# Comparative Study of Nd:YAG Laser-Induced Breakdown Spectroscopy And Transversely Excited Atmospheric CO2 Laser-Induced Gas Plasma Spectroscopy on Chromated Copper Arsenate Preservative-Treated Wood

# Comparative study of Nd:YAG laser-induced breakdown spectroscopy and transversely excited atmospheric $CO_2$ laser-induced gas plasma spectroscopy on chromated copper arsenate preservative-treated wood

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Taking advantage of the specific characteristics of a transversely excited atmospheric (TEA) $CO_2$ laser, a sophisticated technique for the analysis of chromated copper arsenate (CCA) in wood samples has been developed. In this study, a CCA-treated wood sample with a dimension of 20 mm × 20 mm and a thickness of 2 mm was attached in contact to a nickel plate (20 mm × 20 mm × 0.15 mm), which functions as a subtarget. When the TEA $CO_2$ laser was successively irradiated onto the wood surface, a hole with a diameter of approximately 2.5 mm was produced inside the sample and the laser beam was directly impinged onto the metal subtarget. Strong and stable gas plasma with a very large diameter of approximately 10 mm was induced once the laser beam had directly struck the metal subtarget. This gas plasma then interacted with the fine particles of the sample inside the hole and finally the particles were effectively dissociated and excited in the gas plasma region. By using this technique, high precision and sensitive analysis of CCA-treated wood sample was realized. A linear calibration curve of Cr was successfully made using the CCA-treated wood sample. The detection limits of Cr, Cu, and As were estimated to be approximately 1, 2, and 15 mg/kg, respectively. In the case of standard LIBS using the Nd:YAG laser, the analytical intensities fluctuate and the detection limit was much lower at approximately one-tenth that of TEA $CO_2$ laser.   © 2012 Optical Society of America

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## 1. Introduction

During the 1960s and 1970s, many houses in Japan were constructed using wood. At that time, in order to protect the wood from spoiling after construction, a chromated copper arsenate (CCA) was widely used as a wood preservative. The CCA-treated wood was used mainly for house foundations. As such houses age, they are demolished and rebuilt. During the demolition of old houses with construction equipment, CCA-treated wood is mixed with non CCA-treated wood. Therefore, a method for the inspection and identification of CCA-treated wood is required in the construction industry to ensure the safety of recycled wood.

Researchers have conducted several studies focusing on the elemental analysis of wood. The techniques commonly employed for wood analysis are atomic absorption spectroscopy and chromatography after treatment of the sample [1–4]. However, rapid and *in situ* analysis cannot be performed using these techniques. Another technique used in the elemental analysis of wood is x-ray fluorescence spectroscopy (XRF) [5]. However, this technique is not generally amenable to online analysis of wood at the recycling factory.

Laser-induced breakdown spectroscopy (LIBS) has become well known as a technique for elemental analysis on various sample types [6–8]. Solo-Gabriele *et al.* have applied LIBS to separate CCA-treated wood from other wood types. However, the technique has limitations when applied to the analysis of wet or rotted wood [5].

Basically, wood is the most difficult to analyze using standard LIBS. This is because wood samples are usually soft and non-homogeneous due to fringe structure. According to our research, the high-temperature plasma required as an excitation source cannot be induced on a soft sample. This is because a strong shock wave cannot be produced due to the lack of repulsion force on the surface when the pulsed laser is directly focused on the surface of the soft sample [9–11]. For this reason, lower detection limits cannot be achieved, making accurate measurement impossible. Additionally, the diameter of the Nd:YAG laser spot is very small at only a few hundred $\mu$m. As a consequence, when the laser beam is focused on different positions on the sample surface, which is non-homogeneous due to the fringe structure, the plasma induced on the sample surface fluctuates widely.

As an alternative to the Nd:YAG laser, we have developed a metal-assisted gas plasma technique which uses a transversely excited atmospheric (TEA) $CO_2$ laser to realize the direct analysis of powder samples [12]. In this case, a metal subtarget was used to induce a strong gas plasma, and atoms from the sample were excited into the gas plasma region.

In this study, we applied the metal-assisted gas plasma technique for the analysis of CCA-treated wood. Also, a comparative study was made between the TEA $CO_2$ laser-induced metal-assisted gas plasma technique and the standard LIBS technique, in which Nd:YAG laser was applied. It should be stressed that our present technique, metal-assisted gas plasma technique, can be used for the semi *in situ* analysis of wood samples at the wood selection facility.

## 2. Experimental Procedure

The experimental setup used in this study was similar to that used in our previous work [13]. A pulsed TEA $CO_2$ laser (Shibuya SQ 2000 laser, pulse energy of 3 J, wavelength of 10.6 $\mu$m, pulse duration of 200 ns at full width half maximum, beam cross section of 3 mm × 3 mm) commercially produced by Shibuya Company for laser marking was used as an energy source for laser plasma generation. The laser beam was focused on a sample surface through a ZnSe window using a ZnSe lens with a focal length of 200 mm. The laser energy was set at 750 mJ by placing an aperture in the path of the laser beam, which resulted in a power density of 0.38 GW/cm². For the experiment using standard LIBS technique, a fundamental Nd:YAG laser (Usho Optical Systems Polaris III, New Wave Research, pulse energy of 160 mJ, wavelength of 1.064 $\mu$m with a repetition rate of 10 hertz, pulse duration of 8 ns at full width half maximum) was employed for plasma generation. A quartz lens with a focal length of 7 cm was used to focus the laser beam onto the sample surface. The power density was estimated to be approximately 10 GW/cm² when the laser energy was set at 60 mJ. In order to achieve a reliable signal to noise ratio (S/N ratio), we used 10 shots of laser irradiation for data acquisition by TEA $CO_2$ laser and Nd:YAG laser.

In order to know how the laser plasma generation depends on the wood characteristics, we used two kinds of commercial wood; namely, a softwood sample (*Cryptomeria*, mass density of approximately 0.5 g/cm³) and a hardwood sample (Japanese cypress, mass density of approximately 0.7 g/cm³). These samples are readily available on the local market in Japan.

For experiments using TEA $CO_2$ laser, a sample with a dimension of 30 mm × 20 mm and a thickness of 2 mm was attached to a nickel plate (30 mm × 20 mm × 0.15 mm), which served as a metal subtarget, as shown in Fig. 1(a). It should be stressed that the metal itself is never damaged or ablated during TEA $CO_2$ laser irradiation because the power density of the laser beam impinging on the metal is lower than the ablation threshold of the metal due to the fact that most of laser energy is absorbed by the strong gas plasma (plasma shielding effect). This phenomenon only occurs when using the TEA $CO_2$ laser and never when using the Nd:YAG laser, which is commonly employed in standard LIBS technique. For Nd:YAG laser experiments, a sample with a dimension of 30 mm × 20 mm and a thickness of 2 mm was prepared without nickel plate. The laser was directly focused on the sample surface.

During experiments, all samples were attached on a holder placed in a metal chamber measuring 12 cm × 12 cm × 12 cm, which was filled with nitrogen gas in order to clean the dust produced by the wood sample during the laser bombardment. In these experiments, the pressure of the surrounding gas in the chamber was set at 1 atmosphere. The flow rate of gas was 4 liters per minute.

The emission spectrum was obtained by optical multi channel analyzer (OMA) system (ATAGO Macs-320) consisting of a 0.32 m focal-length spectrograph with a grating of 1200 grooves/mm, a 1024-channel photodiode detector array, and a micro-channel plate image intensifier to detect the laser plasma radiation. The spectral resolution of the OMA system was 0.2 nm. The light emission of the laser plasma was collected by optical fiber fed into the OMA system. The fiber was bundled fiber with the diameter of each fiber measuring 0.5 mm. The entrance and exit fibers were of different shapes; namely, the entrance fiber was circular with a diameter of 2 mm and the exit fiber was slit-shaped with a dimension of 4.5 mm × 1 mm. For the TEA $CO_2$ laser, one end of the fiber was placed at a distance of 4 cm from the focus of the laser light and set inclining 25 degrees from the perpendicular path of the laser beam. For the Nd:YAG laser, the distance
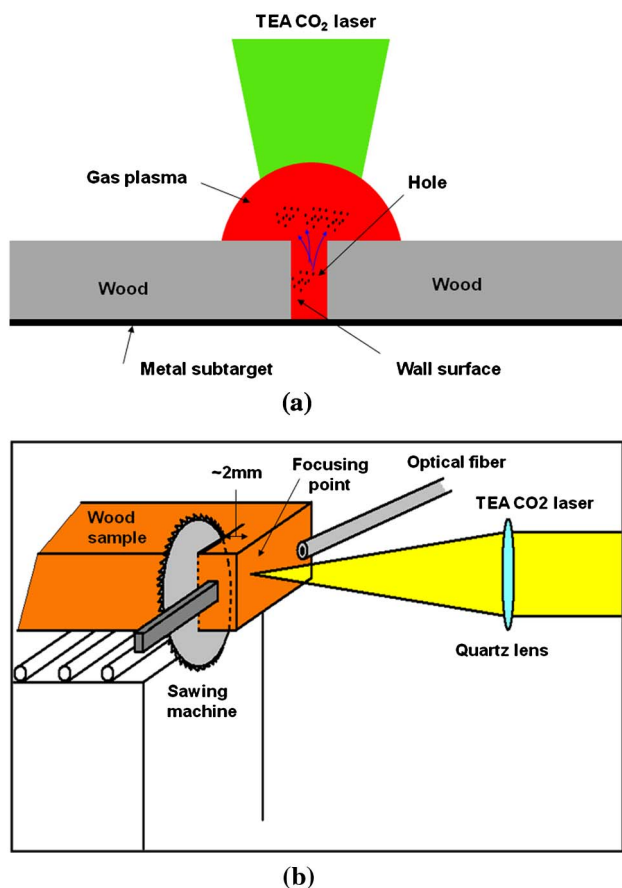


**(a)**



**(b)**

Fig. 1. (Color online) (a) Illustration of the gas plasma and the sample holder used in this study. (b) Illustration of the metal-assisted gas plasma system used for semi *in situ* analysis of wood samples at a recycle production factory.

of the optical fiber was set much closer at 1 cm from the focal point because of its small plasma. For the sensitive analysis of wood samples, a high-resolution monochromator (Jobin-Ybon HRS-2, $f = 640$ mm, 2400/mm, spectral resolution of 0.02 nm) attached to an OMA system (Lambda vision LVICCD 1012) was used.

For quantitative analysis, wood samples treated with various concentrations of CCA (chromated copper arsenate) were employed. The samples were produced by one of the laboratories of this research group (Hokkaido Research Organization). The samples consisted of 4 sets of wood samples. Sample a contained 231, 101, and 77 mg/kg of Cr, Cu, and As, respectively. Sample b contained 1536, 673, and 512 mg/kg of Cr, Cu, and As, respectively. Sample c contained 3003, 1317, and 975 mg/kg of Cr, Cu, and As, respectively. Sample d contained 7446, 3265, and 2482 mg/kg of Cr, Cu, and As, respectively.

Prior to preparing CCA-treated wood samples, a standard liquid containing CCA (chromated copper arsenate) was prepared using $K_2Cr_2O_7$, $CuSO_4.5H_2O$, and $H_3AsO_4$. For Cr, 137.5 g of the $K_2Cr_2O_7$ was dissolved into 1 liter of water, resulting in a liquid containing 48,600 mg/l of Cr. For Cu, 83.75 g of the $CuSO_4.5H_2O$ was dissolved into 1 liter of water, resulting in a liquid containing 21,300 mg/l of Cu. For As, 51.16 g of the $H_3AsO_4$ was dissolved into 1 liter of water, resulting in a liquid containing 27,000 mg/l of As. The liquids were then diluted from 10 to 500 times by adding water. For the CCA-treated wood samples, Peisugi wood with a dimension of 30 mm × 36 mm × 15 mm was dried in a room with a temperature of 60 °C for 2 days. Then, the dried wood was sunk into liquid containing different concentrations of CCA. Under vacuum condition, the water was then removed and the wood was pressed at a pressure of 5 kg/cm². Following this, the concentration of CCA in treated wood samples was determined using the Japanese analytical standard (JAS) method.

## 3. Results and Discussion

It is well known that LIBS is very convenient as a method for rapid analysis on any sample including solids, liquids, and gases. This is because the samples can be analyzed without pretreatment and plasma can be easily induced by focusing the laser onto the sample surface. However, in order to obtain reliable quantitative analysis, we should have a good understanding of the physical mechanism of plasma generation. Influence of sample characteristics, such as hardness, on the plasma generation should be considered. These considerations are especially important when applying the LIBS technique to soft and non-homogeneous samples such as wood.

The significant issue in wood sample analysis is that the depth of the crater created by the laser bombardment on the sample surface increases, and plasma emission intensity decreases with the increased depth of the crater. Figure 2 shows the emission intensities of Ca II 393.3 nm taken from hardwood and

softwood samples with respect to the number of laser shots. Usually, the wood sample contains calcium at a concentration of approximately 2%. The laser bombardment was directed at a fixed position on the sample surface with a laser energy of 60 mJ. The laser was directly focused on the sample surface, as shown in the inset of Fig. 2. It is clearly seen that at the initial stage, the emission intensities of Ca II 393.3 nm taken from the hardwood sample are very high. With an increase in the number of laser shots, the emission intensity of Ca II 393.3 nm decreases steeply. For the softwood sample, the Ca II 393.3 nm emission intensity is nearly constant up to 10 shots of laser irradiation and finally decreases with the number of laser shots. Based on this result, for wood analysis we should take the data from the initial 10 shots of laser bombardment with the laser focused at a fixed position on the sample surface.

From a practical perspective, laser irradiation has to be directed randomly on the sample surface because rapid analysis is the most important requirement. Thus, we examined how the analytical data fluctuate depending on the position selected by random choice. Figure 3 shows how the emission intensity of Ca II 393.3 nm changes with the different position on the wood sample surface. The gate delay time and gate width of OMA system were set at 1 and 50 $\mu$s, respectively. The laser energy was set at 60 mJ. The numbers 1 to 6 in graph have no meaning because the laser irradiation was directed randomly on the sample surface. Each item of data was derived from the spectrum taken by 10 shots of initial laser irradiation. It is seen that the Ca II 393.3 nm intensity fluctuates with the different position for both hardwood and softwood samples.

The TEA $CO_2$ laser wavelength and pulse duration are quite different from the Nd:YAG laser. Thus, we expected that the TEA $CO_2$ laser might be used for wood analysis because the wood sample has high absorbance in the TEA $CO_2$ laser wavelength. However,



Fig. 3. (Color online) Emission intensities of Ca II 393.3 nm taken from the hardwood sample and the softwood sample at the different positions on the sample surface by using standard LIBS technique, in which Nd:YAG laser is employed.

as we reported in our previous work [13], the TEA $CO_2$ laser could not be used to generate plasma when the laser was directly focused on a soft sample. In order to generate plasma on a soft sample using the TEA $CO_2$ laser, we have developed a metal-assisted gas plasma technique. With the aid of a metal subtarget, gas plasma can be induced. The sample was vaporized and the atoms were excited into the gas plasma region. We have successfully demonstrated this technique for powder analyses, as reported in our previous papers [12,14].

For the wood analysis performed in this study, we used the same metal-assisted gas plasma technique employed in powder analysis. Specifically, the metal was placed in tight contact with the backside of a wood sample, as shown in the insert of Fig. 4. Figure 4 shows how the emission intensities of Ca II 393.3 nm taken from the hardwood sample and the softwood sample change with the number of laser shots. The gate delay time and gate width of the OMA system were set at 10 and 100 $\mu$s, respectively. The laser energy was set at 750 mJ. It was clear that the emission intensities of Ca II 393.3 nm of both the hardwood
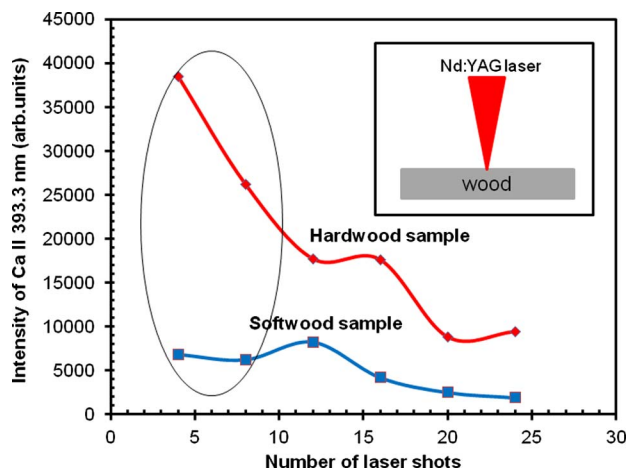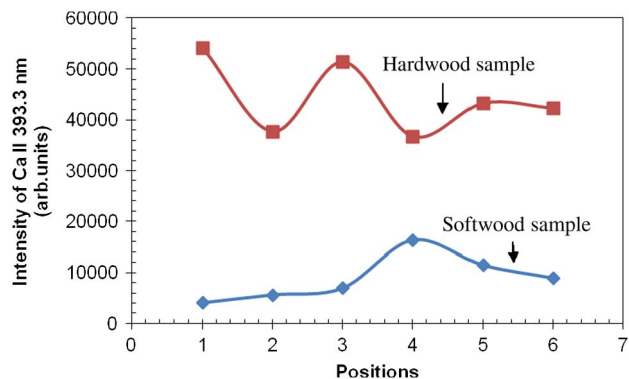


Fig. 2. (Color online) Emission intensities of Ca II 393.3 nm taken from the hardwood sample and the softwood sample corresponding to the number of laser shots by using standard LIBS technique, in which Nd:YAG laser is employed.
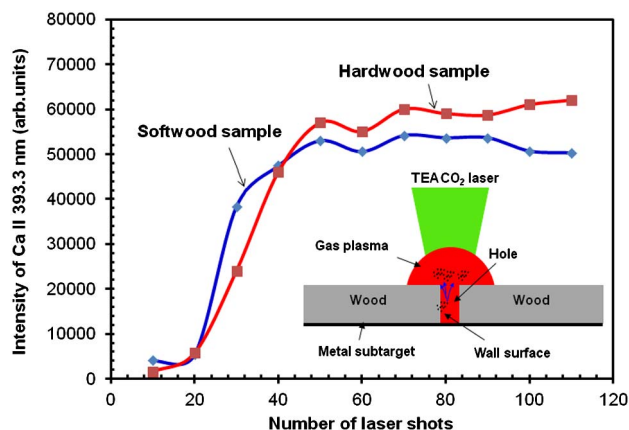


Fig. 4. (Color online) Emission intensities of Ca II 393.3 nm taken from the hardwood sample and the softwood sample corresponding to the number of laser shots by using the metal-assisted gas plasma technique, in which TEA $CO_2$ laser is employed.

and softwood samples were initially very weak. The intensities then sharply increased up to 50 shots of laser bombardment and finally became constant up to 110 shots of laser irradiation. At initial laser irradiation, the laser directly contacted the sample surface and the sample is vaporized, but no plasma generation was observed. With the number of laser shots, a hole was created inside the sample and at 30 shots of laser irradiation, some parts of the laser beam directly contact on the metal subtarget placed in tight contact on the backside of the wood sample to induce gas plasma. At around 50 shots of laser irradiation, the hole inside the sample was completed, where the emission intensity of Ca II 393.3 nm became constant. Thus, it was concluded that the laser beam was completely impinged on the metal subtarget and induced strong gas plasma.

It is thought that the mechanism of gas plasma generation in the case of TEA $CO_2$ laser is as follows [12]; when a TEA $CO_2$ laser is focused onto a metal surface, electrons are released from the surface due to a multiphoton absorption process that occurs at the focal point of the laser light. These electrons are then accelerated to high energy in the low frequency electric field of the laser light, which induces cascade ionization of the atoms in the gas and generates an initial gas plasma. Once this initial plasma has been produced, the laser light is completely absorbed in the gas plasma by inverse bremsstrahlung via free-free transitions. This absorption is much stronger for the TEA $CO_2$ laser than for the Nd-YAG laser as the plasma absorption coefficient is proportional to the inverse square of the frequency of the laser light. Furthermore, the pulse duration of the TEA $CO_2$ laser is relatively long (200 ns), approximately 20 times longer than for the Nd-YAG laser, which means that nearly all the energy from the TEA $CO_2$ laser is absorbed by the gas plasma. The gas plasma produced is, therefore, very strong and has a high temperature and high heat capacity. For the wood sampling process it is assumed that during the expansion of the gas plasma, the fine particles of the wood sample are vaporized inside the sample. The vaporized particles then move to the strong and high-temperature gas plasma region to be atomized and excited. The atomization and excitation of the fine particles proceed well because the temperature of the gas plasma is high with a sufficiently high heat capacity.

Figure 5(a) shows how the emission intensity of Ca II 393.3 nm changes with the different position on the wood sample surface under TEA $CO_2$ laser irradiation. The emission lines of Ca II 393.3 nm were taken from the hardwood and softwood samples as used in the Nd:YAG laser case. Each point was made by 10 laser shots after 100 shots of laser pre-irradiation, where the emission intensity of Ca II 393.3 nm has already become constant. It is seen in Fig. 5(a) that the emission intensities of Ca II 393.3 nm both from the hardwood and softwood samples are almost constant, regardless of position. Figure 5(b) shows a

photograph of the holes created inside the softwood sample by TEA $CO_2$ laser bombardment. Each hole was made by 100 shots of laser irradiation, where the emission spectrum was taken for analytical study. The metal subtarget placed in the backside of the wood sample was removed for the photograph. This good result is probably due to the fact that the spot size created by the laser bombardment inside the sample is very big at approximately 2 mm in diameter compared to the case of Nd:YAG laser of approximately 200 $\mu$m in diameter. The emission intensity of Ca II 393.3 nm for the TEA $CO_2$ laser is a result of the average of the wide area in the sample, causing a quite stable plasma emission. It is also believed that the interior surface of the 2 mm hole is ultimately involved in the plasma-material interaction, and that the resulting signal is bound to be more precise and more representative of the sample bulk than any ensemble of measurements taken on the surface. It should also be noted that, in the case of the TEA $CO_2$ laser, the fringe structure of the wood sample does not exert a significant influence on plasma emission. This is because the plasma is induced
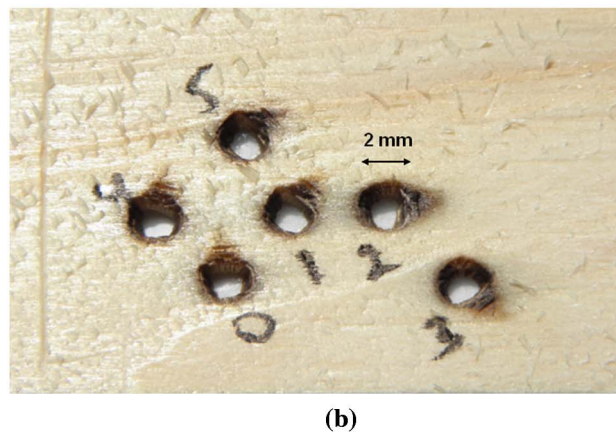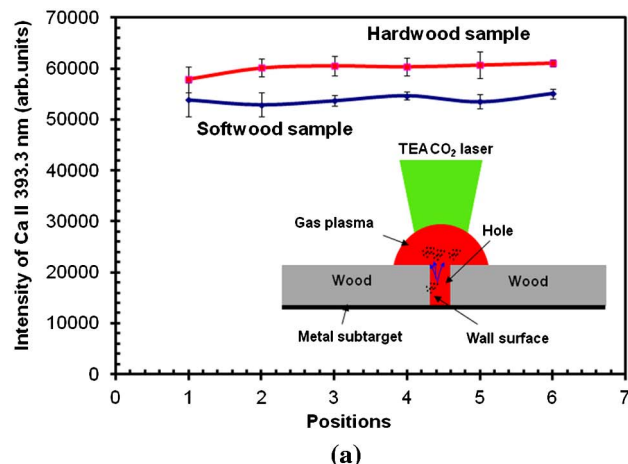


(a)



(b)

Fig. 5. (Color online) (a) Emission intensities of Ca II 393.3 nm taken from the hardwood sample and the softwood sample at the different positions on the sample surface by using the metal-assisted gas plasma technique, in which TEA $CO_2$ laser is employed. (b) Photograph of the holes created inside the softwood sample after data acquisition of (a).

by the metal subtarget placed in tight contact on the backside of the sample rather than being generated by the wood surface as in the case of the Nd:YAG laser. The fluctuation of plasma emission for the Nd:YAG laser is due to the small spot size of the laser on the sample surface. Some may think that a good result would be obtained even with the Nd:YAG laser if the spot were enlarged. However, a large laser spot size cannot be employed because the power density of the laser on the sample surface becomes too low to induce the plasma.

In order to compare the quality of analytical performance between the Nd:YAG and TEA $CO_2$ lasers, we compared the emission spectra taken from the CCA-treated wood samples. Figure 6 shows emission spectra of (a) Cr, (b) Cu, and (c) As, taken from wood samples containing 231, 101, and 975 mg/kg of Cr, Cu, and As, respectively, using the standard LIBS technique, in which the Nd:YAG laser was employed. The laser energy was set at 60 mJ. The laser was directly focused on the wood sample surface. The emission spectra were taken from the initial 10 shots of laser irradiation. The gate delay time and gate width of the OMA system were 1 and 20 $\mu$s, respectively. Figure 7 shows the emission spectra of (a) Cr, (b) Cu, and (c) As, taken from the same sample as used in Fig. 6, using the metal-assisted gas plasma technique, in which the TEA $CO_2$ laser was employed. The emission spectra were taken using 10 laser shots after 100 shots of laser pre-irradiation, where the plasma emission intensity has already become constant. The laser energy was set at 750 mJ. The gate delay time and gate width of the OMA system were 10 and 100 $\mu$s, respectively. By comparing the spectra in Figs. 6 and 7, in the case of Cr and Cu, the emission spectrum profile is almost the same in both cases of the Nd:YAG laser and the TEA $CO_2$ laser; however, the spectrum quality, namely the signal and noise ratio (S/N), is better for the TEA $CO_2$ laser. On the other hand, for As, the spectrum profile quality with the TEA $CO_2$ laser is significantly superior to that of the Nd:YAG laser, namely some lines at shorter wavelengths such as As I 228.8 nm do not appear in the Nd:YAG laser case; however, they clearly appear in the TEA $CO_2$ laser case.

Finally, in order to examine the effectiveness of our present technique in terms of quantitative analysis, calibration curves were obtained using the preservative wood samples containing different concentrations of Cr. Figure 8(a) shows the calibration curve obtained using the Nd:YAG laser (standard LIBS technique), and Fig. 8(b) is for the TEA $CO_2$ laser (metal-assisted gas plasma technique). Each point plotted on the calibration curves of Figs. 8(a) and 8(b) was an average of five spectra taken from different positions on the sample surface. It is clearly seen in Figs. 8(a) and 8(b) that the linearity of calibration curve for the TEA $CO_2$ laser [Fig. 8(b)] is much better than that of the Nd:YAG laser [Fig. 8(a)]. The nonintercept zero might be because the Cr I 425.4 nm line overlaps with the unknown line in the spectrum. In

addition, we have confirmed by JAS method that the non-treated wood (blank wood) does not contain chromium. In order to compensate for the uncontrolled fluctuation of the laser plasma intensity produced on the sample, internal standardization was carried out using the background emission employed in our previous work [15]. The standard deviation was
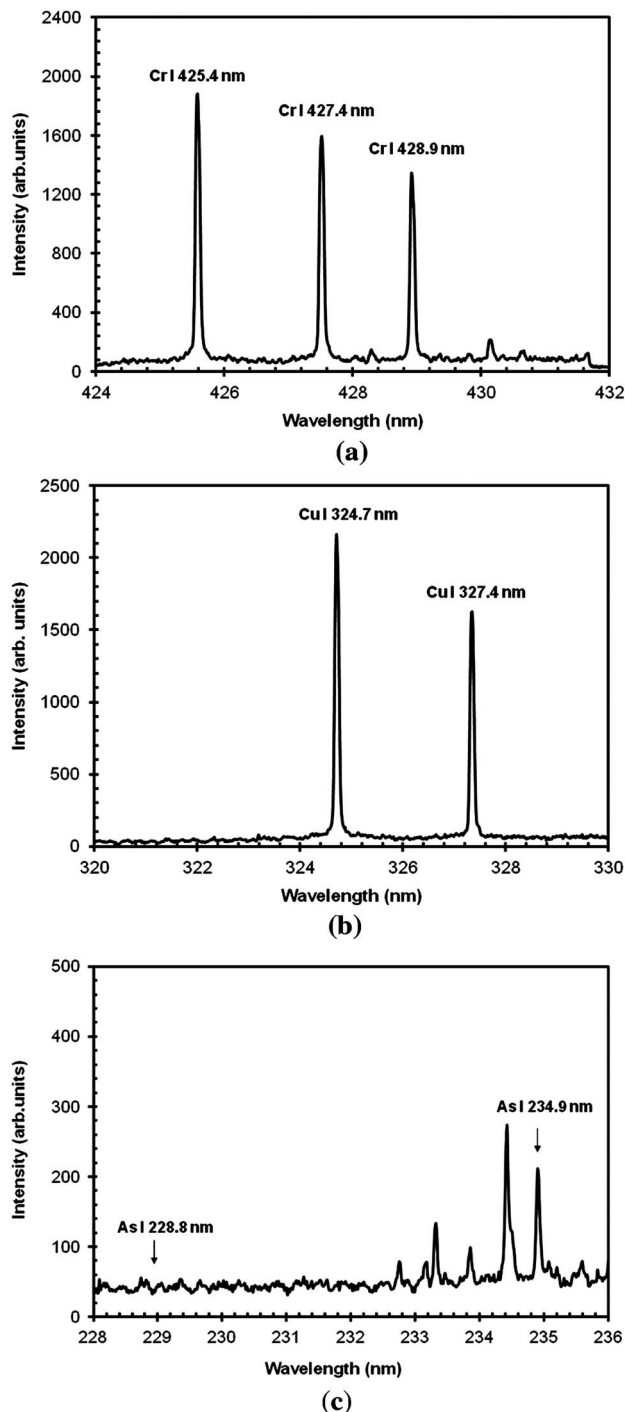


Fig. 6. Emission spectra of (a) Cr, (b) Cu, and (c) As taken from the CCA preservative-treated wood by using standard LIBS technique, in which Nd:YAG laser is employed. The spectra were taken using 10 shots of laser irradiation and the laser energy was 60 mJ.

found to be approximately 20% to 36% for the Nd:YAG laser and 2% to 5% in the case of the TEA $CO_2$ laser.

The detection limits of Cr, Cu, and As in the wood sample using the Nd:YAG laser were approximately 11, 8, and 130 mg/kg, respectively, and for the case of TEA $CO_2$ laser, namely metal-assisted gas plasma technique, the detection limits were approximately 1, 2, and 15 mg/kg for Cr, Cu, and As, respectively. The detection limit was derived by calculating the signal concentration which yielded 3 times the noise level because this was clearly identified as a signal that could be distinguished from the noise [16]. These results clearly indicate that wood analysis by metal-assisted gas plasma technique, in which the TEA $CO_2$ laser is employed, is significantly superior in precision and sensitivity compared to the standard LIBS technique, in which the Nd:YAG laser is used as an energy source. It should also be noted that compared to the technique developed by Solo-Gabriele et al. [5], our present metal-assisted gas plasma technique is significantly superior because analysis could be performed even on very soft wood samples such as rotted wood.

It should also be noted that, for the case of the TEA $CO_2$ laser, even without metal subtarget, the plasma can be induced by successive laser irradiation, namely when a hole with a sufficient depth (approximately 3–4 mm) is produced. Although, the plasma emission intensity is lower by one-tenth compared to the case of the metal-assisted gas plasma technique, direct irradiation of TEA $CO_2$ laser irradiation without subtarget can also be used for analytical application only when the CCA concentration is very high. It is estimated that 100 shots of TEA $CO_2$ laser irradiation on wood sample enables nearly the same degree of data sensitivity as the Nd:YAG laser. However, it should be stressed that the advantage of the lower fluctuation that the metal assisted gas plasma
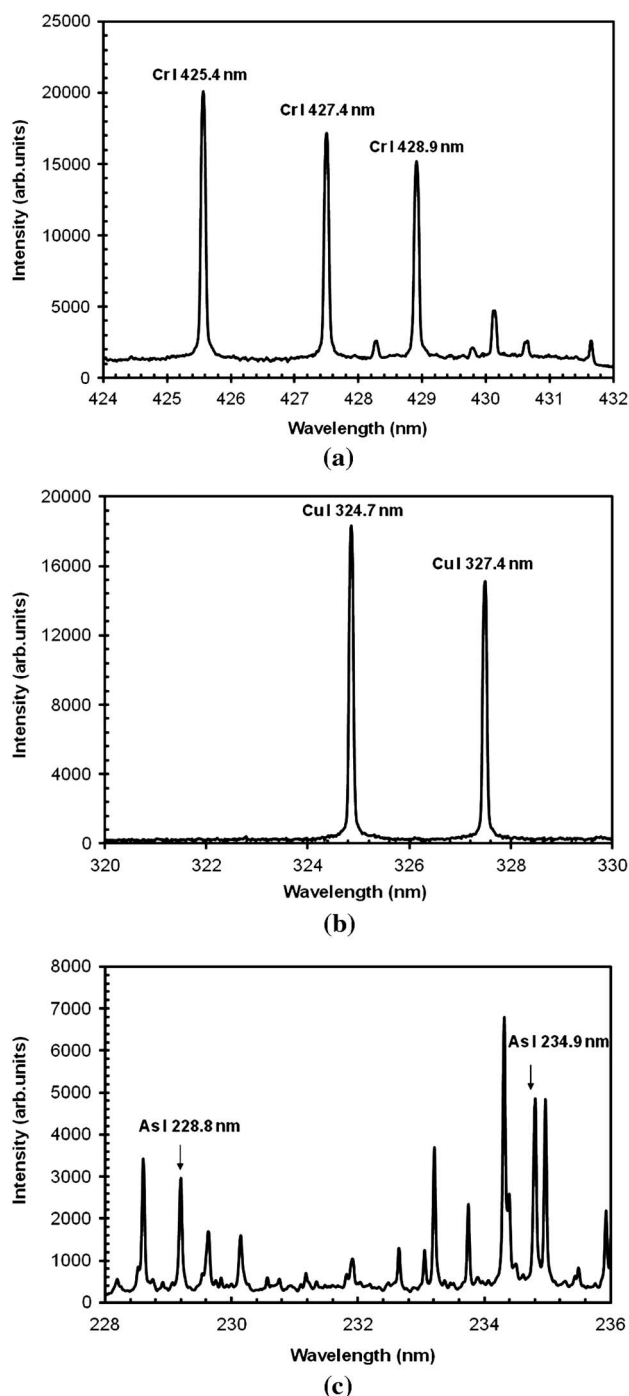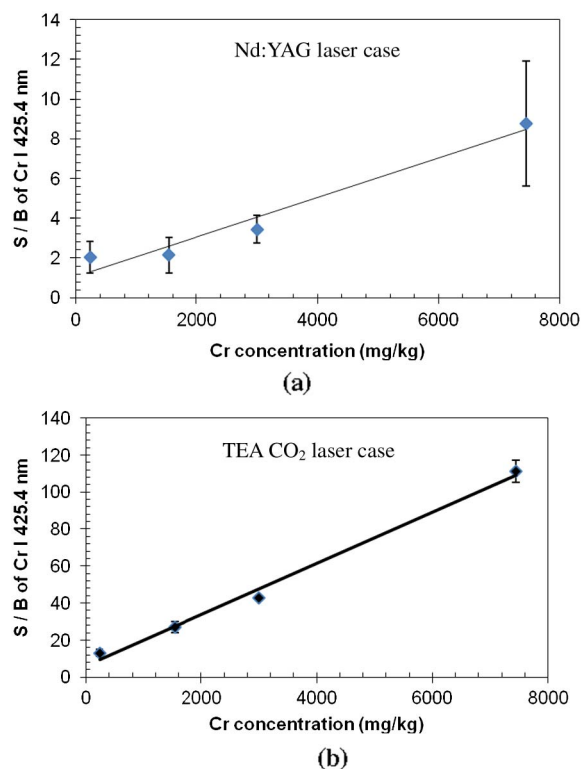


Fig. 7. Emission spectra of (a) Cr, (b) Cu, and (c) As taken from the CCA preservative-treated wood by using the metal-assisted gas plasma technique, in which TEA $CO_2$ laser is employed. The spectra were taken using 10 laser shots after 100 shots of laser pre-irradiation and the laser energy was 750 mJ.



Fig. 8. (Color online) Calibration curve of Cr contamination in the wood sample by using (a) the Nd:YAG laser, and (b) the TEA $CO_2$ laser.

technique resulted in is maintained because of the large sampling size. We assume that the hole effect observed in the TEA $CO_2$ laser is most likely due to the confinement effect reported in our previous paper [17]. The effect can be explained based on the shock wave model. In the initial stage, the plasma emission is very weak, probably due to the fact that the ablation process proceeds slowly with long duration. This is because the softwood surface absorbs the recoil energy, and the atoms gushing from the primary plasma do not acquire sufficient speed, resulting in the lack of the compression in the shock wave generation stage. When a hole with a sufficient depth is produced inside the sample, the ablated atoms are confined in the hole so that the compression process is enhanced, generating a shock wave.

As mentioned in the introduction, recently, *in situ* wood analysis has been in great demand for use in the screening of wood with and without CCA preservative in the recycle process. Some might think that application of our metal-assisted gas plasma technique is difficult for *in situ* analysis. It is expected that the metal-assisted gas plasma technique developed in this study can be applied easily utilizing the system illustrated in Fig. 1(b). The recycled wood to be selected is sawed by the sawing machine to a thickness of approximately 2 mm. The saw metal remains inside the wood and serves as a metal subtarget. The TEA $CO_2$ laser is then directly focused on the sawed wood, in which the saw metal remains. After several dozen laser shots, a hole is completed inside the sample so that the laser beam directly impinges on the saw metal surface.

## 4. Conclusion

CCA-treated wood analysis has been successfully demonstrated by standard LIBS and metal-assisted gas plasma techniques. In the case of standard LIBS technique, in which the Nd:YAG laser was employed, the results showed that serious emission fluctuation occurs mainly due to the fringe structure of the wood sample. Thus, the precision is quite poor. Furthermore, because the wood includes soft samples, highly sensitive analysis is difficult to realize as high plasma temperature cannot be produced due to the lack of repulsion force on the sample surface [18,19]. In the metal-assisted gas plasma technique, in which the TEA $CO_2$ laser was employed, high precision and highly sensitive analysis can be carried out because of the stability of the plasma emission. In this study, calibration curves have successfully been obtained from CCA-treated wood samples containing different concentrations of Cr using the standard LIBS and the metal-assisted gas plasma techniques. The standard deviation was found to be approximately 20% to 36% for the Nd:YAG laser and 2% to 5% in case of the TEA $CO_2$ laser. The detection limits of Cr, Cu, and As in the wood sample using the standard LIBS technique are approximately 11, 8, and 130 mg/kg, respectively; and for the case of TEA $CO_2$ laser, namely the metal-assisted gas plas-

ma technique, the detection limits are approximately 1, 2, and 15 mg/kg for Cr, Cu, and As, respectively. The results indicate that in the case of TEA $CO_2$ laser, improved quantitative analysis can be realized. The precision and sensitivity of the results using the metal-assisted gas plasma technique are much higher than with the standard LIBS technique. The present metal-assisted gas plasma technique has potential for use in the semi *in situ* analysis of wood sample at a recycle production factory.

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