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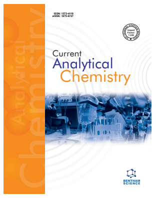

Emission Characteristics of Hydrogen and Carbon in Various Ambient Gases using Pulsed-CO_2 Laser-Induced Breakdown Spectroscopy

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Abstract: *Background*: Hydrogen (H) and Carbon (C) are major elements that occur in various materials, including organic matter. The identification and analysis of C and H are necessary for several fields. LIBS is an excellent method for such analysis because it is rapid, and can be conducted remotely. The technique has been employed for the analysis of H in zircaloy metals. However, few studies on the emission characteristics of H and C in various gases have been undertaken because of the difficulty of identifying H and C using standard LIBS techniques. In this work, the emission characteristics of H and C were studied using pulsed CO_2 LIBS. H and C elements were obtained from ethanol vapor. Various gas environments were employed, including Nitrogen (N_2), Argon (Ar), and Helium (He) gases, in order to study the stability of the laser-induced plasma, the plasma lifetime, and the excitation mechanisms of H and C.

Methods: The LIBS system used in this work consisted of a pulsed TEA CO_2 laser (Shibuya SQ 2000), pulse generator, and optical multichannel analyzer. In this work, the laser with a wavelength of 10.6 µm, pulse duration of 200 ns, and pulse energy of 3 J, was used as the irradiation source. The laser energy used was 1.5 J. The laser was irradiated, and focused, using a 200 mm zinc selenide (ZnSe) lens, onto a metal surface in order to initiate and induce a luminous plasma. The sample used in this study was ethanol vapor, obtained from ethanol (99.5%, Merck). For this purpose, 10 mL ethanol was poured into a glass beaker, and this was placed into a closed chamber that could be evacuated by ambient gases including N_2, Ar, and He gases.

Results: Identification of H emission line has been successfully carried out using this present technique demonstrated in various gases including N_2, Ar, and He. From the results, it was observed that in N_2 gas, the H_α I 656.3 nm emission line was clearly expressed, with a wide, full-width half-maximum, and quite a low emission intensity.

Conclusion: The emission characteristics of H and C in laser-induced plasma, produced in various ambient gases, including N_2, Ar, and He, were studied. The emission spectra of H_α and H_β were expressed clearly, with high intensity and low background emission, in He, while they were broad and had high background emissions in N_2 and Ar. Based on the time-resolved emissions, the H_α emission had a longer lifetime in Ar and He. It was assumed that the metastable atoms of Arand He were predominant in the excitation process of H and C. The characteristics of the H and C emissions in various gases are important in selecting a suitable ambient gas for the study of light atomic emission in the medical field, which mostly deals with organic materials containing H, C, and oxygen.

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1. INTRODUCTION

Hydrogen (H) and Carbon (C) are major elements that occur in various materials, including organic matter [1]. In the materials industries, unwanted amounts of H and C can significantly affect the mechanical properties of many metals [2-4]. In the field of biomedical science and engineering, H and C are important major elements, being constituents of all organs. Furthermore, these elements are also primary components of bacteria and viruses [5-7], which are sources of disease in humans. Therefore, the identification and analysis of C and H are necessary for several fields.

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The commonly used method to identify and analyze H is gas chromatography [8, 9]. During analysis, the material is melted in a C furnace prior to identification of the element. This requires tedious sample pretreatment and cannot be employed to perform rapid or in-situ analyses. Another method used for the identification and analysis of H and C is laser-induced plasma spectroscopy, also known as Laser-Induced Breakdown Spectroscopy (LIBS).

LIBS is an excellent method for such analysis because it is rapid, and can be conducted remotely [10-13]. In this method, a pulsed neodymium-doped yttrium aluminium garnet (Nd:YAG) laser is usually employed to induce a luminous plasma on a sample target.

In LIBS, certain parameters, including laser wavelength, laser pulse width, gas environment, and type of sample, have a significant influence on the obtained atomic emission spectra [14-16]. Compared to other conventional atomic emission methods, LIBS offers robust and rapid analysis, less sample pretreatment, and is a relatively low-cost technology. In LIBS, a pulsed Nd:YAG laser is generally used as the excitation source. LIBS has been applied to various materials, including liquids, gases, and solids. The method has also been used for the detection of H and C in solid samples; however, few studies have been undertaken on H analysis because of H disturbance from the water in gas and the sample surface, and the effects of Stark broadening and mismatching of spectral lines.

Despite this, we have successfully developed some sampling techniques for the LIBS of H and C utilizing a pulsed Transversely Excited Atmospheric (TEA) CO_2 laser. The technique has been employed for the analysis of H in zircaloy metals, as reported elsewhere [17-19]; however, few studies on the emission characteristics of H and C in various gases have been undertaken because of the difficulty of identifying H and C using standard LIBS techniques.

In this work, the emission characteristics of H and C were studied using pulsed CO_2 LIBS. H and C elements were obtained from ethanol vapor. Various gas environments were employed, including Nitrogen (N_2), Argon (Ar), and Helium (He) gases, in order to study the stability of the laser-induced plasma, the plasma lifetime, and the excitation mechanisms of H and C.

2. EXPERIMENTAL PROCEDURE

The setup of the experiment is shown in Fig. (**1a**). A pulsed TEA CO_2 laser (Shibuya SQ 2000), with a wavelength of 10.6 µm, pulse duration of 200 ns, and pulse energy of 3 J, was used as the irradiation source. The laser energy used was 1.5 J. The laser was irradiated, and focused, using a 200 mm Zinc Selenide (ZnSe) lens, onto a metal surface in order to initiate and induce a luminous plasma. The effect size of the beam at the focusing point on the metal plate was 2 x 2 mm^2, resulting in a power per unit area of the surface of 0.19 GW/cm^2.

Ethanol vapor, obtained from ethanol (99.5%, Merck), was used as the sample. For this purpose, 10 mL ethanol was poured into a glass beaker, and this was placed into a closed chamber that could be evacuated by ambient gas. The ethanol naturally produced ethanol vapor in the chamber. Pure nickel (Ni, 99.9%) was used as the subtarget for attachment of the ethanol vapor inside the chamber, and to assist in plasma generation, as illustrated in Fig. (**1b**). During data acquisition, the metal was rotated so that the laser beam always impacted new vapor onto the metal surface. Three kinds of ambient gas -high-purity N_2 (99.999%), Ar (99.999%), and He (99.999%) - were circulated inside the chamber during the experiment. The gas flow rate was controlled at 2 L per minute.

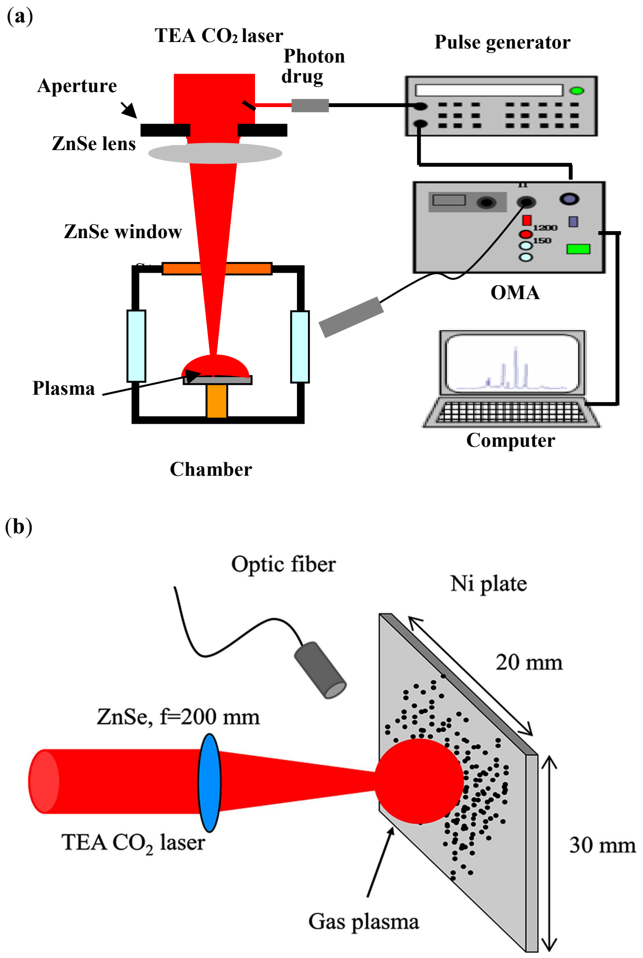

Fig. (1). (**a**) Experimental setup used in this work. (**b**) Illustration of ethanol vapor deposited on metal subtarget.

To obtain the emission spectra, an optical multichannel analyzer (OMA system, ATAGO Macs-320) was used. To this end, the laser-induced plasma emission was sent to the OMA system *via* an optical fiber, which was connected to the OMA. The repetition rate of the pulsed laser was 10 Hz.

3. RESULTS AND DISCUSSION

The initial mechanism of plasma generation, utilizing a pulsed TEA CO_2 laser, assisted by a metal subtarget, has been reported in our previous work [20]. Plasma generation using a TEA CO_2 laser, assisted by a metal subtarget, is significantly different from the standard LIBS method, using a pulsed Nd:YAG laser. When the laser beam was irradiated and focused on the metal subtarget, electrons were emitted from the metal subtarget through a photoelectric effect due to a multiphoton absorption process. The emitted electrons are accelerated by the electrical fields associated with the optical pulse in the period between collisions, which acts to thermalize the electron energy distribution. As the electron energies grow, collisions produce ionization, other electrons, more energy absorption, and an avalanche occurs, resulting in obtaining the initial gas breakdown plasma. Immediately after the gas breakdown plasma is produced, the plasma further absorbs the latter part of the laser pulse energy through free-free transition (inverse Bremsstrahlung). The produced plasma is much stronger using the TEA CO_2 laser than the Nd:YAG laser because the plasma absorption coefficient depends strongly on the laser light frequency, it is proportional to the inverse square of the frequency of the laser light. Moreover, the pulse duration of the TEA CO_2 laser is relatively long, at around 200 ns, which is about 20 times longer than typical for a Nd:YAG laser. As a result, in the TEA CO_2 laser case, almost all the laser light energy is converted into gas breakdown plasma, inducing a strong, large volume of this. It should be stressed that, in this case, the metal subtarget is never damaged or ablated due to the fact that the strong gas breakdown plasma absorbs most of the laser energy (plasma shielding effect), thus no damage occurs to the metal surface. In this case, the metal surface works only as the source of the electrons initiating the gas breakdown plasma.

First, identification of H and C was carried out using metal-assisted LIBS. Fig. (**2**) illustrates the emission spectrum of Hα at 656.3 nm, obtained from the ethanol vapor deposited on the Ni metal target with various circulating gases - (a) N_2, (b) Ar, and (c) He. From Fig. (**2**), it can be seen that, in N_2 gas, the H_α I 656.3 nm emission line was clearly expressed, with a wide, full-width half-maximum, and quite a low emission intensity. An unknown wide line was also strongly expressed at around 647 nm. It should be noted that, in the emission spectra, including the N_2, Ar, and He gases, no Ni emission lines contributed by the Ni metal were observed, although a large volume of plasma, with a diameter of around 10 mm, was produced. This result confirmed that, when the laser beam, with an energy of 1500 mJ and focusing point of 200 mm, was irradiated on the Ni plate, no ablation of Ni metal occurred, and the luminous plasma came only from the gas in the environment. Thus, no Ni emission line was detected. This is because the power density of Ni metal is much higher than the power density of laser irradiation on a Ni metal surface. Therefore, the laser beam cannot ablate the Ni metal plate, as reported in our previous study [20].

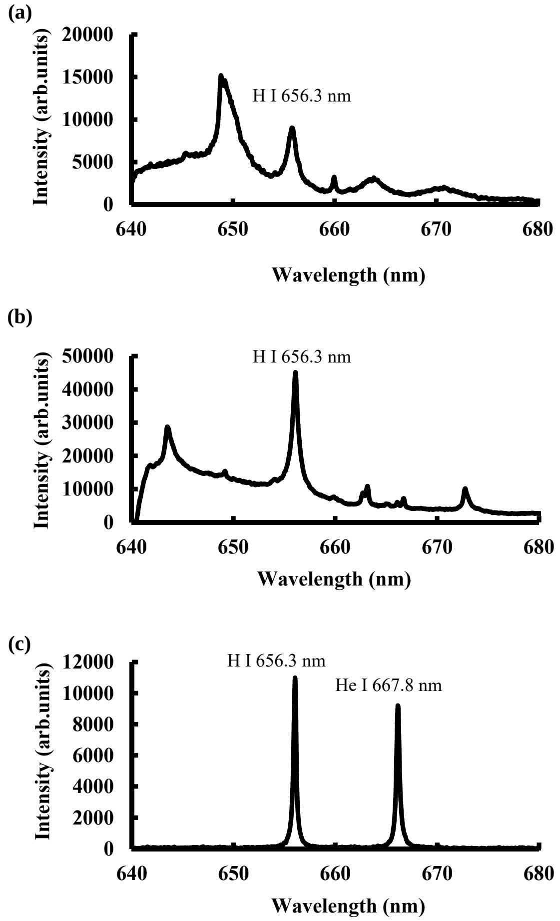

Fig. (2). Emission spectra of Hα (H I 656.3 nm) obtained from various surrounding gases, (**a**) N_2, (**b**) Ar, and (**c**) He, using LIBS with a pulsed CO_2 laser.

In this study, the Ni metal only works as a subtarget. It should be understood that, in LIBS, the sample target used for analysis needs to possess certain characteristics in order to be able to induce a plasma with a high temperature. A strong repulsion force needs to be induced for high-temperature plasma generation. A strong repulsion force can be induced only when the sample target surface is hard. Therefore, in case of film analysis present in this study, hard Ni metal served as the support for initiating the luminous plasma.

Figs. (**2b** and **2c**) show the emission line of H_α I at 656.3 nm, obtained from ethanol vapor in Ar and He gas, respectively. The H emission line from the Ar and He gases has a higher emission intensity than the N_2 gas (Fig. **2a**), Specifically, the H line in He gas has a much narrower spectral width and is more sharp, compared to the Ar and N_2 gases. It can be expected that, with a low atomic mass, He will equilibrate with H atoms produced by the thermal decomposition of ethanol (Fig. **2c**), whereas broadening (Figs. **2b** and **2c**) occurs due to inelastic energy transfer. We assumed that, in the excitation process of the H atoms in the laser-induced plasma, two excitation mechanisms would take place. First, the excitation process of H occurs in the high-temperature region of the shock-wave plasma because a strong shock-wave is induced in the laser-induced plasma, resulting in a high plasma temperature. The second possible mechanism is excitation of the H taking place *via* metastable states. It is known that the excitation energy of H I 656.3 nm is 12.1 eV. When metastable atoms have a higher energy than 12 eV, they might play a role in the excitation process.

It is known that the metastable energies of N_2, Ar, and He are 6.2 eV, 11.7 eV, and 19.8 eV, respectively [19]. As seen in Fig. (**2**), in the case of N_2 gas, the emission spectrum is quite broad, with low emission intensity. We assume that, in the case of N_2, the excitation process of H takes place in the high-temperature plasma *via* the shock-wave plasma mechanism, rather than *via* the metastable state because the energy of the metastable level of N_2 is much lower than the excitation energy of H. Thus, the excitation process happens in the initial stage of plasma generation, resulting in Stark broadening, as seen in Fig. (**2a**). The high background emission is due to the low ionization energy of N_2 (15.6 eV), which results in a high probability of N_2 gas being ionized, thereby increasing the population of ionized N_2 and free electrons in the plasma region.

In the case of Ar gas, as shown in Fig. (**2b**), it is assumed that the excitation process takes place *via* Ar metastable atoms due to the fact that the energy level of metastable Ar is 11.7 eV, similar to the H I 656.3 eV. The wide spectral width and high background emission are due to many free electrons being produced in the plasma because the ionization energy of Ar is only 15.75 eV, which gives a high probability of producing free electrons and ions. Those electrons and ions still remain in the later stage of plasma emission because of the low ionization energy of Ar. The free electrons and ions are responsible for the Stark broadening effect, which results in a wider spectral emission.

For the He gas, we assumed that the excitation process occurred through metastable He atoms, rather than the shock-wave plasma mechanism. This is because the energy of metastable He is much higher (19.8 eV) than the excitation energy of H I 656.3 nm. In the case of excitation *via* metastable atoms, the process takes place at a later stage, when the electrons and ions, which contribute to the Stark broadening effect, have been disappeared. Therefore, the emission spectrum of H I 656.3 nm has a narrow spectral line, with low background emission intensity, because Stark broadening did not contribute to the excitation process. The assumption of an excitation process *via* metastable He atoms in this study was confirmed using the time-resolved emission of H I 656.3 nm, as presented below.

Fig. (**3**) illustrates the emission spectra of H_β (H I 486.1 nm) taken from ethanol vapor in the gas environment of (a) N_2, (b) Ar, and (c) He. From this, it can clearly be seen that many unknown analytical lines occur in the spectrum of the N_2 gas environment; however, the H_β emission line does not appear completely (Fig. **3a**). When the gas was changed to an Ar environment, the H_β line still did not appear due to the disturbance of many Ar lines that occurred as depicted in Fig. (**3b**). Other phenomena occurred when He gas was introduced as the gas environment. Namely, the H_β emission line became clearly detectable at a wavelength of 486.1 nm, as shown in Fig. (**3c**). In addition, other lines contributed by the gas environment were observed. The upper level energy of H_β is 12.7 eV.

Another experiment was carried out to determine the effects of the various gases in the environment on the emission spectrum of C. Fig. (**4a**) shows the emission spectrum of C taken from ethanol vapor using the presented technique in N_2 gas. An emission line of neutral C, at a wavelength of 247.8 nm, is present with high emission intensity. The high intensity of the C line was also clearly detected when the gas environment was replaced by Ar (Fig. **4b**). Also, the intensity of the background emission was high in both the N_2 and Ar gases, as shown in Figs. (**4a and 4b**), respectively; however, a different spectral pattern was exhibited in the case of the He gas environment (Fig. **4c**), with the emission line of C being detected with high emission intensity, but low background emission, which is dissimilar to that of N_2 and Ar. The high background emission shown in the C emission spectrum in Ar gas can be explained by the differential ionization energies of He (24.58 eV) and Ar (15.75 eV). Ar thus has a higher potential for being ionized, thereby increasing the population of Ar and N_2 ions and free electrons. This supposes that the excitation process of C in He gas takes place through metastable He atoms, as in the case of H.

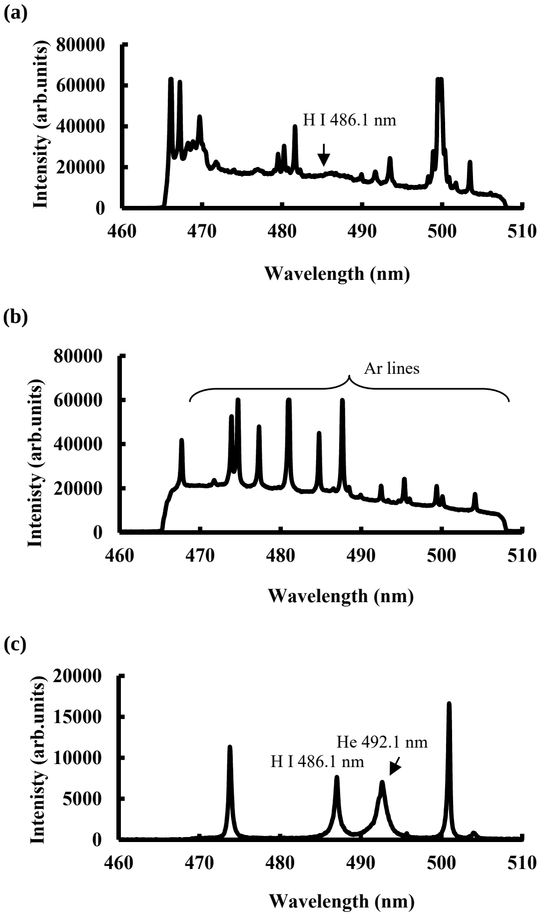

Fig. (3). Emission spectra of H_β(H I 486.1 nm) obtained from various circulatinggases, (**a**) N_2, (**b**) Ar, and (**c**) He, using LIBS with a pulsed CO_2 laser.

In order to study the characteristics of H and C in the gas plasma induced in various gases, plasma reproducibility was examined through a number of laser shots. Plasma stability is necessary in order to apply the present method in a quantitative analysis. Fig. (**5**) illustrates the effect of the number of

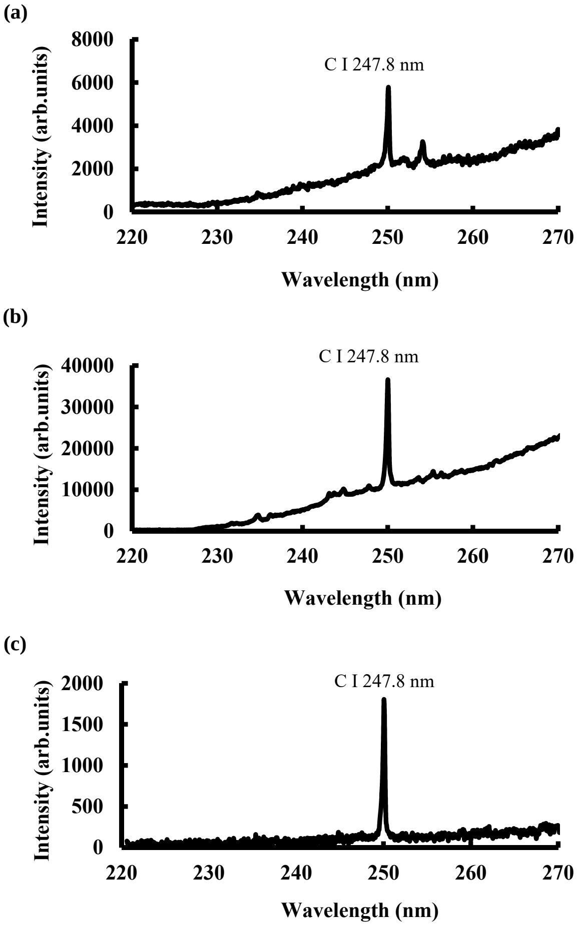

Fig. (4). Emission spectra of C I 247.8 nm obtained from various circulating gases, (**a**) N_2, (**b**) Ar, and (**c**) He, using LIBS with a pulsed CO_2 laser.

laser shots on the emission intensities of H_α (H I 656.3 nm), H_β (H I 486.1 nm), and C taken from ethanol vapor in the various gas environments of (a) N_2, (b) Ar, and (c) He. During acquisition, the gate delay and gate width of the OMA system were 5 µs and 50 µs, respectively. Each point plotted in the curve was obtained using 10 shots of laser bombardment. As seen from Fig. (**5**), the emission intensities of H and C are almost constant with the number of laser shots, regardless of gas environment. This confirmed that the present technique can be used to study the emission characteristics of H and C.

In order to examine the excitation processes of H and C using the present technique, the time-resolved emissions of H_α (H I 656.3 nm), H_β (H I 486.1 nm), and C were examined. To this end, the gate width of the OMA system was set at 0.5 µs for each point of the gate delay time. Fig. (**6a**) shows how the Hα intensity changed with plasma lifetime. It can be seen that, with N_2 gas, the intensity of Hα sharply increased up to 3 µs, and then decreased, with a plasma emission time of 15 µs. For Ar, the emission intensity increased up to 3 µs, and then decreased slightly, becoming almost stable up to 50 µs. For He, the intensity sharply increased up to 3 µs, and then decreased to 30 µs. A peculiar phenomenon occurred with Ar and He, in which the emission intensity lifetime was much longer than that of N_2.

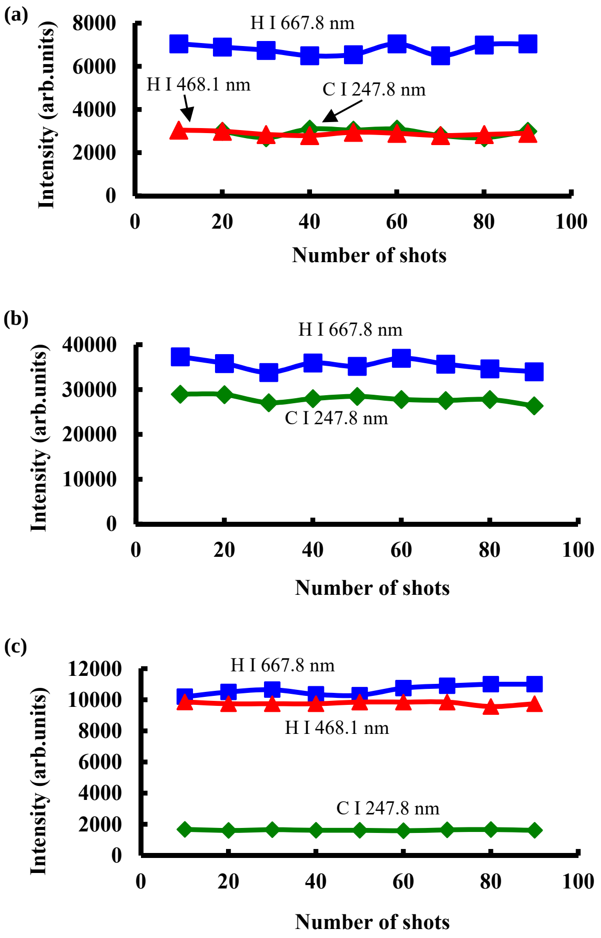

Fig. (5). Emission intensities of Hα (H I 656.3 nm), H_β (H I 486.1 nm), and C (I 247.8 nm) *versus* number of laser shots obtained from various surrounding gases, (**a**) N_2, (**b**) Ar, and (**c**) He, using LIBS with a pulsed CO_2 laser.

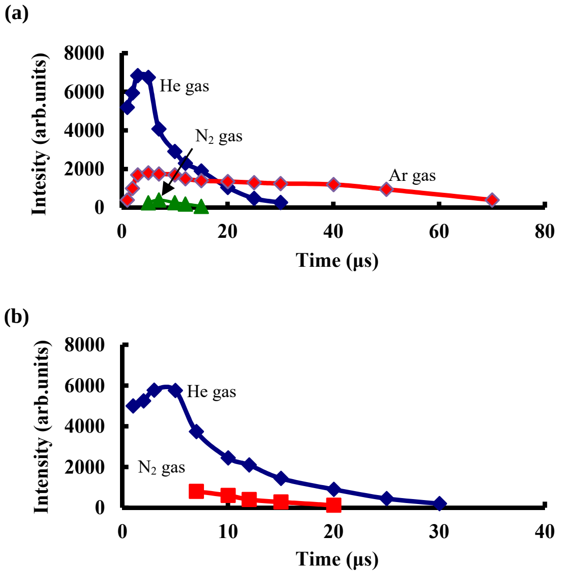

Fig. (6). Time-resolved emission of (**a**) Hα (H I 656.3 nm) and (**b**) H_β (H I 486.1 nm) using LIBS with a pulsed CO_2 laser.

The emission spectra of H_α in N_2 and CO_2 gases are much shorter than that in He gas. This might be due to different excitation processes of H_α in the different gases. Based on our assumption above, and our previous study [21], the excitation process of elements in He takes place through metastable He atoms, which have a long lifetime in the plasma region. Therefore, the emission of H_α has a long lifetime because the metastable He atoms continually supply the energy to excite the H emission. With the other gases, however (N_2, Ar, and CO_2), the excitation process happens *via* high temperature in the shock-wave plasma during initial laser plasma generation. Therefore, in the case of N_2 gas, the lifetime of H_α emission is quite short, at around 15 μs, because the plasma temperature in the later stage decreases due to the recombination of free electrons and ions. For Ar and He, the excitation process *via* metastable state is predominant because the Ar and He metastable energy is much higher than the excitation energy of H. As presented in a previous study [17], in the case of excitation through metastable atoms, the emission lifetime of the atoms is prolonged because the excitation process takes place at a later stage, after the recombination process occurs. The emission lifetime of Hα in the case of Ar is the longest because the ionization energy of Ar is only 15.75 eV, which has the high potential to produce free electrons and ions, and therefore produce many metastable atoms, thus resulting in a longer emission lifetime. In order to support our assumptions, the time-resolved emission of H_β was also determined, as illustrated in Fig. (**6b**). This shows consistency with our assumption that, for He, the lifetime of H_β remains long compared to N_2. For Ar, we could not produce a time-resolved emission because the H_β emission disappeared as a result of the disturbance of the Ar emission lines. These results are consistent with those from our previous study that showed that, in the case of H in He gas, the excitation process takes place through metastable He atoms.

CONCLUSION

The emission characteristics of H and C in laser-induced plasma, produced in various ambient gases, including N_2, Ar, and He, were studied. The emission spectra of H_α and H_β were expressed clearly, with high intensity and low background emission, in He, while they were broad and had high background emissions in N_2 and Ar. Based on the time-resolved emissions, the H_α emission had a longer lifetime in Ar and He. It was assumed that the metastable atoms of Ar- and He were predominant in the excitation process of H and C. The characteristics of the H and C emissions in various gases are important in selecting a suitable ambient gas for the study of light atomic emission in the medical field, which mostly deals with organic materials containing H, C, and oxygen.

ETHICS APPROVAL AND CONSENT TO PARTICIPATE

Not applicable.

HUMAN AND ANIMAL RIGHTS

No animals/humans were used for studies that are the basis of this research.

CONSENT FOR PUBLICATION

Not applicable.

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CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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Declared none.

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