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Reconstruction of chemical fingerprints from an individual’s time-delayed, overlapped fingerprints via laser-induced breakdown spectrometry (LIBS) and Raman spectroscopy

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Abstract

Laser-induced breakdown spectroscopy (LIBS) is a method for atomic emission analysis that can be used to analyze the chemical composition of samples in the forensic investigations. The combined effort of extracting, analyzing, and restoring latent fingerprints at crime scenes is an important step toward successful arrests, and hence, the purpose of this research is to estimate the temporal sequence at which a fingerprint was imprinted from an individual. The difference in the laser spectrum from a latent fingerprint at times from 0 to 60 minutes after it was left was analyzed using LIBS and Raman spectroscopy, both of which require no chemical pre-treatment of the sample. We found that the signal intensity changes with time, 60 min after the imprint was made for the wavelengths of CN band, fatty acid, amino acid, and oil components. Based on these preliminary findings, the chemometric analysis was performed on the spectrum data obtained from 60 minutes of exposure time and the time-sequenced overlapping fingerprints were distinguished, which were imprinted at intervals of 10, 20, 30, and 40 minutes using SIMCA and PLS-DA classification methods.

Keywords: LIBS (laser-induced breakdown spectroscopy), latent fingerprint, overlapping fingerprints, Raman spectroscopy, sequence detection, aging factor, PCA (principal component
analysis).

1. Introduction

Laser-induced breakdown spectroscopy (LIBS) generates a plasma from a sample produced by a high-energy laser [1, 2]. The laser energy is absorbed by the sample and the material is then liquefied or vaporized, depending on the state of the material. Repeated ablations result in a plasma. Atoms in the irradiated region maintain their excited state for 200 ~ 300 ns, and then emit light when they relax to the ground state. The wavelengths and amplitudes of light emitted during relaxation differ for different elements in the sample, allowing spectroscopic analysis of atomic components in a sample. LIBS can produce this laser spectrum in real time, and even a small sample can be analyzed reliably without risk of contamination. The optical equipment for LIBS is simple and allows for remote sensing. Based on these advantages, LIBS has been used in a wide range of applications that include forensic analysis [3-12].

A latent fingerprint is a specific pattern formed by the line of the swollen glands on the skin of the fingertip, and creates a figure when the ridges touch a surface. A human fingerprint has a shape from birth that does not change over time, and is not easily changed by external conditions. The shape of the fingerprint is used as a means of identifying an individual because of the fingerprint’s uniqueness. At a crime scene, criminal investigators detect fingerprints in the form of oil imprints. Ridges and valleys on fingertips can produce latent fingerprints in the form of oil when the fingertip is imprinted on an object. Therefore, finding latent fingerprints at crime scenes is an important step toward arresting suspects. In addition, the chemical features of the latent fingerprint vary according to eating habits and living environment [13-18]. It is possible that the unique chemical composition of each person’s skin oils can be detected with LIBS, providing an additional piece of data for the forensic investigation. LIBS is also used to
study fingerprint detection. Abdelhamid et al. [19] studied laser spectrum detection of explosive debris in fingerprints. Taschuk et al. used a femtosecond laser to reduce the extent of the laser craters, which enables LIBS to detect and recover partial fingerprints [20]. Each of these studies focuses on restoring a single fingerprint; however, in practice, perfect fingerprints are rarely found, and forensic scientists often need to analyze more than one fingerprint on a surface.

The chemical composition of latent fingerprints may change with lifestyle of the person, and in particular, the finger oil composition can change with the environmental exposure and aging [21-27]. As can be seen in Archer et al. [21], the oil components of the fingerprint change over time. Researchers have also found changes in amino acid and fat composition [22]. Antoine et al. [23] found that fingerprint composition varies according to the age of the person, and that the composition varies over time. In addition, image processing and chemical composition analysis have shown that the thickness of the oil imprint and the chemical composition of the oil change over time and with exposure to temperature [24-27]. Consequently, in the present investigation, changes in the chemical signature of oil imprints over time were measured using LIBS and Raman spectroscopy.

Overlapping latent fingerprints often appear in crime scenes [3, 4, 28-33], where they belong to two different sources or a single source of imprints on the same surface with a time delay. These overlapping fingerprints have traditionally presented a challenge for forensic investigators. Image processing with computer software offer a limited access to discriminating two images from an overlapping sample. Feng et al. [28] studied an algorithm for separating overlapped fingerprints that measures the orientation of components in the image. The fingerprints can be separated by sensing the directions of the ridges. Stojanović et al. [29]
developed a technique for separating fingerprints using a neural network. Bradshaw et al. [30] took a chemical approach to separate overlapping fingerprints. They used matrix-assisted laser desorption ionization (MALDI) with multivariate analysis to separate fingerprints that had different chemical compositions. In our previous study, LIBS was used to measure the chemical compositions of human fingerprints via the intensity of the laser spectra [3, 4]. This allowed us to separate overlapped fingerprints from different sources.

The present study is focused on distinguishing the overlapping fingerprints from an individual by the times at which they were deposited. Fingerprints from the same person have identical chemical signatures when they are first imprinted, so chemical analysis is not as useful as imaging analysis for fingerprints that were all left at the same time. However, as time goes on, changes in the oil and amino acid content of the fingerprints can be estimated with LIBS and Raman spectroscopy that provide measurements in real time. Laser spectra from overlapping fingerprints yield chemical data that can be categorized using multivariate analysis. We separated overlapping fingerprints left 10, 20, 30, and 40 mins before the measurement and successfully estimated the imprinting sequence by analyzing LIBS and Raman spectroscopic data.

2. Material and methods

2.1 Preparation of overlapping fingerprint sample

We prepared sample fingerprints on aluminum plates in the following steps. In order to minimize the influence of the environment, the test subject’s index finger and forehead are cleaned with 99.8% alcohol (Sigma Aldrich) cotton swabs. Then the oil on the subject’s forehead is placed on the index finger for about 10 s. The index finger is then pressed lightly
on the aluminum plate for 5 s. When creating samples of overlapping fingerprints, two fingerprints were imprinted at 10, 20, 30, and 40 min intervals. After that, LIBS analysis was immediately applied inside the chamber to minimize potential environmental contamination. Four different males in their 20’s and 30’s provided their fingerprints for the samples.

![Diagram of single person's overlapping fingerprints](image)

![Diagram of LIBS scanning system](image)

**Fig 1.** (a) Preparation of overlapping fingerprint and (b) LIBS scanning system.

### 2.2 Optical experimental setup and data acquisition

Our LIBS system uses a 1064-nm-wavelength Q-switch Nd:YAG laser for ablation and plasma generation (RT250-Ec, Applied Spectra Inc.). Figure 1(b) depicts the experimental apparatus. The pulse duration of the laser was set at 5 ns. We set the laser energy to approximately 10 mJ to minimize the area of craters created by the ablation process, which enhances the resolution of the laser scanning process. A beam expander was also used to minimize the beam area. The gate delay was set to 1.05 ms, and the distance from laser to the sample was fixed at 10 cm. Each point for laser scanning had a distance of 125 um to enhance the resolution. The laser repetition rate was set at 1 Hz. Using a six-channel CCD spectrometer,
we set the CCD sensor to detect wavelengths from 198 to 1050 nm. The resolution of the spectrometer was set at 0.1 nm for ultraviolet to visible wavelengths, and 0.12 nm for visible to near-infrared. To detect the chemical distribution of the fingerprint, laser-beam scanning is utilized. The distance between the laser and the sample was also adjusted with z-axis movement. A chamber capable of controlling atmospheric pressure and temperature was used to minimize the change of signal intensity due to the high temperature and high pressure of the plasma.

A 532-nm-wavelength Q-switch Nd:YAG laser (Surelite 1, Continuum Inc.) was used for Raman scattering. This laser has a pulse duration of 5–7 ns and uses a second-harmonic generator for the dominant wavelength. To avoid scattering caused by laser ablation during these measurements, the area irradiated with the laser was larger than that of the LIBS laser (~200 μm), and a pulse energy of 9 mJ or less was used. The gate delay is 0 μs for these irradiations. The repetition rate was set at 2 Hz. A CCD Czerny-Turner spectrometer (MonoRA320i Andor, iStar Andor) capable of measuring the Raman scattering signal was used. The spectral resolution was set to 7 cm⁻¹, with 10-μm slits and 1200 gr/mm. The grating and gate width were fixed at 1200 grooves and 0.1 ms. A longpass filter (LP03-532RU-25, Thorlab) was used to remove Rayleigh-scattered light. A 600-μm optical fiber was used to focus the Raman-scattered light.

Unscrambler X 10.1 (CAMO PROCESS AS, Oslo, Norway) and MATLAB R2016a software were used for data processing and multivariate analysis. Origin Pro 8.5.1 (Origin Lab Corporation, Northampton, MA, USA) was used for drawing graphs.

3. Results and discussion

3.1 Analysis of aging factor from latent fingerprints using LIBS
We first need to identify a latent fingerprint signal without time exposure using LIBS and Raman spectroscopy before applying the aging factor to separate overlapped fingerprints. Figure 2 shows the LIBS spectra of latent fingerprints from four different people. Each laser spectrum is the result of averaging laser spectra from 100 points of the latent fingerprint. Each LIBS spectrum is offset by 25,000 for ease of reading. The NIST atomic spectra database is used to analyze the composition of the LIBS spectra [34]. The major emission lines in data from the four fingerprints we tested are summarized in Table 1. The LIBS spectra do not clearly indicate differences in chemical composition between fingerprints from the four individuals we tested. In previous studies [3, 4], we focused on the signal intensities from a few elements such as sodium and potassium, and we were able to discriminate between fingerprints from different individuals. However, when fingerprints from the same person are overlapped, the basic chemical composition will be the same. With LIBS data alone, then, we concluded that overlapping fingerprints can be separated only when they come from different individuals.

However, in other recent work, we confirmed that environmental influences such as drying, dehydration, degradation, and migration change the binding pattern of fatty acids and amino acids over time and increase the number of double or triple CN bond. The signal intensity from the CN band is determined by the concentration of nitrogen in the air or the proportion of carbon in the targeted sample composition in conventional LIBS analysis for making recombination process of CN formation [35-38]. Furthermore, LIBS emission intensity was affected by contaminants of carbon and nitrogen in the plasma atmosphere [36, 38]. However, several conventional studies have confirmed that CN-band signal intensity increases slightly when the number of CN bands is increased or double or triple bonds form, if the proportions of carbon and nitrogen are nearly equal [34]. Based on this observation, we expect that an
increase of double CN bonds due to time-delayed aging will increase the CN-band signal intensity when a latent fingerprint is exposed to the nitrogen in air over a long period.

![Average LIBS spectra for latent fingerprints from four different individuals.](image)

**Fig. 2.** Average LIBS spectra for latent fingerprints from four different individuals.

<table>
<thead>
<tr>
<th>Element</th>
<th>Emission line (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td>388.29, 387.08, 386.14, 385.44, and 358.03</td>
</tr>
<tr>
<td>Mg</td>
<td>279.51</td>
</tr>
<tr>
<td>K</td>
<td>766.49, 769.90</td>
</tr>
<tr>
<td>Na</td>
<td>588.1, 589.59</td>
</tr>
<tr>
<td>Ca</td>
<td>393.36, 396.85</td>
</tr>
</tbody>
</table>

*Table 1. Main emission lines from four latent fingerprints.*
Figure 3 shows the LIBS spectra over the wavelengths from 384 to 390 nm measured for 60 min after four different fingerprints were imprinted at intervals of 10 min. The wavelength bands at 388.29, 387.08, 386.14, 385.44, and 385.03 nm, which correspond to the CN-band signal, was selected following the method. The signal-to-noise ratio (SNR) of the CN band is small compared to other atomic signals, but it is still approximately 1000 or more, so we averaged over 100 laser spectra to improve the reliability of the results. Figure 4(a) shows the simple signal intensity including error bars for 100 laser spectra, and (b) shows the relative increase of 100 laser spectra for every 10-min interval.

The laser spectrum of each latent fingerprint was measured at intervals of 10 min. As shown in Figs. 3 and 4, these data confirm that the intensity of the CN-band signal increases slightly over time. As shown in Fig. 4(b), the signal intensity increases by 150% over 60 min. Changes of other atomic components with high SNR are not detected consistently, as shown in Fig 5. As a result, we judge that the concentration of metals in the imprints does not change significantly over time. However, the signal intensity of the CN band increases not only by the fingerprint material but also by any contaminants of carbon and nitrogen in the plasma atmosphere. The fingerprints were tested in a chamber with constant internal temperature of 25°C and relative humidity of 60% to diminish effect of plasma atmosphere. This maintained environment suggests that atomic composition of the fingerprint hardly changes, and the fluctuation of bonding between C and N molecules may be caused by not only the aging phenomena, such as drying, dehydration, and degradation. This indicates that the signal intensity of CN band increases such that the shape of the molecule changes, as reported previously [35].
Fig. 3. Average LIBS signal lines from four latent fingerprints.

Fig. 4. Temporal change of CN band. (a) Signal intensity and (b) ratio to initial intensity.
Fig. 5. Temporal change of signal intensity for (a) potassium (766.587 nm), (b) calcium (393.36 nm), (c) sodium (588.91 nm), and (d) magnesium (279.51 nm).

3.2 Validation of LIBS via Raman spectroscopy

Raman spectroscopy measures the vibrational and rotational motion of a molecule as driven by inter- or intra-molecular interactions. When a laser beam irradiates a sample, part of the light is scattered by vibrations and rotations of the molecules in the sample. The degree of this Raman scattering for each wavelength indicates the molecular arrangement and composition of a sample. Since Raman spectroscopy requires mostly the same optics as does LIBS, Raman spectroscopy data can complement the LIBS data in the present analysis [39, 40].
Figure 6 shows the change in Raman spectra over 20 min for a latent fingerprint on an aluminum plate. Table 2 lists the main emission lines. The latent fingerprint consists of glycine, serine, acetic acid, aspartic acid, pyruvic acid, and lactic acid. The signal intensity from fatty acids, amino acids, oils, and CN bonds increases over time. This result confirms that aging increased the density of fatty acids, amino acids, and oils, and that double and triple CN bonds also increased. The Raman spectroscopy data can therefore increase the accuracy of fingerprint sequence detection by complementing the LIBS data.

![Raman Spectra](image)

**Fig. 6.** Average Raman spectra for time-delayed fingerprints

<table>
<thead>
<tr>
<th>Element</th>
<th>Emission line (1/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td>1610-1665 (double), 2249 (triple)</td>
</tr>
<tr>
<td>Isobutyric acid</td>
<td>800, 1100</td>
</tr>
<tr>
<td>Compound</td>
<td>Raman Shifts</td>
</tr>
<tr>
<td>-------------------</td>
<td>--------------</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>800, 1100</td>
</tr>
<tr>
<td>Aspartic acid</td>
<td>~1475-1580</td>
</tr>
<tr>
<td>Serine</td>
<td>550</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>~1475-1580</td>
</tr>
<tr>
<td>Pyruvic acid</td>
<td>~1475-1580</td>
</tr>
<tr>
<td>Glycine</td>
<td>1670</td>
</tr>
</tbody>
</table>

Table 2. Selective Raman peaks from the latent fingerprint.

Fig. 7. Average Raman spectra for two different latent fingerprints.

Figure 7 shows Raman spectra for two different persons’ latent fingerprint from 700 to 3100 cm\(^{-1}\). In the laser spectra from the latent fingerprints between 0 and 60 min, the signal intensities from amino acids, fatty acids, oils, and CN bands increased continuously, but the signal intensities remained constant after 60 min. Figure 8 shows the temporal changes, around the CN band and oil signals, in Figure 7. The signal intensities from oils and CN bands doubled over 60 min, and did not change from 70 min on.
Fig. 8. Temporal change of CN band using Raman spectroscopy. (a) Signal intensity and (b) ratio to initial intensity.

3.3 Time-sequence detection and multivariate analysis of aging factor

Figure 9 shows the LIBS signal intensities normalized to the maximum intensity of each laser pulse around the CN band signal (388.29 nm) for measurements taken with each fingerprint over 60 min. Figure 9(a) shows that the signal intensity increases in a roughly linear fashion. The time-sequence detection based on this linear increase in signal intensity is possible because the results from the four other latent fingerprints show similar linear trends.
Fig. 9. Change in the intensity of CN signal during 60 mins. (a) Signal intensity and (b) intensity relative to initial measurement.

Fig. 10. Successful PCA results according to the origin and aging factor

Figure 10 shows the result of grouping the LIBS data from four different people's fingerprints often applying the principal component analysis (PCA). Each oil fingerprint lies in an independent region; measurements at different times are grouped within those regions. This plot shows that classification schemes such as SIMCA and PLS-DA can be further used to automatically recognize time differences in the fingerprint laser spectra.

We conducted sensitivity and robustness tests to determine the reliability of these results following previous works [4, 41, 42]. The difference between sensitivity and robustness is in whether the test relies on data from the first 100 fingerprints or requires additional extracted
spectral data. After selecting 30 data points for the prediction class, 20 other data points were selected randomly, and tests were repeated 100 times. For the sensitivity test with SIMCA, the classification accuracy was 92.86%, 4.78% of classifications were inadequate, and 2.36% of the data points were not classified. Using PLS-DA, the average classification accuracy was 96.17%, 0.75% of classifications were inadequate, and 3.08% of the data points were not classified. The averages of the robustness tests were 91.50%, 7.30%, and 1.20%, respectively. These tests confirmed that fresh latent fingerprints can be classified according to the time they were deposited with an accuracy of more than 90%.

3.4 Separation of overlapped fingerprints with aging factor

The above tests confirmed that multivariate analysis with methods like PCA, SIMCA, and PLS-DA can accurately classify the time sequence in which fingerprints were deposited when they come from the same source. Next, we used multivariate analysis to distinguish overlapping fingerprints laid in sequence, and utilized the obtained data to reconstruct the image of the ridge lines for two overlapping fingerprints.

First of all, 30 laser spectra from each latent fingerprint were extracted for setting the prediction class for PCA. The laser spectrum data from each point on the sample were then converted into PCA data, and the classification algorithm applied to these PCA plots. In case of an overlapping fingerprint without the aging factor, we could not reconstruct the separate fingerprint lines, as seen in Fig. 11. However, as seen in Fig. 12, this process allowed us to separate clearly the two overlapping fingerprints and to reconstruct the images of each. To obtain the two-dimensional images in Figs. 11 and 12, laser-beam scanning is used. Each point for laser scanning is distanced at 125 um for enhancing the resolution.
Fig. 11. Unsuccessful separation of an individual’s overlapping fingerprints when aging factor is not applied.
Figure 12. Successful reconstruction of an individual’s overlapping fingerprints when aging factor is utilized

4. Conclusion

An individual’s overlapped fingerprints were reconstructed by considering the aging factor using laser spectroscopic methods. Environmental influences such as drying, dehydration, and degradation are known to increase and strengthen the CN band on the latent fingerprints. Using
the proposed LIBS and Raman spectroscopic analysis, estimating the imprinting sequence is possible based on the increased CN-band intensity for each time interval. The classification methods such as SIMCA and PLS-DA are also applied to classify the fingerprints with their distinct time of imprints. Nevertheless, the proposed spectroscopic analysis is not intended to replace the generic forensic techniques such as powder, nynhydrin, and light source methods. However, the combined methods of LIBS and Raman together with chemometry may offer advantage in the evidence collection leading to a successful crime investigation.

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References


Highlights

- Aging factor of latent fingerprint was analyzed using LIBS and Raman
- Time sequencing of an individual’s latent fingerprints was performed
- Time-delayed, overlapped fingerprints were separated.