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Forensic soil analysis using laser-induced breakdown spectroscopy (LIBS) and Fourier transform infrared total attenuated reflectance spectroscopy (FTIR-ATR): Principles and case studies



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ABSTRACT

Soils are crucial trace evidence that can establish or exclude the relationship between a suspect, victim, or an object at a particular scene, which could contribute to building a case. Laser-induced breakdown spectroscopy (LIBS) and Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectroscopy have been demonstrated to be effective techniques for soil characterization owing to its being rapid, nondestructive, and convenient analysis with little sample preparation requirements. Therefore, the principles of LIBS and FTIR-ATR techniques for soil forensic analysis in typical soil samples were investigated and their practical feasibility was tested by applying the techniques to forensic soil samples in two criminal cases. Principal component analysis (PCA) of a typical soil sample indicated that five typical soil types were clearly distinguished by LIBS and FTIR-ATR spectra. Variations in the soil elements (i.e., Si, Mg, Al, Ca, K, O, and N) and functional groups (i.e., O-H/N-H, C=C/C=O, Si-O, CO_3^{2-} , Al-OH, and NL_2) are crucial indicators for soil identification. The casework results demonstrated that both LIBS and FTIR-ATR show great potential for forensic soil analysis in future cases.

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1. Introduction

Soil is highly variable in terms of its composition, texture, and formation process [1], and its physical, biological, and chemical properties can change significantly depending on the sampling location [2]. In the course of criminal investigations, soil samples are very important tracing evidence as they are frequently moved from one place to another [3] and can be easily collected and analyzed [4]. Generally, the physical, biological, and chemical properties of the soil samples collected from the hands, shoes, clothes, vehicles, etc. of the suspect can be compared with the soils collected from the crime scene or victim [3]. Thus, the connection between a suspect, victim, or object with a particular scene can serve as forensic evidence that can contribute to the determination of criminal cases [5]. For instance, Petraco et al. reported four successful cases using forensic soil examinations and indicated that forensic soil examination provides the forensic science community with a quick, simple procedure for the accurate

http://dx.doi.org/10.1016/j.forsciint.2020.110222 0379-0738/© 2020 Elsevier B.V. All rights reserved. inclusion and/or elimination of questioned and known soil specimens in real life forensic casework [6].

The color, elemental analysis, and microbiological analysis of soils are commonly used approaches for forensic soil examination [3,7]. However, the color examination is only suitable for soils with large color variations. During microbiological analysis of soils, samples are susceptible to contamination at the crime scene (as a result of soil transfer effects) and laboratory [8]. In addition, the time lapses between the crime and collection of reference samples may also influence the results [8]. Elemental analyses of soil are relatively stable due to the stability of soil element composition over time. A number of elemental analysis techniques can be used, including atomic absorption spectrometry (AAS) [9], inductively coupled plasma-atomic/optical emission spectroscopy (ICP-AES/ ICP-OES) [10], and inductive coupled plasma mass spectrometry (ICP-MS) [11]. However, these methods are environmental unfriendly, expensive, not available in all forensic science laboratories, and require well-trained operators [3].

Laser-induced breakdown spectroscopy (LIBS), also called laser-induced plasma or laser spark spectroscopy [12], is an emerging analytical technique first reported in 1962 by Brech and Cross [13]. LIBS can obtain soil fingerprint which involve plentiful information of soil element contents and soil texture [14]. This feature makes the LIBS technique more reliable for soil

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| I adde I | | | | | |
|---------------|------------------|------|---------|------|--------|
| Details of th | e representative | soil | samples | used | herein |

| Soil type ID | Number | Soil type | Location | Coordinates |
|--------------|--------|------------------|--|------------------------------------|
| SHD | 20 | Fluvo-aquic soil | Yucheng county, Shandong province | 116°22′-116°45′ E, 36°40′-37°12′ N |
| JS | 20 | Paddy soil | Suzhou/Wuxi/Zhenjiang, Jiangsu province | 119°22'-121°00' E, 30°54'-32°01' N |
| JX | 20 | Red soil | Dongxiang county/Yanshan county, Jiangxi province | 116°20'-118°00' E, 27°48'-28°30' N |
| HLJ | 20 | Black soil | Hailun county/Bei'an county, Heilongjiang province | 126°14′-127°53′ E, 46°58′-48°33′ N |
| NM | 20 | Chestnut soil | Bayannur, Inner Mongolia | 107°23'-108°46' E, 40°43'-41°11' N |

identification than conventional physicochemical analysis. In addition, due to its small sample requirements and simple equipment, LIBS technique is suitable for forensic soil analysis in the extreme conditions with small quantities of samples. Some researchers have used LIBS for forensic soil analysis because of its rapid, real-time, on-site, and non-destructive analysis, without the need for sample preparation. For example, Jantzi and Almirall successfully discriminated soil samples from two sites in Dade Country, Florida with a corrected classification rate of 99.4 % using liner discriminant analysis with leave-one-outvalidation [4]. Jantzi and Almirall indicated that the soils from Miami-Dade County could be discriminated with clear groupings and correct classification rates of > 94 % [15].

Fourier transform infrared-attenuated reflectance spectroscopy (FTIR-ATR) is a commonly used technique for forensic soil examination. Cox et al. proposed that the FTIR spectra of the organic portions of soil is served a useful purpose in for forensic investigations [16]. Woods et al. indicated that FTIR-ATR could be effectively used as a screening test for discrimination of forensic-sized soil samples prior to submission for more detailed analyses by a

soil expert [17]. Different from LIBS technique, soil FTIR-ATR spectra carry the structure information of soil, including structure of minerals and organic matters [16]. Thus, we hypothesize that the combination of LIBS and FTIR-ATR techniques could simultaneously obtain the soil element compositions and soil structures, which could greatly improve the reliability of soil identification. However, there are few reports on the application of LIBS as well as the combination of LIBS and FTIR-ATR for real life forensics analysis.

In this context, this study characterized and identified the soil samples collected from different geographical areas of China using LIBS and FTIR-ATR spectra. The soil identification capabilities of LIBS and FTIR-ATR spectra were investigated and compared by applying principal component analysis (PCA). Furthermore, LIBS and FTIR-ATR were used for analyzing soils in two criminal cases to evaluate their potential application. The specific objectives of this study were: (i) to evaluate and compare the soil identification capabilities of LIBS and FTIR-ATR; (ii) to investigate the principles of soil identification by LIBS and FTIR-ATR spectra; and (iii) to evaluate the performance of these methods for forensic soil identification in practical cases.



Fig. 1. Parameter optimization in the MPLS baseline correction algorithm for the LIBS spectra. (a) RMSE of the baseline corrected LIBS spectra with different $\log(\lambda)$ values and window sizes; (b) MPL of the baseline corrected LIBS spectra with different $\log(\lambda)$ values and window sizes; (c) baseline corrected LIBS spectra at 600 to 700 nm under different $\log(\lambda)$ values and window sizes; (d) relative BCEC of the baseline corrected LIBS spectra with different $\log(\lambda)$ values and window sizes.

Table 1

2. Materials and methods

2.1. Soil sampling and preparation

The 100 soil samples used for the current study were collected from five major region of China including Shandong, Jiangsu, Jiangsu, Heilongjiang, and Inner Mongolia. All collected soil samples with their sample type ID and location descriptions are listed in Table 1. Before spectral analysis, the soil samples were airdried at room temperature (25 ± 1 °C) and subsequently sieved to < 2 mm. No attempt was made to remove any components in soil. The soil tablets for LIBS measurement were pelletized using an applied pressure of ~ 55 MPa for 1 min using a tablet machine (YP-2, China). The soil samples in criminal cases are further described in Section 3.4.

2.2. Instruments and spectra acquisition

The LIBS spectra were obtained using a MobiLIBS system (IVEA, France) controlled by AnaLIBS control software. The laser beam was generated using a fourth-harmonic Nd:YAG laser

(Quantel, France) at 532 nm with a 5 ns pulse duration. The frequency of the laser was 20 Hz and the delivery energy was 16 mJ. A lens with a 15 cm focal length was used to focus the laser output onto the surface of the pelleted sample with a spot diameter of 50 µm. The emission line of the resulting plasma was transmitted from the light collector to a Mechelle 5000 Echelle spectrometer (Andor Technology Ltd., Northern Ireland) at a resolving power of $\lambda / \Delta \lambda$ = 4000. An intensified charge-coupled device (ICCD) camera (iStar, Andor Technology, Ltd., Northern Ireland) collected the diffracted light. The delay time and gate width were controllable and were adjusted to 370 µs and 7.0 ms, respectively. For each soil sample, 5×5 matrix shot sites on the sample surface were used with three-layer shots at each site. Thus, a total of 75 LIBS spectra were obtained for each soil sample. The FTIR-ATR spectra of the sieved soil samples were acquired in the mid-infrared range (4000-650 cm^{-1}) at a 2.87 cm^{-1} resolution using an attenuated total reflectance infrared spectrophotometer (TruDefender FT, Thermo Scientific, USA). Prior to each soil sample measurement, the FTIR-ATR crystal was cleaned and a background spectrum was obtained for subsequent baseline correction



Fig. 2. The LIBS spectra and heat-map plot of 100 representative soil samples from 200–400 nm (a), 400–600 nm (b), and 600–1000 nm (c). SHD, soil samples from Shandong; JS, soil samples from Jiangsu; JX, soil samples from Heilongjiang; NM, soil samples from Inner Mongolia.

2.3. Statistical analysis

Prior to the investigation of LIBS spectra, the raw LIBS spectra were baseline corrected using the morphological weighted penalized least squares (MPLS) algorithm. The MPLS algorithm requires neither prior knowledge regarding the background nor an iteration procedure or manual selection of a suitable local minimum. The theories and principles of the MPLS algorithm were described in detail by Li et al. [18]. In MPLS, the adjustable parameters of λ and window size are the main factors affecting the baseline correction effectiveness. To optimize the parameters, the root mean square error (RMSE) and maximum peak height (MPH) of baseline corrected spectra were used:

$$RMSE = \sqrt{\frac{1}{N} \sum_{i=1}^{N} (y_i - z_i)}, \qquad (1)$$

$$MPH = \max(y_i - z_i), \tag{2}$$

where y_i and z_i are the *i*th variables of the raw spectrum and estimated baseline, respectively; *N* is the variable number of the spectrum. The optimal baseline corrected spectra should exhibit a

Table 2

Selected emission lines with high LIBS intensity variations.

low RMSE and high MPH values. Thus, we defined a relative baseline correction evaluation coefficient (BCEC) according to the RMSE and MPH values. A high BCEC value indicates optimal efficiency of the baseline correction.

$$BCEC_{ij} = \frac{MPH_{ij} - \min(MPH)}{|\max(MPH) - \min(MPH)|} - \frac{RMSE_{ij} - \min(RMSE)}{|\max(RMSE) - \min(RMSE)|}.$$
(3)

After baseline correction, the LIBS and FTIR-ATR were smoothed using the Savitzky-Golay filter [19] and subsequently averaged and normalized.

PCA is an extensively used multivariate statistical technique in chemometrics and represents a powerful tool for data dimensionality reduction [20]. PCA orthogonally transforms a set of observations of possibly correlated variables into a set of values of linearly uncorrelated variables called principal components (PCs), where the number of PCs is less than or equal to the number of original variables. After the reduction of variables in the data set, PCA allows for the identification and observation of variation sources [21]. Herein, PCA was applied to reduce the dimensionality of the spectra and provided intuitionistic classification results of soil according to the scatterplots of the first PCs. The spectral

| Element | Wavelength (nm) | Sorting by LIBS intensity |
|---------|---|--|
| Si I | 251.4 and 288.2 | $JX > JS \approx HLJ > SHD > NM$ |
| Mg I | 517.3 and 518.4 | $SHD \approx NM > HLJ \approx JS > JX$ |
| Mg II | 279.3 and 280.0 | SHD \approx JS \approx HLJ > NM > JX |
| Al I | 309.2 | $JX > JS \approx HLJ > SHD > NM$ |
| Ca I | 422.5, 429.8, 445.4, 526.4, 558.8, 615.6, 645.1, 714.8, and 720.2 | SHD \approx NM > HLJ > JS > JX |
| Ca II | 315.7, 317.7, 393.0, 396.5, 732.3, 854.2, and 866.2 | SHD \approx NM > HLJ > JS > JX |
| Ca III | 642.5 and 648.3 | SHD \approx NM > HLJ > JS > JX |
| NI | 818.25, 819.3, 821.7 and 824.3 | $SHD \approx NM \approx JS > HLJ > JX$ |
| 0 I | 777.1 and 844.6 | $JX > JS > HLJ \approx SHD > NM$ |
| O II | 655.6 | $JX > JS > HLJ \approx SHD > NM$ |
| K I | 766.3 and 769.8 | JX > JS > HLJ > SHD > NM |

SHD, soil samples from Shandong; JS, soil samples from Jiangsu; JX, soil samples from Jiangxi; HLJ, soil samples from Heilongjiang; NM, soil samples from Inner Mongolia.



Fig. 3. The FTIR-ATR spectra and heat-map plot of 100 representative soil samples from 4000–650 cm⁻¹. SHD, soil samples from Shandong; JS, soil samples from Jiangsu; JX, soil samples from Heilongjiang; NM, soil samples from Inner Mongolia.

pre-processing, PCA, and statistical analyses were implemented in MATLAB R2016a (The Math Works, Natick, USA).

3. Results and discussion

3.1. Baseline correction

Fig. 1 shows the parameter optimization results (λ and window size) in the MPLS baseline correction algorithm. It is clear that the RMSE values were affected by λ value and were relatively low when at $\lambda = 10^{0}$ to 10^{3} . Both the RMSE and MPH values were quite low at low log(λ) values, resulting in a loss of several informational peaks. In contrast, the RMSE values increased with increasing λ , resulting in overcorrection of the LIBS spectra. In Fig. 1c, the corrected LIBS spectrum showed a peak loss (blue line) at a low λ

Table 3

Selected spectrum bands with high FTIR-ATR intensity variations.

and presented an overcorrection (green line) at a high λ and low window size. Thus, the relative BCEC was applied for parameter optimization. The highest BCEC value was obtained at log(λ) of 3 and window size of 30. Thus, the λ value and window size in the MPLS baseline correction algorithm were set as 10^3 and 30, respectively.

3.2. Features of soil spectra

3.2.1. LIBS spectra

Fig. 2 shows the LIBS spectra and heat-map plot with respect to different types of soils where the C I emission line was observed at 247.8 nm [22]. The signals at 343.7, 498.2, 498.9, 499.9, 500.6, 501.6, 503.0, and 633.1 nm were attributed to the N II emission line [23], and the signals at 742.3, 744.2, 746.8, 818.25, 819.3, 821.7, and

| Vibrations | Wavenumber (cm ⁻¹) | Components | Sorting by FTIR-ATR intensity |
|------------------------------|--------------------------------|--|--|
| Clay O—H stretching | ~ 3620 | Clay mineral | JX > SHD > HLJ > NM > JS |
| O—H/N—H stretching | 3200-3500 | Carboxyl, alcohols and phenols/amine and amide, hydroxyl groups | HLJ > SHD > JX > NM > JS |
| C=C/C=O stretching | ~ 1630 | Amides, COO ⁻ /aromatics/O–H stretching | $JS \approx HLJ > SHD > JX > NM$ |
| CO_3^{2-} | ~ 1440 | Carbonates | $NM > SHD > JS > JX \approx HLJ$ |
| Si—O stretching | ~ 1000 | Silicates | $JX > SHD \approx NM > JS \approx HLJ$ |
| NH ₂ out of plane | ~ 780 | Primary amine | $JX > JS > SHD \approx NM > HLJ$ |

SHD, soil samples from Shandong; JS, soil samples from Jiangsu; JX, soil samples from Jiangxi; HLJ, soil samples from Heilongjiang; NM, soil samples from Inner Mongolia.



Fig. 4. Principal component score distributions (a, b, and c) and principal component loading plots (d, e, and f) of the first three principal components from the LIBS spectra of 100 representative soil samples. SHD, soil samples from Shandong; JS, soil samples from Jiangsu; JX, soil samples from Heilongjiang; NM, soil samples from Inner Mongolia.

824.3 nm were attributed to the N I emission line [23-25]. The O I emission lines were observed at 777.1 and 844.6 nm, whereas the O II emission line was observed at 655.6 nm and the O III emission line at 794.6 nm [26]. The strong emission lines at 766.3 and 769.8 nm corresponded to the K I emission [27,28]. Abundant Ca emission lines were observed as Ca I emission lines at 422.5, 429.8, 445.4, 526.4, 558.8, 615.6, 645.1, 714.8, and 720.2 nm; Ca II emission lines at 315.7. 317.7. 373.5. 393.0. 396.5. 732.3. 854.2. and 866.2 nm: and Ca III emission lines at 642.5 and 648.3 nm [29–32]. The signals at 279.3 and 280.0 nm were attributed to the Mg II emission lines and those at 382.9, 383.5, 517.3, and 518.4 nm arose from Mg I emission [27,32-36]. An Al I emission line was observed at 309.2 nm [27,32]. Two Si I emission lines were observed at 251.4 and 288.2 nm [27,30,34,37,38], and many Fe I and II emission lines were observed at 460.6 and 487.7 nm as well as at 237.1, 259.7, 262.8, 274.4, 323.2, 534.7, and 669.9 nm. From the heat-map, the wavelengths with high LIBS intensity variation were selected and are summarized in Table 2. High LIBS intensity variations were observed in the emission lines of Si, Mg, Al, Ca, N, O, and K, indicating the high variation of these elements in different soils.

3.2.2. FTIR-ATR spectra

The FTIR-ATR spectra of the soils and a representative heat-map plot are shown in Fig. 3. Two CO_3^{2-} stretching bands from carbonates were observed at $\sim 1440 \text{ cm}^{-1}$ [39–41], and the peak at $\sim 925 \text{ cm}^{-1}$ was associated with the Al–OH stretching of kaolinite

and smectite in soil [39,42]. The large band at ~ 1000 cm⁻¹ originated from the Si–O stretching from quartz [43] and that at ~ 1630 cm⁻¹ was attributed to the vibrations of amides (C=O) [39,44,45] and aromatics (C=C) [46,47] in organic compounds. The broad band spanning 3500–3200 cm⁻¹ was assigned to O–H vibration from water, alcohols, carboxylic acids, phenols, and N–H vibration from amides [48,49]. The peak at 3620 cm⁻¹ originated from the stretching vibration of O–H in the clay minerals [43]. Significant variations of FTIR-ATR intensity were observed at the clay O–H stretching band (~ 3620 cm⁻¹), O–H/N–H (3200–3500 cm⁻¹), C=C/C=O (~ 1630 cm⁻¹), Si–O (~ 1000 cm⁻¹), CO₃^{2–} (~ 1440 cm⁻¹), and NH₂ out of plane (~ 780 cm⁻¹; Table 3). These results suggested that the silicates, carbonates, and organic matter varied significantly between soil types.

3.3. Identification of soils by PCA

Although both the LIBS and FTIR-ATR spectra showed large intensity variations at some wavelengths and wavenumbers for different soil types, it was difficult to directly distinguish the soil type according to spectral intensity difference. To intuitively differentiate the soil type, PCA analysis was performed on the full LIBS and FTIR-ATR spectra.

The explained variances of the first (PC1), second (PC2), and third (PC3) principal components from the LIBS spectra were 69.54 %, 12.31 % and, 6.80 %, respectively, and the total explained



Fig. 5. Principal component score distributions (a, b, and c) and principal component loading plots (d, e, and f) of the first three principal components from the FTIR-ATR spectra of 100 representative soil samples. SHD, soil samples from Shandong; JS, soil samples from Jiangsu; JX, soil samples from Heilongjiang; NM, soil samples from Inner Mongolia.



Fig. 6. Principal component score distributions from the LIBS (a) and FTIR-ATR (b) spectra of the soil samples in case 1. C1-1, soil samples on the riverbank; C1-2, soil samples on the victim's shoes.

variance was 88.65 % (Appendix S1, Fig. S1a). PC1, PC2, and PC3 could be used to distinguish the soil type via scatterplots (Fig. 4a-c). Surprisingly, the five soil types were accurately divided into five groups according to the PC1-PC2 scatterplot (Fig. 4a). Among these groups, the JS soil group showed a small boundary distance with the HLJ soil group, indicating a low capacity of PC1 and PC2 from the LIBS spectra to distinguish JS and HLJ soils. The PC1–PC3 scatterplot also showed an obvious partition of the five soil types, except for two NM soil samples (Fig. 4b). However, the soils were hardly differentiated according to the scatterplot of PC2 -PC3 (Fig. 4c). These results indicated that PC1 and PC2 from the LIBS spectra played a vital role in distinguishing soil types. To better understand variable interpretability, the PC loading of the LIBS spectra is presented in Fig. 4d-f. High absolute value of PC1 loading from the LIBS spectra was observed at the wavelengths corresponding to the emission lines of Si, Mg, Al, Ca, K, O, and N (Fig. 4d), consistent with the variations of LIBS intensity for the different soil types. High absolute values of PC2 and PC3 loadings were also observed at the Fe, Si, Mg, Al, Ca, K, O, and N emission lines. In addition, negative values for PC1 loading were observed at the Ca emission lines, whereas positive values for PC1 loading were observed at the Si, K, and O emission line wavelengths. This suggested that more Ca but less Si, K, and O were present in NM and SHD soils compared to HLJ, JS, and JX soils, in agreement with the results presented in Table 2. The variation of Si, Mg, Al, Ca, K, O, and N in soil was reflected by the intensity difference of their characteristic LIBS lines and was a significant indicator of soil identification in PCA.

For the FTIR-ATR spectra, the explained variances of first three PCs accounted for 48.1 %, 21.8 %, and 12.1 % of the total variance, respectively (Fig. S1b). Fig. 5a-c shows the scatterplots of the first three principal components (PC1-PC3) from the FTIR-ATR spectra that were used to identify soil type. The IX and HLI soils were well distinguished from SHD. IS. and NM soils by PC1. The SHD. IS. and NM soils were easily distinguished by the scatterplot of PC1-PC2 (Fig. 5a). Although the JX and HLJ soils were hardly differentiated according to the PC1-PC2 scatterplot, they were clearly differentiated by the PC1-PC3 scatterplot (Fig. 5a and b). Only the JS soil was obviously distinguished from the other by the PC2-PC3 scatterplot (Fig. 5c). These results highlight the significance of PC1, PC2, and PC3 from the LIBS spectra for distinguishing soil types and the first three PC loadings are shown in Fig. 5d-f. As expected, high absolute values of PC1, PC2, and PC3 loadings were observed at the wavenumbers of the clay O—H (\sim 3620 cm^{-1}), O—H/N—H (3200– 3500 cm⁻¹), C=C/C=O (\sim 1630 cm⁻¹), and Si–O (\sim 1000 cm⁻¹) vibrations as well as those of $\text{CO}_3{}^{2-}\,(\sim1440~\text{cm}^{-1}),\,\text{Al}-\text{OH}\,(\sim925$ cm⁻¹), and NH₂ (\sim 780 cm⁻¹). The positive value observed at the wavenumber (\sim 1440 cm⁻¹) of the CO₃²⁻ vibration and the negative value observed at the of Si-O vibration ($\sim 1000 \text{ cm}^{-1}$) for PC1 loadings indicated that more carbonates and fewer silicates were present in NM, SHD, and JS soils compared to JX and HLJ soils. Therefore, the identification ability of FTIR-ATR spectra for different soil types was related to soil minerals, including carbonates and silicates.

Although individual LIBS or FTIR-ATR spectra showed good distinguishing capability for some soil types, it remained difficult to distinguish JS and HLJ soils by individual LIBS spectra and JX and HLJ soils by individual FTIR-ATR spectra. Thus, combination of LIBS and FTIR-ATR spectra for distinguishing different soil types is recommended. Combining the results of PC loading from the LIBS and FTIR-ATR spectra as well as spectral analysis, it was concluded that the NM and SHD soils contain abundant calcium carbonate and little organic matter, whereas the HLJ soil has abundant organic matter and little calcium carbonate. The JX soil contains a significant amount of silicate, and the variations of the mineral and organic matter contents in different soil types are crucial indicators for soil identification. Understanding these variations is of great significance for distinguishing and identifying soils in forensic trace evidence.

3.4. Case studies

Section 3.3 indicated the usefulness of LIBS and FTIR-ATR spectra for soil identification in forensic trace evidence. In the following sections, LIBS and FTIR-ATR techniques were applied to two practical criminal cases to support their practical feasibility.

3.4.1. Case 1

In mid-summer, the body of a female was found at the bottom the Jurong River near Hushu Sub-District in Jiangning District, Nanjing. Autopsy results indicated the victim was approximately 9 years old and 135 cm tall, but uncovered no direct evidence indicating whether the victim had fallen and drowned or had been murdered. Thus, soil samples were collected from riverbank (C1-1), river bottom (C1-2), and the sole of the victim's shoes

| Table 4 | | | | | | | |
|--------------|--------|--------|---------|----|------|----|--|
| Descriptions | of the | e soil | samples | in | case | 2. | |

| Sample ID | Soil number | Location description |
|-----------|-------------|--|
| В | 4 | Next to the body of the boy victim |
| G | 3 | Next to the body of the girl victim |
| SLS | 20 | On the suspect's left shoe |
| SRS | 8 | On the suspect's right shoe |
| SS | 4 | On the bottom of shallow area of the river |
| SD | 4 | On the bottom of deep area of the river |



Fig. 7. Principal component score distributions from the LIBS (a) and FTIR-ATR (b) spectra of the soil samples in case 2. B, soil samples next to the boy's body; G, soil samples next to the girl's body; SLS, soil samples on the suspect's left shoe; SRS, soil samples on the suspect's right shoe; SS, soil samples on the bottom of shallow area of the river; SD, soil samples on the bottom of deep area of the river.

(C1-3), and sent to the laboratory for LIBS and FTIR-ATR analysis. Prior to spectral analysis, the soil samples were air-dried at room temperature (25 ± 1 °C) and sieved to < 2 mm. No attempt was made to remove any components in soil sample. Each soil sample was measured in quintuplicate for the LIBS spectra and quadruplicate for the FTIR-ATR spectra.

The LIBS and FTIR-ATR spectra of the three soil samples are shown in Fig. S2. PCA analysis was applied to the LIBS spectra from 200 to 1000 nm and to the FTIR-ATR spectra from 4000 to 650 cm⁻¹. The explained variances of PC1, PC2, and PC3 from LIBS spectra were 43.52 %, 18.27 %, and 8.30 %, respectively (Fig. S3), and the explained variances of PC1 and PC2 from the FTIR-ATR spectra were 47.89 % and 28.89 %, respectively. The scatterplots of the PC scores showed that the C1-1 soil sample could be clearly distinguished from the C1-2 and C1-3 soil samples using both LIBS and FTIR-ATR spectra (Fig. 6). However, C1-2 and C1-3 soil samples were distributed in the same group according to PC score scatterplots. That is, the C1-3 and C1-2 soils were highly homologous. The PC loadings showed that Si, Ca, Mg, K, O, and N in the soil could be used for identifying soil according to LIBS spectra, and the soil mineral and organic components played an important role in the FTIR-ATR spectra for identifying the soil source (Fig. S4). If the victim drowned, the soil on her shoes should be homologous to that on the riverbank. Instead, the soil in victim's sole likely originated from the bottom of the river than from the riverbank. Therefore, the victim may have been deliberately pushed into the river. The forensic trace evidence of the soil provides useful information for the determination of this case.

3.4.2. Case 2

The bodies of two children were found on the Beihe River in Dizhuang village, Peixian County, Jiangsu of a 6 year old boy and 3 year old girl who were both drowned. A young woman at the scene, wearing no shoes, claimed that she was trying to save the two children. Her shoes were found in the river afterwards. The young woman is the stepmother of the two children and was usually unfriendly to them, according to a survey. Before the accident, villagers witnessed the woman leaving the village with her two step-children. However, no witnesses or video records of the accident were recovered. To obtain direct evidence, the soil samples next to the bodies, from the woman's shoes, and from the river bottom were collected for spectral analysis. The specific descriptions of collected soil samples are shown in Table 4. Prior to spectral analysis, the soil samples were air-dried at room temperature (25 \pm 1 °C) and sieved to < 2 mm. No attempt was made to remove any components in soil sample. For the acquisition of the LIBS spectra, each sample was shot 25 times according to 5×5 matrices and the average spectra were obtained. For the acquisition of the FTIR-ATR spectra, each sample was measured four times to obtain the average spectra.

The LIBS and FTIR-ATR spectra of the different soil samples are shown in Fig. S5. The LIBS spectra from 200 to 1000 nm and FTIR-ATR spectra from 4000 to 650 cm^{-1} were used for PCA analysis. The variances change by the number of principal components, as shown in Fig. S6. The explained variances of PC1 and PC2 from the LIBS spectra were 60.12 % and 16.52 % respectively, and those from the FTIR-ATR spectra were 47.89% and 28.89%, respectively. Hence, the PC1–PC2 scatterplot was used for soil identification (Fig. 7). Both the PCA scatterplots of LIBS and FTIR-ATR spectra showed two clearly distinguished groups which could divide the soil samples into two sources. The left group from LIBS spectra contained the soil samples next to the bodies of the boy (B) and girl (G), and the soil samples from the river bottom (SD) and partial soil samples from the woman's left shoe (SLS) were also analyzed. The left group from FTIR-ATR spectra contained the soil samples B. G. SD. part of SLS, and the soil samples from the shallow river bottom (SS). Combining the PCA analysis of the LIBS and FTIR-ATR spectra, it was concluded that part of the soil sample from the woman's left shoe (SLS) was highly homologous to the soil samples next to the bodies. In other words, the young woman's shoes were exposed to the soil at the bottom of the river and the soil where the child drowned. If, as the woman claimed, she was saving the two children, she would have had no time to take her shoes off during the crisis. Even if she had taken her shoes off to save the two children, her shoes would not have contacted the soil next to the children's bodies. These claims were deduced from the forensic trace soil evidence obtained using LIBS and FTIR-ATR spectra, providing useful clues for the determination of this case.

4. Conclusions

This study investigated the availabilities and principles of soil identification in China for forensic trace evidence based on LIBS and FTIR-ATR spectra by PCA. The developed methodology for forensic soil examinations based on LIBS and FTIR-ATR spectra was applied to two criminal cases to evaluate forensic performance. The results suggested that five soil types could be clearly distinguished by LIBS and FTIR-ATR spectra. The elemental, mineral, and organic matter variations in the different soil types are crucial indicators for soil identification based on LIBS and FTIR-ATR in the two case studies provides an application example of soil analysis for forensic

investigations, indicating great potential for applying LIBS and FTIR-ATR spectra in the practice of forensic science.

CRediT authorship contribution statement

Xuebin Xu: Methodology, Formal analysis, Investigation, Writing - original draft. **Changwen Du:** Conceptualization, Funding acquisition, Project administration, Writing - review & editing, Supervision. **Fei Ma:** Writing - review & editing. **Yazhen Shen:** Writing - review & editing. **Jianmin Zhou:** Project administration.

Declaration of Competing Interest

None.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at https://doi.org/10.1016/j.forsciint.2020.110222.

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