

# Fire debris analysis for forensic fire investigation using laser induced breakdown spectroscopy (LIBS)☆☆☆



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## 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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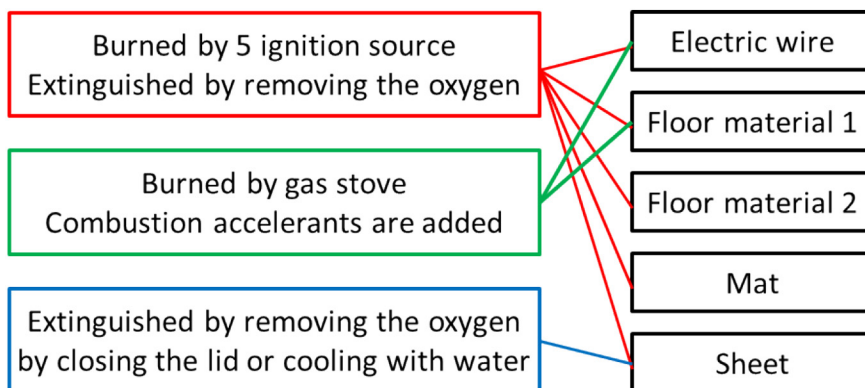


Fig. 1. Experimental matrix.

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 analyzed 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

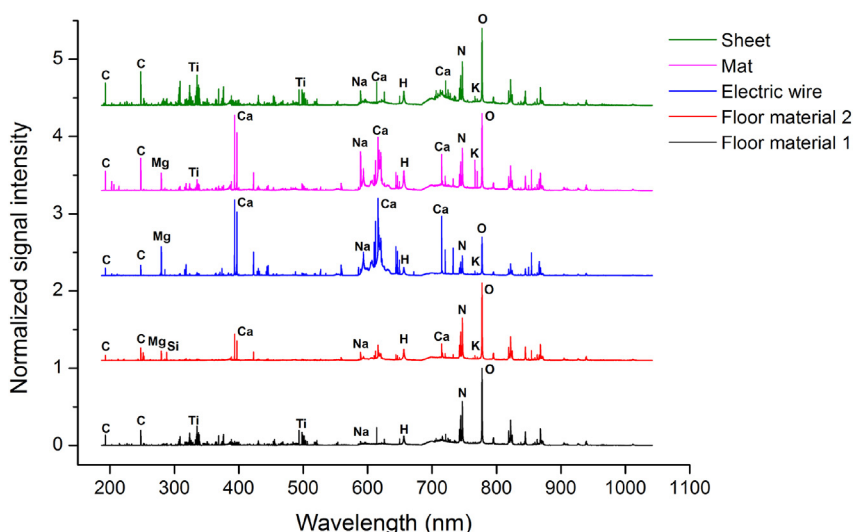


Fig. 2. LIBS spectra of original samples.

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