unknown particle is compared with that of finger residue to determine whether the interfering peaks of finger residue are present. The spectrum can be searched in the library directly if no interfering peak is present, or the interfering peaks of finger residue must be subtracted before identification.

Conclusions

This work shows that it is feasible to detect and identify explosive particles in fingerprints by ATR-FTIR spectromicroscopy. The particles of explosives and finger residues can not normally be discriminated by their morphology alone, however their infrared spectra can differentiate between them. Particles as small as $20\text{ }\mu\text{m}$ in fingerprints can be analyzed by the ATR-FTIR spectromicroscope. Even though the analyzed particles are pressed by the ATR-FTIR probe, this does not disturb the line pattern of the fingerprint because the region over which the probe contacts the specimen is much smaller than the width and spacing of the fingerprint lines. Therefore, ATR-FTIR spectromicroscopy can be used as a nondestructive technique for analyzing explosive particles in fingerprints. The explosive particles can be identified by searching their spectra in an infrared spectral library in order to find matching spectra of known materials. The explosive particles can thereby be directly identified. The spectrum of AN was found in the library and matches those spectra obtained from the fingerprints. As the library used in this work is neither specific for explosives nor is it complete, perfectly matched spectra of TNT and TNB were not found. However, the closely matched spectrum of DNB can provide identification information for analysis of TNT and TNB. The particles in the contaminated fingerprints can be a mixture of explosives and finger residue. Therefore, great attention should be taken before searching the spectrum in the library in order to confirm that there is no interference from finger residue.

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