Fire debris analysis for forensic fire investigation using laser induced breakdown spectroscopy☆

Soojin Choi, Jack J. Yoh *

Department of Mechanical and Aerospace Engineering, Seoul National University, 1 Gwanakro, Gwanakgu, Seoul 151-742, Republic of Korea

ABSTRACT

The possibility verification of the first attempt to apply LIBS to arson investigation was performed. LIBS has capabilities for real time in-situ analysis and depth profiling. It can provide valuable information about the fire debris that are complementary to the classification of original sample components and combustion residues. In this study, fire debris was analyzed to determine the ignition source and existence of a fire accelerant using LIBS spectra and depth profiling analysis. Fire debris chemical composition and carbon layer thickness determines the possible ignition source while the carbon layer thickness of combusted samples represents the degree of sample carbonization. When a sample is combusted with fire accelerants, a thicker carbon layer is formed because the burning rate is increased. Therefore, depth profiling can confirm the existence of combustion accelerants, which is evidence of arson. Also investigation of fire debris by depth profiling is still possible when a fire is extinguished with water from fire hose. Such data analysis and in-situ detection of forensic signals via the LIBS may assist fire investigation at crime scenes.

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1. Introduction

In 2016 over 43,000 fires were reported in South Korea. Of those, 986 were arson [1]. Fire damage is expected to increase with increasing property values and larger scale fires. Therefore, the importance of fire prevention and investigation is becoming more important. Fire investigators try to determine the point of origin, cause, and development of a fire or explosion. The ultimate goal of fire investigation is to establish measures for preventing future fires.

Fire investigation has three major steps. First, initial burning area is isolated by fire dynamics evaluation and burn pattern analysis. Then the initial burning area is analyzed to determine the ignition point of origin. During this step the potential ignition source, such as candle, cigarette, electrical source, etc., is also determined. The final step is analysis to determine the actual ignition source and cause of the fire. Fire caused by arson is also identified in this step.

Chemical analysis plays an important role in fire debris investigation. It can determine the fuel constituent and type of ignition source. Fire debris from the point of origin is analyzed to determine if a fire accelerant is present. Accelerant presence is the key factor for determining the fire cause as accident or arson. The applicability of the fuel used can be

estimated by analyzing fuel tank residues. Analyzing residue on electrical wires can establish arson disguised as a short circuit. Chemical analysis of fire debris provides information about fire causes that can be used to prevent future accidental fires and dissuade arson. Typically, five steps are required to analyze fire debris; preliminary debris examination, extracting ignitable liquid residues, analyzing the extract, interpreting results, and reporting [2]. The analysis methods for fire investigation have been reviewed [3,4].

Gas chromatography (GC) is the most widely used method for analyzing fire debris to discover evidence of a flammable liquid. Krüger et al. detected ignitable liquids in fire debris using gas chromatography–mass spectrometry (GC–MS) from real scale room fire experiments [5]. They considered the presence, position, and amount of fire accelerant. Nowlan et al. confirmed the applicability of the ignitable liquid absorbent (ILA) by full scale room fire experiments [6]. GC–MS results were compared to accelerant detection results using canines. Almirall et al. also performed GC–MS analysis to characterize the background and pyrolysis products after burning [7]. Vos et al. analyzed arson accelerants using gas chromatography coupled with ion trap mass spectrometry [8]. Ueta et al. suggested a needle extraction device to extract fire accelerants for GC analysis [9]. The fire accelerants were detected from uncombusted and combusted samples. Ugena et al. identified brands of fuels such as gasoline and diesel by GC [10]. This method has close to 100% accuracy by combining neutral network algorithms with GC. Sampat et al. analyzed neat white spirits for forensic application using GC based analytical methods [11]. Principal component analysis (PCA)

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 * Corresponding author.
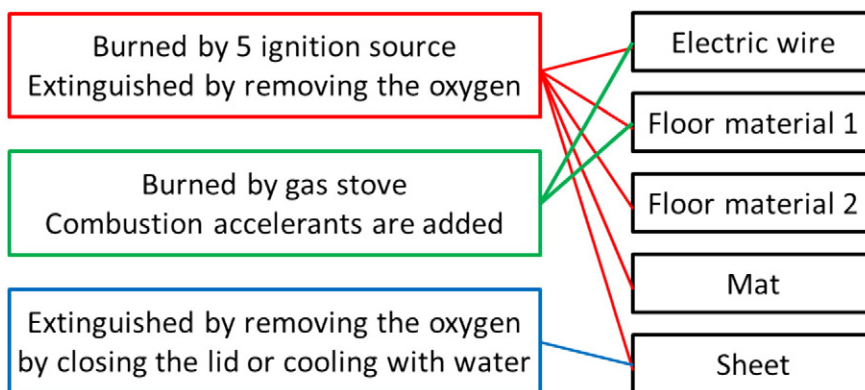 *E-mail address:* jjyoh@snu.ac.kr (J.J. Yoh).

Fig. 1. Experimental matrix.

was used for discrimination of sample brand and temporal variations of production. Visotin et al. detected ignitable liquids on different substrates to confirm the detection ability of a portable GC–MS system [12]. The portable system detected and classified ignitable liquid residues successfully. As part of fire investigation safety, semi/nonvolatile fire debris components were analzed by pressure ionization GC triple quadrupole mass spectrometry to discover firefighter exposure risks (Organtini et al. [13]).

A number of efforts are being made to apply other chemical analyses to fire investigation. Martin et al. employed LIBS for environmental and forensic applications [14]. They analyzed annual tree growth rings before and after the fire. Saitoh et al. identified various ignitable liquids on various background materials using fluorescence spectra [15]. The effect of the excitation wavelength on signal intensity was also studied. Chen et al. performed depth profiling analysis of electrical arc residues using secondary ion mass spectrometry (SIMS) [16]. Primary and secondary arc beads are identified by analyzing the carbon and chlorine signals. McCurdy et al. suggested vapor phase ultraviolet spectroscopy as a complementary method to GC arson accelerant analysis [17]. González et al. studied headspace mass spectrometry (HS-MS) as an alternative GC–MS analytical technique for fire debris analysis [18]. They suggested that HS-MS is a faster, safer, and more ecologically friendly method. Rodgers et al. identified arson accelerants using Fourier transform ion cyclotron resonance mass spectrometry [19]. This method also discriminated between unweathered and weathered arson accelerants. Rostad classified commercial fuels without sample preparation

using negative electrospray ionization/mass spectrometry [20]. This noted that minor components in refined fuels can be determined. Marshall et al. used ultrahigh resolution Fourier transform ion cyclotron resonance mass spectrometry to identify crude oils [21]. They suggested possible forensic applications to identify accelerants consisting of complex components.

The present study suggests a laser induced breakdown spectroscopy (LIBS) for fire investigation because it has capabilities for in-situ analysis and depth profiling. LIBS is an atomic emission spectroscopy that utilizes plasma. When a high power pulsed laser is focused on a sample surface, plasma is generated as the chemical bonds of the sample break. The emitted plasma signal contains information about electrons, ions, atoms, and molecules. Real time in-situ analysis at a fire scene is possible since LIBS analysis does not require sample extraction or preparation. Depth profiling using LIBS allows determining the degree of carbonization of combusted samples.

In this study, fire debris was analyzed to determine ignition source and accelerants existence using LIBS. Five selected materials were combusted using five ignition sources with and without fire accelerants. To compare the effect of fire extinguishing method, the fire is extinguished with two methods. By comparing LIBS spectra of original and combusted samples, the type of ignition source was determined. Depth profiling analysis was performed on combusted sample carbon and CN layers to determine the degree of sample carbonization. The depth profiling process also reveals whether or not flame was the ignition source. Also, the existence of fire accelerants can be determined for
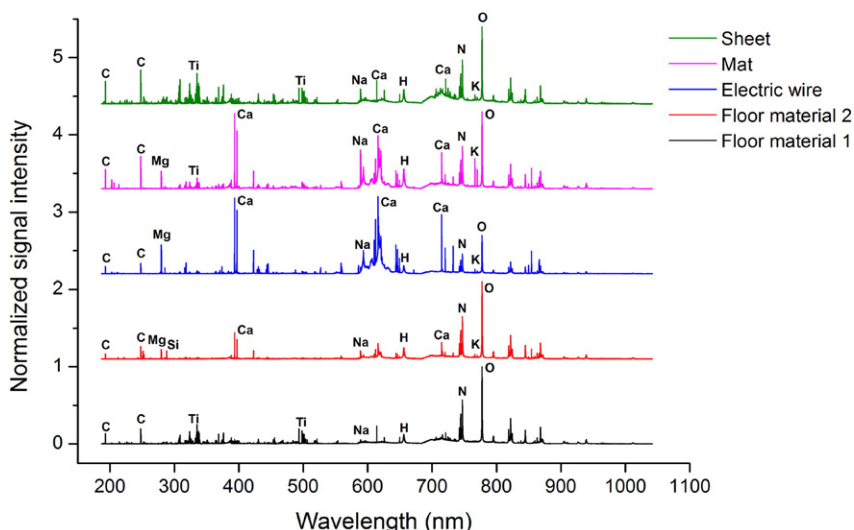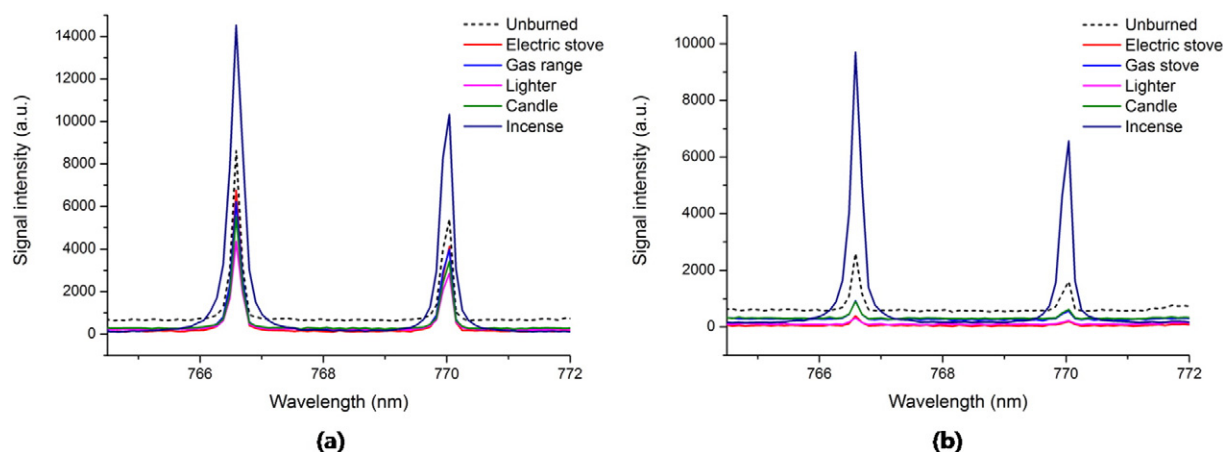

Fig. 2. LIBS spectra of original samples.

Fig. 3. Effect by ignition source on potassium signal (a) mat, (b) electric wire.

evidence of arson. The first attempt to investigate fire debris for arson investigation using LIBS successfully provided information about ignition source and fire accelerants.

2. Experimental setup

A commercial LIBS instrument (RT250-Ec, Applied Spectra Inc.) with Nd:YAG laser and 6 channel-CCD spectrometer was used to carry out the experiments. The Nd:YAG laser operated at 1064 nm, with a pulse energy of 21 mJ and pulse duration of 5–7 ns at 1 Hz repetition rate. 5 to 30 pulses were irradiated to the sample surface and this was repeated at 5 locations in each case. The spectrometer spectral range was 196 to 970 nm. A 0.5 μs time delay and 1.05 ms gate width were applied.

Electric wire, two types of floor materials, mats, and sheets were selected as samples. For sample burning, five types of ignition sources were used. Gas stove, disposable lighter, and candle were used as ignition sources relying on hydrocarbon fuels for combustion. An electric stove was used as a heat flux ignitor without burning hydrocarbons. Aroma incense was used for conduction combustion. All of the selected samples, ignition sources, and flammable liquids are widely used in everyday life.

We conducted three experiments (Fig. 1). First, to investigate the ignition source, five selected samples were combusted using five ignition sources. Second, electric wire and floor material 1 were combusted by gas stove using lighter oil and olive oil in order to determine the existence of accelerants. Third, fire was extinguished by removing oxygen by closing the lid or by dousing with water to compare the effect of fire extinguishing method. A stainless steel container was used for fire extinguishing.

3. Results and discussion

The original sample chemical components were analyzed before depth profiling to determine the degree of sample carbonization. Most samples consisted of carbon, hydrogen, nitrogen, and alkali elements; while some of the samples contained titanium and silicon (Fig. 2).

Fig. 3 shows the effect by ignition source on potassium signals of the mat and electric wire. The sample component signals after combustion are lower than original (unburned) sample because the sample component evaporated during the combustion process. The exceptionally high intensity of the potassium signal in the incense spectra was caused by adsorption of the potassium from the incense. Therefore, it is possible to estimate that the ignition source contains high potassium concentration. This means that combustion by hydrocarbon fuel such as a gas stove, disposable lighter, and candle can be excluded.

Fig. 4 shows the carbon signal of floor material 1 and electric wire by various ignition sources. Carbon is a major component of the original samples and hydrocarbon fuels. In case of electric wire, as shown in Fig. 4(b), the hydrocarbon content in the fuel is responsible for debris containing carbon, while a LIBS signal from the electric stove has a very low carbon level. However, a sample combusted by electric stove can also emit a carbon signal (Fig. 4(a)) since all of the samples contain carbon. Therefore, LIBS raw data alone may be inaccurate for determining the ignition source.
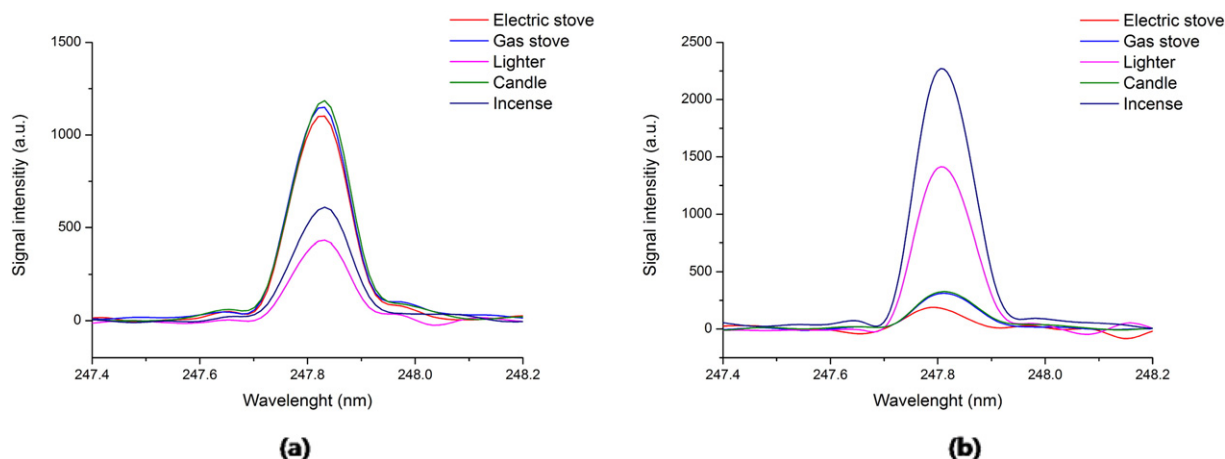

Fig. 4. Effect by ignition source on carbon signal (a) floor material 1, (b) electric wire.
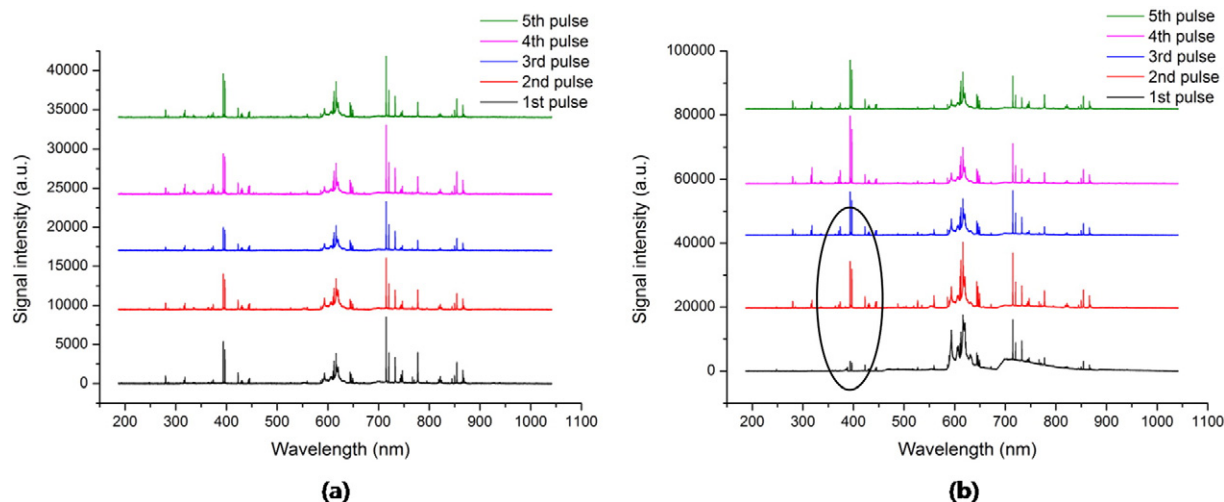
Fig. 5. Pulse-to-pulse variation of combusted electric wire by (a) electric stove, (b) gas stove.

Depth profiling analysis was performed to improve the accuracy of determining the ignition source. In a general case of combustion, original sample component remains inside the combusted sample because the heat and oxygen are not enough to completely burn the sample. Therefore, sample's surface and interior have difference in chemical compositions. This involves the ignition source, burning velocity, and degree of carbonization. As shown in Fig. 5(a), combustion by heat flux (e.g. electric stove) does not create a carbon layer, so original sample chemical composition is detected on the debris surface as well as inside the debris. On the other hand, a sample surface combusted by flame (e.g. gas stove) is covered by a carbon layer, so the component of original sample appears several pulses later. These results show the possibility of estimating ignition source by depth profiling analysis.

To identify the ignition source, carbon signal pulse-to-pulse variation was analyzed (Fig. 6). The signal intensities were determined by peak intensity after background subtraction using Origin program after user defined baseline creation process. The carbon signal from combustion flame (gas stove, disposable lighter, and candle) decreases in the second pulse due to the carbon layer formation while the signal from the electric stove is not significantly changed. If there is large carbon intensity drop in the first pulse, the component of ignition source can be adsorbed at the sample surface during combustion (e.g. incense). Fire debris from heat flux, flame, and conduction have different depth compositions.

In contrast, original sample compositions such as calcium by the flame have the smallest intensity in the first pulse because the carbon layer generated by the combustion covers the debris surface (Fig. 7).
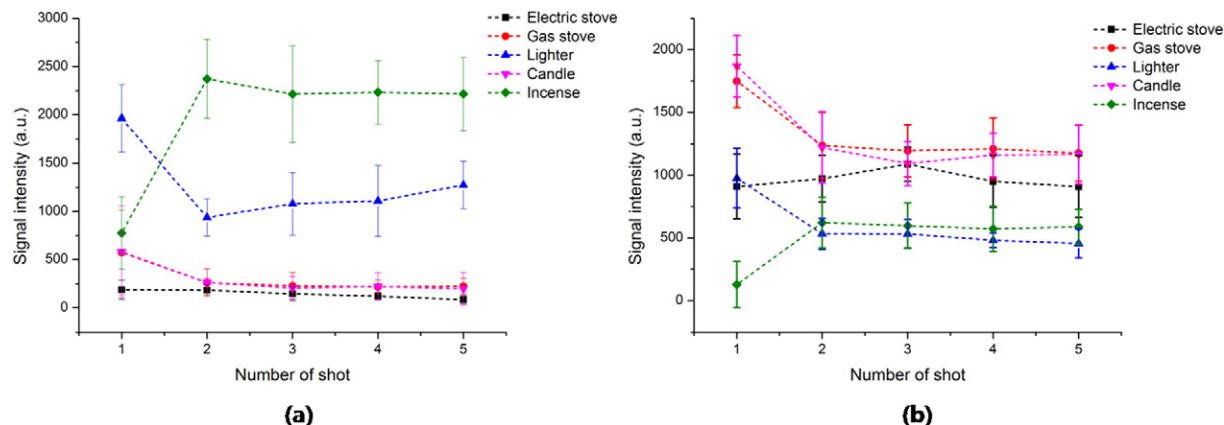
On the other hand, the signal from the electric stove is not significantly changed like the carbon signal in Fig.6. These results mean that the fire debris surface signal provides the information needed to determine the ignition source chemical composition.

Fig. 8 shows the LIBS pulse-to-pulse spectra of the combusted original floor material 1 with and without combustion accelerants. Extensive burn damage on a surface could indicate that a flammable liquid was poured and ignited. In the case of the combusted sample without accelerant, a thin carbon layer is generated. Then the original sample component clearly appears in the second laser pulse. When olive oil is added to the combustion, a weak original sample signal appears from the fifth laser pulse since a thicker carbon layer is formed. Moreover, combustion with a lighter oil (similar to kerosene) causes a thicker carbon layer that represents the high degree of sample carbonization. This suggests that the burning rate is increased by the temperature increase. In this case, the original sample components are partially detected several pulses later.

Fig. 9 shows the signal intensities that normalized to maximum intensity of each laser pulse. As shown in Fig. 9(a), carbon layer from lighter oil lasts for ten pulses whereas the original and olive oil samples formed a thin carbon layer. Additionally, the original sample component from lighter oil appears strongly after 20 pulses (Fig. 9(b)). Depth profiling can confirm the existence of a combustion accelerant that is evidence of arson.

The effect of the fire extinguishing method was studied by; i) removing the oxygen by closing the container lid, and ii) removing the heat with water. The samples extinguished using water were allowed to air
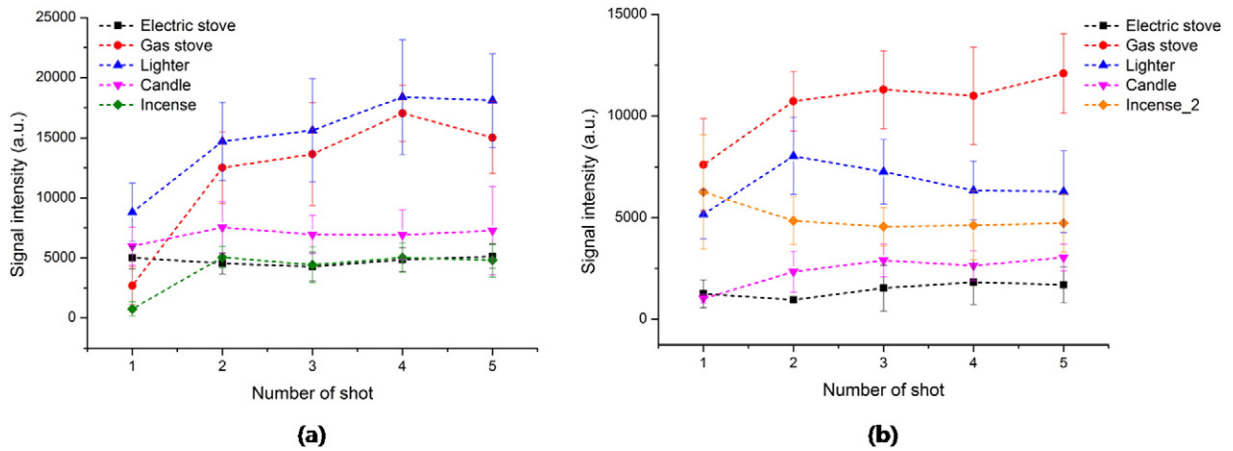

Fig. 6. Pulse-to-pulse variation of carbon (a) electric wire, (b) floor material 1.

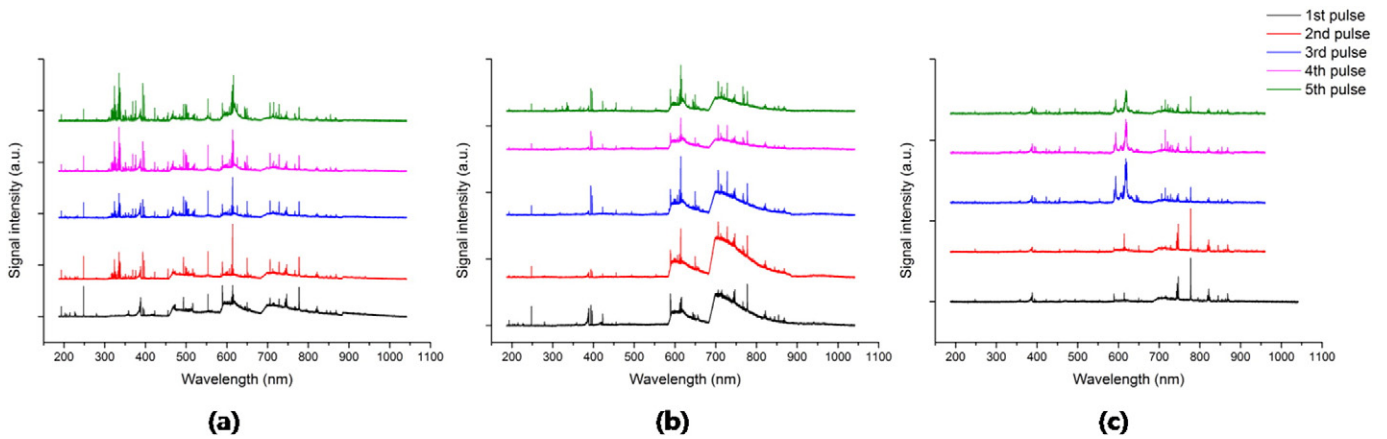**Fig. 7.** Pulse-to-pulse variation of calcium (a) electric wire, (b) floor material 1.

Fig. 8. Pulse-to-pulse LIBS spectra of combusted floor material 1 (a) without combustion accelerants, (b) with olive oil, (c) with lighter oil.

dry for 6 h. As shown in Fig. 10, extinguishing a fire using water causes a decrease of alkali elements (Na, Ca, K) due to its water soluble characteristics. However the sample surface carbon layer still remains when the fire extinguished using water (Fig. 11). Therefore, fire debris investigation by depth profiling is possible, regardless of the fire extinguishing method.

4. Conclusion

Fire debris residues were analyzed to determine the ignition source and presence of accelerants using LIBS. By the proposed depth profiling method, estimating the ignition source is possible. Combustion by lighter oil (similar to kerosene) causes a thicker carbon layer, due to the
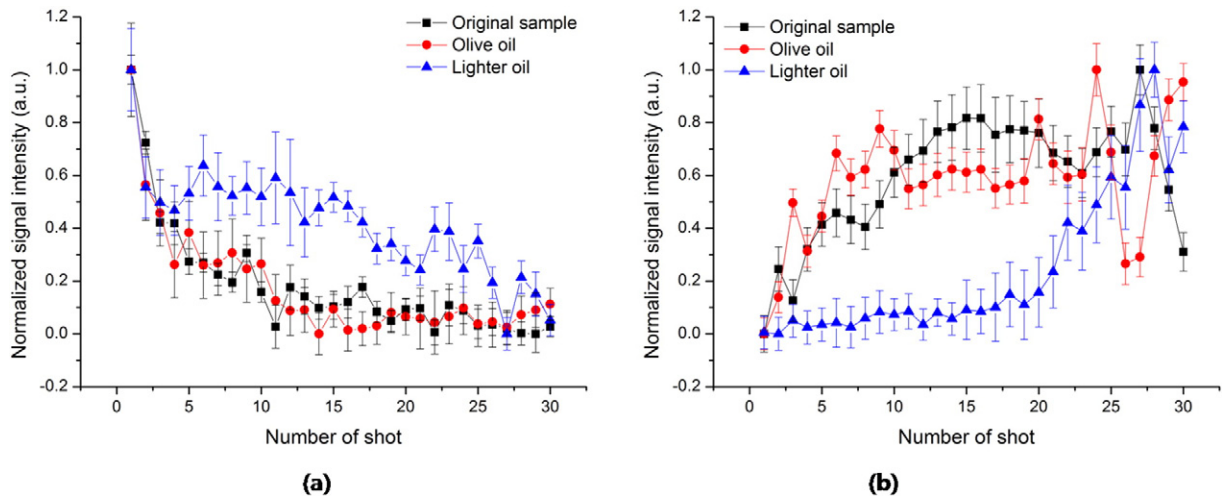

Fig. 9. Effect of combustion accelerant of floor material 1 (a) carbon, (b) calcium.
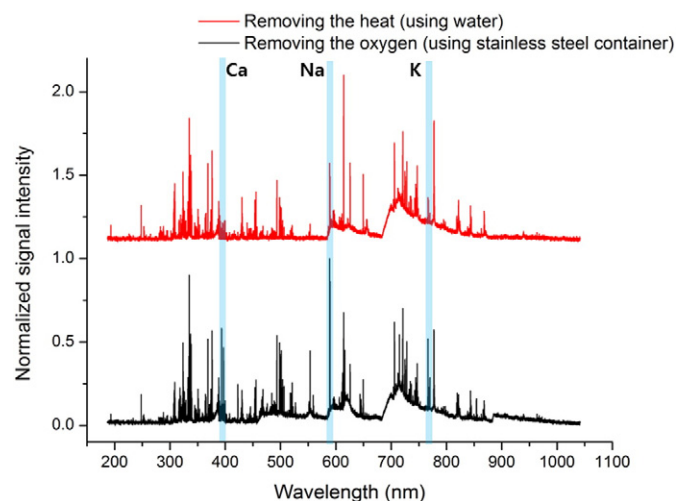
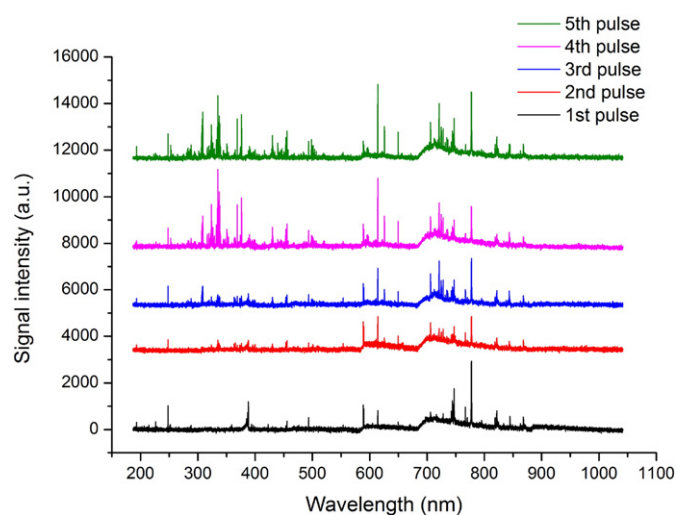Fig. 10. Effect of fire extinguishing method (sheet, 5th pulses).

Fig. 11. Effect of fire extinguishing method (sheet).

extensive burn damage on a surface. Depth profiling can confirm the existence of combustion accelerant, suggesting when arson is the cause of the fire. When a fire is extinguished with fire hose, investigation of fire debris by depth profiling is still possible. LIBS analysis cannot fully replace usual analytical methods such as gas chromatography, but LIBS data analysis and in-situ forensic signal detection may assist fire investigation at crime scenes.

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