

Rapid identification of CCA-treated wood using laser-induced breakdown spectroscopy

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Abstract As chromated copper arsenate (CCA) contains copper, chromium and arsenic, waste CCA-treated wood must be separated from other treated wood because of environmental pollution by chromium and arsenic when it is incinerated and the regulation. Therefore, a method to identify CCA-treated wood was developed using laser-induced breakdown spectroscopy (LIBS). Using the LIBS apparatus assembled in our laboratory, plasma on a wood surface was generated by a 4 ns pulse of 1064 nm (55 mJ/mm²) emitted from Nd:YAG laser. Fluorescence from the plasma was collected by an ellipsoidal mirror and analyzed by a spectrometer in the range of 190–300 nm. The results showed that the 228.7 nm line from As and 267.6 nm line from Cr were useful for the identification of CCA-treated wood. As the discrimination capacity was confirmed by the elemental composition analysis by X-ray fluorescence, it was concluded that LIBS can specifically identify CCA-treated wood.

Keywords CCA · CCA-treated wood · Laser-induced breakdown spectroscopy · Identification

Introduction

Lumber and wood materials used for houses and exterior purposes have been impregnated with chemicals to reduce decay and avoid damage from termites. Chromated copper arsenate (CCA), which contains chromium, copper and arsenic compounds, was one of the standard preservatives.

CCA-treated was introduced in Japan in 1963 and no longer in use from 1997 by the voluntary action of the wood preservative industry [1]. The reasons were emissions of Cr compounds to factory effluent and incinerated ash [2], and As compounds to flue gas [3], though CCA treatment has been effective for the preservation of wood. As the estimated volume of CCA-treated wood waste at demolition sites will reach its peak at 130,000 m³ in 2015 and then gradually decreases to almost zero for the next hundred years, a guideline for the disposal of CCA-treated wood was established under the act for the recycling of building materials. However, a method that can rapidly and accurately identify CCA-treated wood at demolition sites has not yet been developed until today.

Several studies about sorting waste CCA-treated wood have been already reported. In those studies, laser-induced breakdown spectroscopy (LIBS) or X-ray fluorescence analysis (XRF) were often used for detection of CCA-treated wood. One is the LIBS which uses a laser to create plasma from atoms in material and can analyze the existence of the atoms in the plasma. The other one is the XRF which observes X-ray fluorescence from materials excited by X-ray. Uhl et al. [4] had analyzed treated wood by LIBS and demonstrated that this technology had a capability to detect heavy metals in wood. Moskal and Hahn [5] also evaluated their online detector system using LIBS for CCA-treated wood detection. However, they observed fluorescence only from Cr and not from As at all. Although Takahashi et al. [6] developed a distinction process of CCA-treated wood, but the detection limit of As was insufficient. Solo-Gabriele et al. [7] compared XRF and LIBS systems, and revealed that both methods had a potential to separate CCA-treated wood from others, though XRF could detect CCA-treated wood better.

Judging from the usability at demolition site, LIBS will be most suitable method for this purpose because of

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transportable possibility, rapid analysis without any pre-treatment and simple operation. However, reliable and practicable identification method by LIBS hasn't established yet. Therefore, we applied LIBS to identify CCA-treated wood from other types of treated wood, such as AAC, BAAC, ACQ, CUAZ, and creosote using a low fluence LIBS system, and herein, we present our results. Spectrum fluctuation, the sampling method, and the accuracy of identification are also discussed.

Experimental

LIBS equipment

A schematic view of the LIBS analyzer used in this study is illustrated in Fig. 1. This setup used an Nd:YAG laser (New Wave Research, Tempest 10) emitting a pulse with a wavelength of 1,064 nm and a pulse duration of 4 ns. The pulse from the laser was focused on the surface of the lumber by a plane convex lens whose focal length was 150 mm to generate a plasma of excited atoms in the layer. The focused spot diameter and fluence were 0.7 mm and 55 mJ/mm², respectively. The fluorescence from the plasma was collected by an ellipsoidal mirror and led into an optical fiber connected to a tiny spectrometer (Stellar-Net, EPP2000HR) whose resolution and analysis range were 0.15 nm and 190–300 nm, respectively. The spectrum can be acquired from the spectrometer within 30 ms after laser irradiation.

Samples

CCA, AAC, BAAC, ACQ, CUAZ, creosote, unknown, and non-treated wood samples from unused sources and waste products were measured in this study. Waste wood samples were collected from demolished houses. All samples were kept in the same room and air-dried before analysis. The analyzed samples are shown in Table 1.

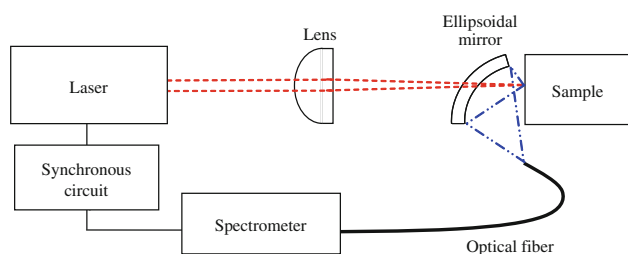


Fig. 1 Schematic of the LIBS analyzer for identifying CCA-treated wood

Data acquisition

The LIBS spectrum is usually affected by background light, pulse energy, the distance between the lens and sample, as well as the heterogeneity of the sample. To minimize these effects, baseline correction and normalization of the spectra were achieved as follows: as carbon fluorescence at a wavelength of 247.8 nm was always observed when the wood was analyzed, this signal was

Table 1 Summary of the wood samples and their characteristics

Preservative	Code	Used age (years)	Usage	Sample symbol
Chromium, copper, arsenic	CCA	–	Unused	C1
		–	Unused	C2
		–	Unused	C3
		>10	Exterior wood	C4
		Unknown	Exterior wood	C5
		30	Sleeper	C6
		30	Sleeper	C7
		13.5	Sill	C8
		30	Sill	C9
		30	Sill	C10
		30	Sill	C11
		27	Exterior wood	C12
		30	Plinth	C13
		16	Sill	C14
		30	Addition part	C15
Ammonium	AAC	4.5	Sill	A1
		4.5	Sill	A2
		4.5	Sill	A3
		4	Floor joist	A4
Boron, ammonium	BAAC	5	Sill	B1
		5	Sill	B2
Copper, ammonium	ACQ	–	Unused	Q1
		–	Unused	Q2
		4	Floor joist	Q3
Copper, azole	CUAZ	Unknown	Unknown	Z1
		Unknown	Unknown	Z2
Creosote	–	40	Plinth	O1
Non-treated	–	–	Unused	P1
		–	Unused	P2
Unknown	–	53	Sill	X1
		53	Sill	X2
		53	Sill	X3
		53	Sill	X4
		Unknown	Sill	X5
		40	Sill	X6
		40	Sill	X7
		40	Sill	X8

chosen as the standard and its intensity was set at 1000. Such an adjustment was thought to be required for every measurement for an accurate analysis. Clear fluorescence was observed for Cr at 267.6, 276.5, 283.5, 284.2, 284.9, and 286.5 nm and for As at 228.7 and 235.0 nm. Fluorescence of Cr at 267.6 nm and that of As at 228.7 nm

were chosen for the identification of these species because the wavelengths provided the most distinct peaks in the range of 190–300 nm. The identification of all atoms was achieved by comparing the observed wavelengths to those reported in the literature [8, 9].

Taking into consideration the surface pollution and the variation of fluorescence intensities, the averages of the peak intensities from the third irradiation of three different locations were determined for identification purposes.

Results and discussion

To determine a more optimal sampling method for the identification of CCA-treated wood, the distribution of Cr and As fluorescence intensities by LIBS were investigated in an area of 20 × 30 mm with a resolution of 1 mm. A surface image and the analyzed result for sample C5 are illustrated in Figs. 2, 3, respectively. As seen in Fig. 2, stains were observed on a part of the sample surface. These stains affected the results of LIBS, although they did not spread into the sample. According to the distribution map of the fluorescence intensity for As at 228.7 nm and for Cr at 267.6 nm in Fig. 3, the effect of the stains on the first and second laser irradiation was clearly observed; however, no effect was observed in the intensity map resulting from the third laser irradiation. Therefore, the fluorescence intensity of the third irradiation was used for LIBS analysis.

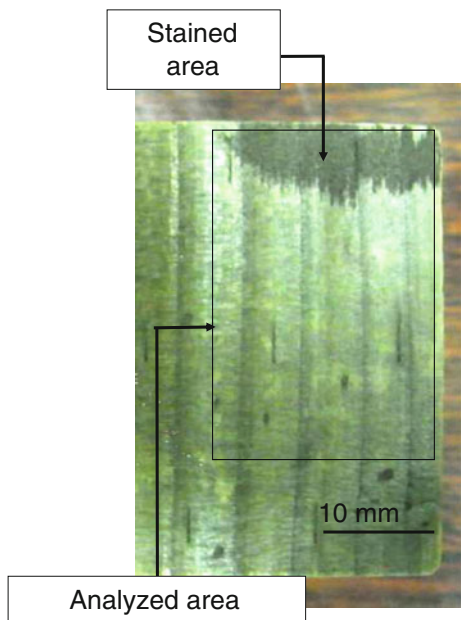
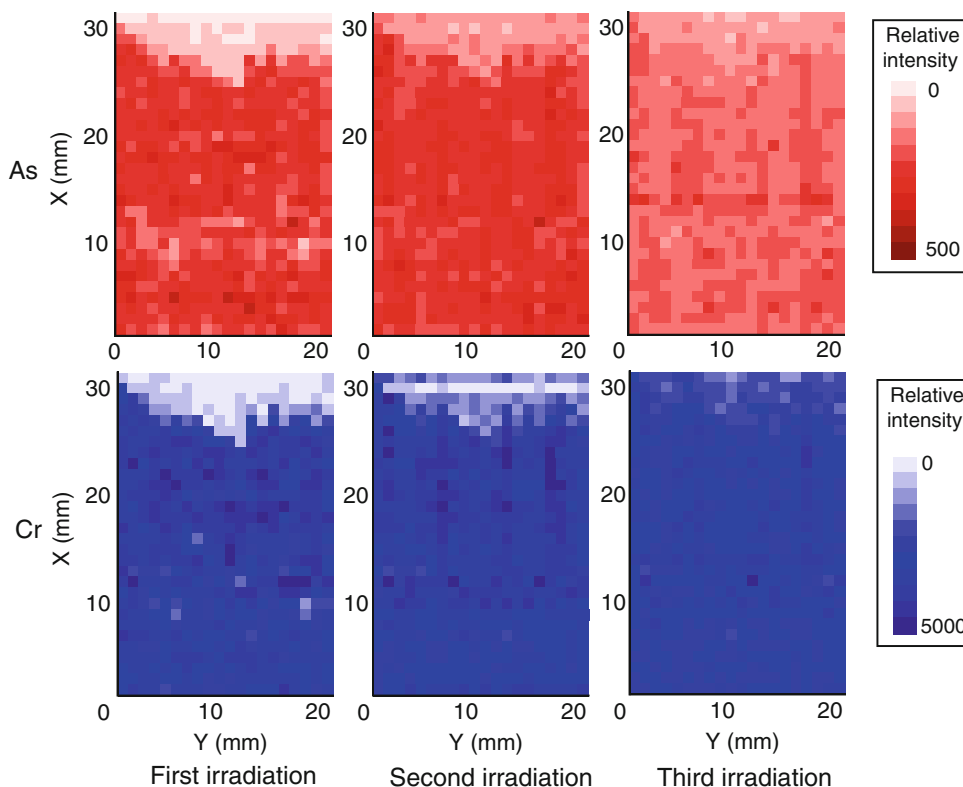


Fig. 2 Image of the wood surface of sample C5

Fig. 3 Distribution of As and Cr fluorescence intensity



The average values of fluorescence intensity of As and Cr from the single-shot irradiation of several CCA samples are shown in Fig. 4, in which the error bars show $\pm 3\sigma$. The strongest fluorescence intensity was observed at the first or second irradiation, except in the stain area. As the standard deviation was considerably large, the error bars for CCA-treated and non-treated wood overlapped each other. Therefore, it was necessary to take an average of multiple measurements from different locations for an accurate identification. Figure 5 shows the averaged intensities of the results from three different locations for the same samples reported in Fig. 4. As the standard deviation clearly decreased compared with that in Fig. 4, the averages of the peak intensities from the third irradiation acquired from three different locations were consequently used for identification.

To test the effectiveness of the method for the identification of As and Cr, one spectrum from the third laser irradiation at three different locations for each sample was

collected. Spectra from all 37 samples of As near 228.7 nm and of Cr near 267.6 nm are shown in Fig. 6.

Strong fluorescence of As at 228.7 and Cr 267.6 nm was observed only in the spectra of CCA-treated samples. The relative fluorescence intensity of As at 228.7 nm varied from 61 to 193 for CCA-treated wood and from 4 to 16 for non-CCA-treated wood. In addition, the relative intensity of Cr at 267.6 nm varied from 348 to 2400 and from 1 to 19 for CCA-treated and non-CCA-treated wood, respectively.

Although the Cr peak in the CCA-treated sample spectra was strong enough to identify samples containing Cr from others, the As peak was not as strong. Therefore, comparisons using a threshold level were required for better identification. Among the non-CCA-treated wood, the strongest fluorescence was shown by samples O1 and Z2 at 228.7 and 267.6 nm, respectively. Therefore, in this test, 3σ of relative fluorescence intensity from each sample was used for As at 228.7 nm and Cr at 267.6 nm threshold. For

Fig. 4 Averages of As and Cr single-shot fluorescence intensities for **a** As at 228.7 nm and **b** Cr at 267.6 nm. Error bars represent $\pm 3\sigma$

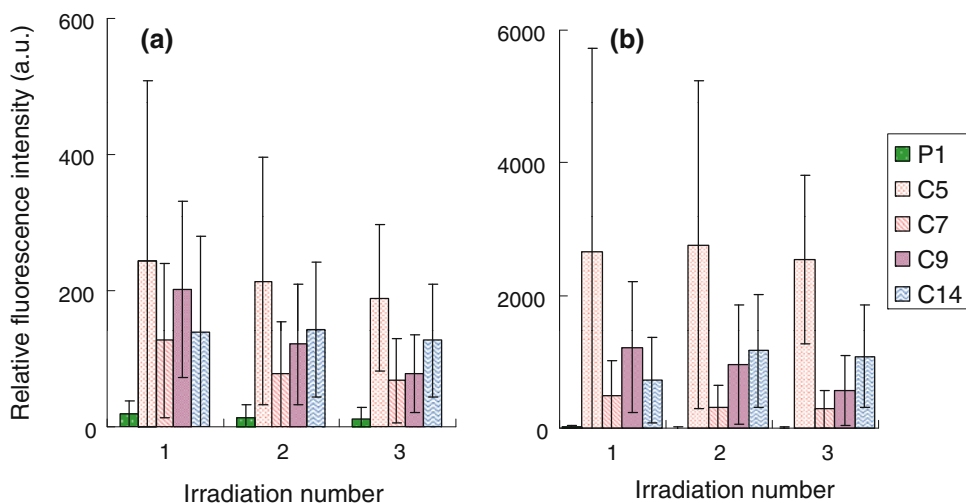


Fig. 5 Averages of As and Cr fluorescence intensities from three different locations are averaged for **a** As at 228.7 nm and **b** Cr at 267.6 nm. Error bars represent $\pm 3\sigma$

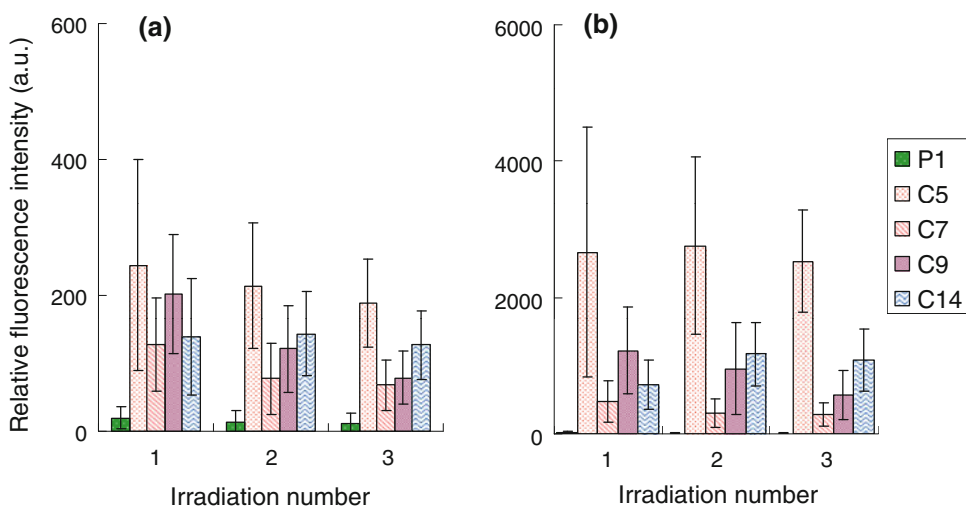


Fig. 6 LIBS spectra from all 37 samples

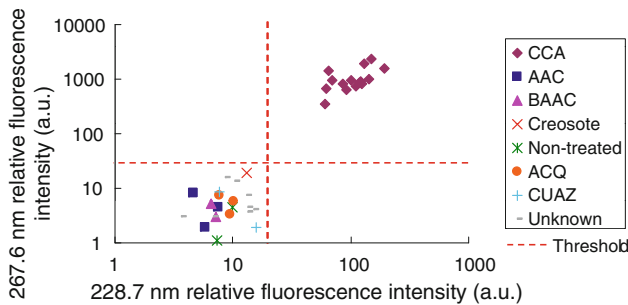
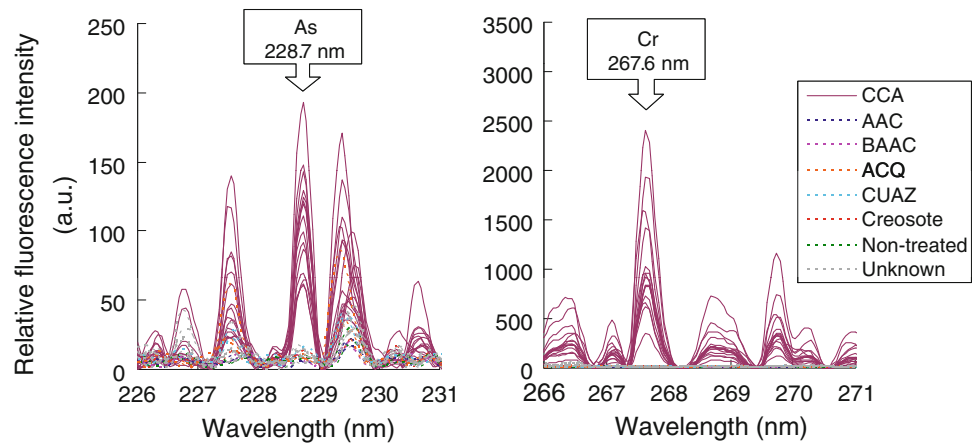


Fig. 7 Identification of CCA-treated wood using the threshold

the discrimination of As and Cr containing samples, the threshold value was set to 27 and 21, respectively. As shown in Fig. 7, CCA-treated wood could be clearly identified from other treated wood samples. The result from LIBS identification corresponded with that from X-ray fluorescence analysis. To obtain more reliable results, it is necessary to analyze samples under various conditions such as wet wood, painted wood, and so on.

Although our apparatus demonstrated an ability to accurately identify CCA-treated wood, the use of a lower fluence or smaller spot diameter on the sample surface needs consideration to develop a more economical and compact LIBS apparatus and such a laser typically has a lower pulse energy and smaller beam diameter compared with that of our laser. As plasma fluorescence intensity is related to ablated sample volume, these factors are thought to affect spectral intensity [10].

Conclusion

Laser-induced breakdown spectroscopy analysis was used to rapidly identify CCA-treated wood among wood samples having various treatments and to develop an rapid identification method using an Nd:YAG laser with the fluence of 55 mJ/mm². The strongest fluorescence intensities of As and

Cr in the range of 190–300 nm appeared at 228.7 and 267.6 nm, respectively. The fluorescence intensity distribution of these peaks and the observed variation suggested that it was necessary to average multiple measurements from different areas to ensure an accurate identification. Consequently, it was determined that the average of the fluorescence intensities from three different areas was sufficient. As peaks from As and Cr were observed only in the spectra from CCA-treated samples, LIBS could accurately identify CCA-treated wood from other treated wood samples, such as AAC, BAAC, ACQ, CUAZ, and creosote, when a threshold calculated from the fluorescence intensity of non-treated wood was used. Therefore, the potential of LIBS for the rapid identification of CCA-treated wood has been demonstrated.

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