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Analytical note

Double pulse spectrochemical analysis using orthogonal geometry with very low ablation energy and He ambient gas

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ABSTRACT

An experimental study of double pulse LIBS is performed for the development of highly sensitive and quantitative analysis of Cl and Ca for the strength evaluation of concrete. The two lasers employed are arranged in orthogonal geometry and operated for delayed ablation with delay time of 10 μs, using He ambient gas at atmospheric pressure. The very large intensity enhancement is obtained over those detected with single pulse operation without generating the He plasma. It is most remarkable that the same sharpness and intensity enhancement observed in the previous double pulse experiment with 37 mJ laser ablation energy is achieved in the present experiment with much lower ablation energy of merely 2.5 mJ, resulting in average crater size of about 10 μm in diameter. Further, a linear relation is obtained between the Cl concentration and its emission intensity in alumina samples, while an estimated limit of detection of 80 ppm is obtained by using concrete sample, which is adequate for highly sensitive quantitative Cl analysis in concrete.

1. Introduction

Thanks to its unique practical advantages over the more conventional spectroscopic methods, the laser induced breakdown spectroscopy (LIBS) first introduced in l962 [1] has enjoyed tremendous growth of applications in industry and research laboratories [2]. Along with its continued technical improvements and increased popularity, intensive studies for overcoming its relatively low sensitivity have also been conducted early on for more than a decade [3–8]. In more recent works on solid samples, double pulse setup were employed in either collinear or orthogonal geometries with various time delays between the two laser pulses [9–16]. All those reports show emission intensity enhancement in most cases over the results obtained by single pulse operation. However, the degree of intensity enhancement varies significantly depending on the sample used and the applied ambient air pressure [17] or the kind of ambient gas used [18]. The samples investigated in those studies are nevertheless limited mostly to metals. The enhancement effect observed in the case of pre-ablation spark employing orthogonal double pulse geometry was shown to be closely related to the increase of ablated material, signifying an increased effectiveness of the ablation process due to the rarefied gas condition created by the preceding laser shot. This was also shown to result in the increase of crater size or the destructive effect [4,15]. On the other hand, in the case of delayed second pulse directed to the ambient air, the enhancement was attributed to reheating effect [4,16].

In the mean time, an alternative approach for enhancing the emission intensity and improving the spectral quality (reducing the background emission and signal line width) has also been pursued by using He ambient gas in place of air. The early studies of the related effects date back to the 1990s [19–22] employing single pulse arrangement. Some of those studies on the effect of He ambient gas have suggested the possible role of meta stable He excited state in providing the energy for the additional delayed excitation of the ablated atoms. It was assumed that as a result of this excitation mechanism, the delayed emission is relatively free from the Stark broadening effect caused by the early presence of charged particles in the plasma. This suggested scenario has offered a plausible explanation for the sharp emission line of Hα observed with He ambient gas at low [23–25] as well as atmospheric pressure [26–32]. The Hα emission line is otherwise known to be poorly detected in ambient air or in nitrogen surrounding gas [33–35]. This experimental result was further corroborated in the detection of deuterium (D) emission line as well as the complete resolution of H and D emission lines of 0.18 nm separation [35]. Assuming the possible role of meta stable He excited state, we were led to contemplate the possibility of

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separating the processes of sample ablation from the excitation of ablated atoms in the separately generated He plasma. In such an experimental arrangement, one is allowed to explore separately the laser energies used as well as the time delay between the two laser pulses, taking into account the need to reduce the thermal and Stark effect, while allowing the He assisted excitation process to play its dominant or perhaps exclusive role without the need of generating the hot plasma consisted of the ablated atoms. This idea was implemented in an orthogonal double pulse scheme for the analysis of zircaloy samples reported recently [36]. While being short of comprehensive experimental support for the solid theoretical explanation of the physical mechanism involved, the reported result clearly demonstrates the benefits of the experiment for intensity enhancement as well as reduction of the ablation energy. In view of the rather remarkable effect observed in that experiment, it is desirable to further verify the result and explore the possibility for further improvement.

The present study is carried out for the above mentioned purpose by applying the same experimental method to the analysis of Cl and Ca of some samples from widely used materials. It is well known that the excessive presence of Cl in concrete will deteriorate its strength and jeopardize its function, and the penetration of chlorine into the concrete structure is a rather common process. An early or regular inspection of Cl content in concrete is therefore necessary especially for buildings located in areas of significant sea water intrusion. The reported limit of detection (LOD) of Cl in concrete achieved with standard LIBS remains so far relatively poor (>5000 ppm) [37,38] which is inadequate for the the required sensitivity. Meanwhile Ca as a host element in cement which is a major material component of concrete, has recently been shown to be useful in its spectroscopic analysis for the estimation of the concrete compressive strength [39]. Apart from verifying the viability of the previously proposed orthogonal double pulse method with He ambient gas, this study is also aimed at two other goals. One is the investigation of concentration–intensity relation for its potential application to quantitative analysis. The other one is to explore the possibility of further reducing the ablated material by applying lower laser ablation energy and thereby minimizing the resulted crater size in order to satisfy the requirement of practically non-destructive spectrochemical analysis.

2. Experimental procedure

The experimental setup used in this work is exactly the same as the one introduced in a previous study [36]. Its schematic diagram is reproduced in Fig. 1 for easy reference. The two Nd–YAG laser systems are set up in orthogonal geometry and both of them are operated in the Q-switched mode with a repetition rate of 10 Hz. They are employed to perform two different tasks. The one operating at its fundamental wavelength of 1064 nm and fixed energy of 110 mJ is focused to generate a small He gas plasma at a spot 5 mm in front of the target. The pressure of the ultra high purity (6 N) He gas in the chamber is maintained in all measurements at 760 Torr by a constant He flow rate of 2 l/min. The second laser was operated at the second harmonic wavelength of 532 nm for the ablation of the solid target, which is switched on 10 μs after the generation of He plasma by the first laser. This choice of the delay time was made on the basis of previous experimental result [36] which shows that more than half of the maximum He emission intensity reached at 5 μs after the He plasma generation is still retained 5 μs later. It implies that a large number of the He atoms in the plasma may remain in their metastable excited state by then, while allowing the He plasma sufficient time to cool itself down. We note further that instead of operating this ablation laser at a fixed energy as we did with the first laser, the energy of the second laser is to be varied in some parts of the experiment as explained later in due places. The emission spectrum from the plasma is collected by an optical fiber with its entrance end facing the plasma and fixed inside the chamber at a distance of 1 cm sidewise from the

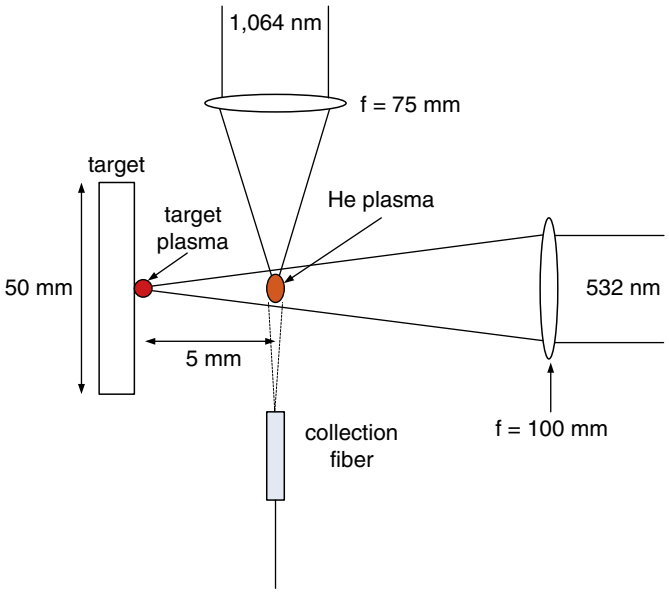

Fig. 1. Diagram of the experimental setup.

He plasma. The other end of the fiber is connected to the detection system consisted of a spectrograph and Optical Multichannel Analyzer which is operated with 50 ns gate delay and 30 μs gate width for all measurements. Each spectral data point presented in this paper is the average of 100 data produced by 100 successive laser shots on the same spot of the sample.

In view of the use of He ambient gas and its suggested possible role in providing the delayed excitation energy source, the two-laser setup employed in the current study is operated with an experimental scheme different from those adopted previously with similar experimental set up cited earlier. Specifically, the experimental setup described above will be operated in two different modes, namely the standard single pulse (SP) LIBS and the double pulse (DP) LIBS operation. In the first case, the short wavelength laser alone is used for simultaneously target ablation and generation of the gas-breakdown-induced hot plasma. In the second case, the short wavelength laser is solely used for target ablation at much lower energy of a few mJ, while the long wavelength laser is operated for the creation and preparation of a cooled He-plasma 10 μs prior to the ablation process. The sample for the study of Ca emission is prepared from a fresh wood of Tectonia Grandii which is widely used for making artifacts, while the study of Cl emission is carried out on sample of black plastic sheet which is extensively found in industrial applications and is known to contain high chlorine concentration. Additionally, a series of alumina samples prepared with different chlorine concentrations are measured for the study of intensity–concentration correlation, and a special concrete sample was also prepared with 0.04% of chlorine for the determination of its estimated limit of detection.

3. Experimental results and discussion

Presented in Fig. 2 are emission spectra of the fresh wood sample measured in the SP LIBS mode with different green laser energies in the spectral range between 418 nm and 426 nm. It is seen that the Ca I 422.6 nm emission line remains faintly observable even with the laser energy raised to 14 mJ. The strong and sharp emission line exhibiting the standard sharp emission spectrum of LIBS as shown in the figure is obtained with laser energy of 135 mJ. This relatively large laser energy is found to leave a crater of about 0.7 mm diameter on the sample surface, which may hardly be suitable for minimally destructive or practically non-destructive analysis required for some important applications.

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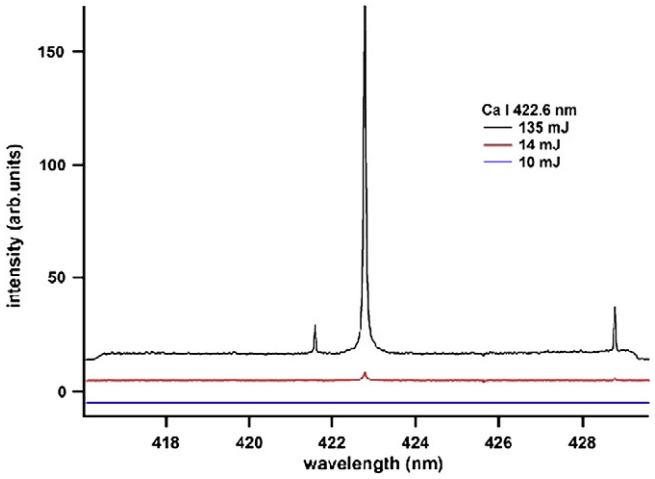

Fig. 2. Fresh wood spectrum showing Ca I 422.6 nm emission line in the wavelength region from 418 nm till 428 nm at different ablation laser energy in the absence of cooled helium plasma. The gate delay and width of the OMA system were set at 50 ns and 30 μs, respectively after the laser-target ablation.

The same sample is then measured in the DP LIBS mode by operating both laser systems in the sequential order described earlier. The resulted emission spectra are shown in Fig. 3(a) and (b) for different ablation energies. In each figure, the result obtained with SP LIBS at the same ablation energy is also presented along for comparison.

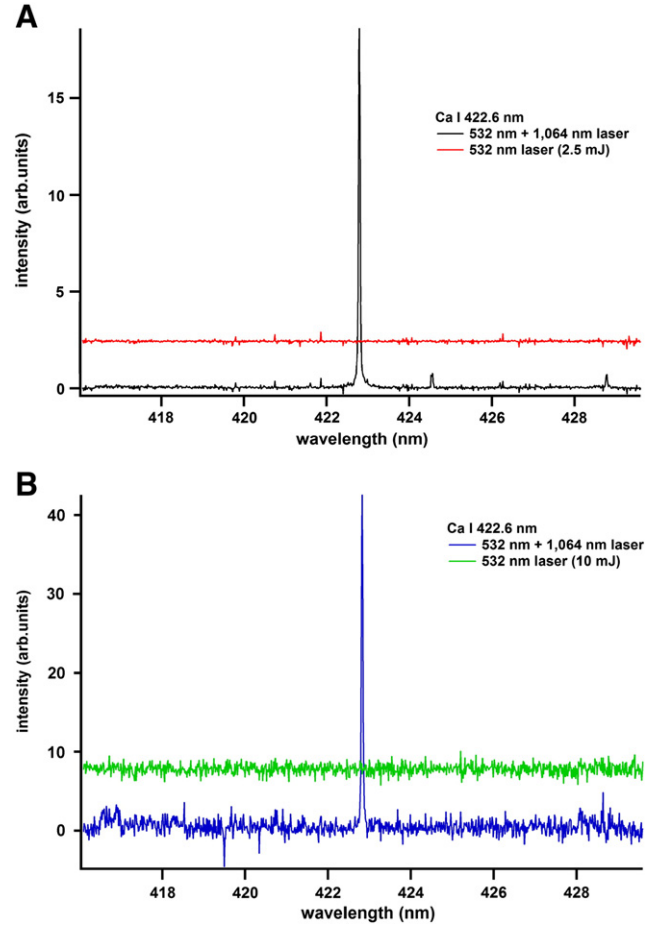

Fig. 3. Fresh wood spectrum showing Ca I 422.6 nm emission line in the wavelength region from 418 nm till 428 nm at different ablation laser energy of (a) 2.5 mJ and (b) 10 mJ in the presence and absence of cooled helium plasma. The gate delay and width of the OMA system were set at 50 ns and 30 μs, respectively after the laser-target ablation.

One observes that the Ca emission produced in the SP LIBS mode is hardly perceptible in either case while the improvement in Ca emission signal detected in the presence of cooled He plasma induced in DP LIBS operation is truly remarkable or even dramatic considering the very small ablation energy (2.5 mJ) employed. It must be pointed out that the detected Ca emission is unlikely to have its major contribution coming from the signal induced in the ablation process near the sample surface, since the geometrical arrangement and the numerical aperture of the light collecting fiber can only collect the light entering the fiber end within the solid angle of 27° subtended by the He plasma. This result therefore offers further indication of the possible role of He assisted excitation effect as suggested previously [36]. Admittedly, no existing theory or experiment result is available for explaining the detailed physical processes responsible for the excitation observed in the specific experimental condition considered here. In analogy with those experimental conditions considered in much earlier studies on Penning collision induced ionization processes [40–45], a Penning like process was proposed to describe the large energy transfer process involved in the hypothesized He assisted excitation process as described below:

$$\mathrm{He}*(1)+\mathrm{X}(2)\rightarrow\mathrm{He}(2)+\mathrm{X}^{+*}+\mathrm{e}(1) \quad (1)$$

where the numerals 1 and 2 are labels for the electron identities associated with their initial atomic hosts and $X^{+*}\rightarrow H^{+}$ in the special case of H atom, with the released electron and the excited ionic state X atom (for X = H, one has $X^{+*}\rightarrow H^{+}$) carrying off the excess energy. The observed emission is then related to the de-excitation process taking place after the subsequent recombination of X^{+} with e(1). Clearly this proposed scenario is in need of further experimental verification. In view of the presence of rarefied gas condition during the ablation process, this is at best regarded as an important partial contribution to the intensity enhancement effect which has also been suggested as arising from the increased effectiveness of the ablation process in the pre-ablation DP experiments.

It is worthwhile to note that the large intensity and sharpness of Ca emission obtained in the DP operation with the much smaller ablation energy of 2.5 mJ is completely comparable with that obtained previously at ablation energy of 37 mJ [36], which is more than one order of magnitude larger. It is further found that the crater created by 2.5 mJ ablation energy is merely about 10 μm in diameter, which is more than one order of magnitude smaller than the 0.6–0.7 mm crater size found in the pre-ablation spark DP LIBS measurement using much higher ablation energy [4]. Further comparison of Fig. 3 (a) with (b) shows that one does not have much to gain by increasing the ablation energy. Namely, the increased intensity is acquired at the expense of undesirable increase of the background emission and very likely a larger crater size as well. We shall therefore stick to the 2.5 mJ ablation energy in the following measurements.

The next sample considered is the black plastic sheet which is known to have high Cl content. Its emission spectrum is measured in both SP and DP modes with varied ablation laser energy. The resulted intensity variations measured with the ablation energy varied over the range from 0.5 to 75 mJ is presented in Fig. 4. It is seen that the Cl emission intensity produced in the DP operation at the very low ablation energy far exceeds the intensity detected without generating the He-plasma (SP operation), although the former rises more rapidly than the latter with increasing ablation energy. The Cl emission spectra measured in both modes at this ablation energy are given in Fig. 5, which displays qualitatively the same variation as the result obtained previously with 37 mJ ablation energy [36]. As it is found in the case of Ca analysis, further increase of ablation energy does not offer significant gain of the resulted DP LIBS spectrum. It is worth noting that despite the faster rise of intensity with increasing laser ablation energy measured in the SP LIBS mode, equalization of the two appears to require the operation at the much higher

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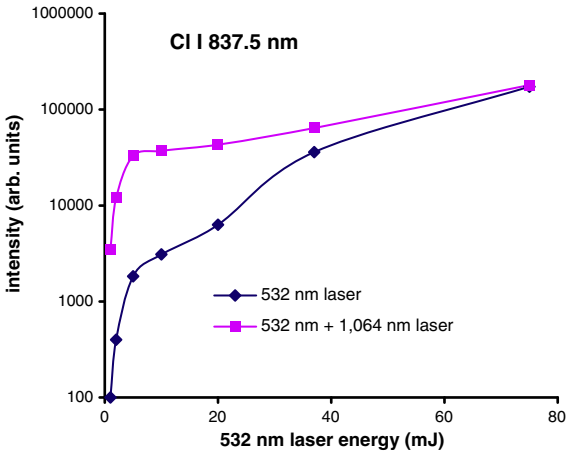

Fig. 4. The measurement of detailed energy-dependent of Cl I 837.5 nm intensity variations of the ablation laser from the cooled He plasma along with those detected at the same spot without generating the He plasma. The gate delay and width of the OMA system were set at 50 ns and 30 μs, respectively after the laser-target ablation.

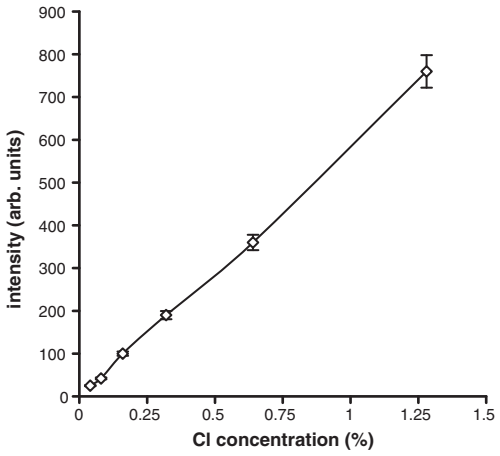

Fig. 6. Calibration relations obtained from alumina samples doped with various concentrations of chlorine impurity (0.04%, 0.08%, 0.16%, 0.32%, 0.64% and 1.28%).

ablation energy of around 75 mJ, which is likely to result in a crater too large to be acceptable for minimally-destructive analysis.

Given the favorable observations described above, we went on to investigate the possibility of its application to quantitative analysis. For this purpose, a series of DP LIBS measurements with 2.5 mJ ablation energy were carried out on a number of alumina samples prepared with different concentrations of doped chlorine. The measurements were repeated on five different spots of the same sample surface. The results of these measurements were found to be highly reproducible, implying the uniformity of the impurity Cl distribution in the sample. The averages of those five measurement results for each of the six samples with different impurity concentrations (0.04%, 0.08%, 0.16%, 0.32%, 0.64%, and 1.28%) are then plotted in Fig. 6. It is seen that the relation between the Cl impurity concentration and its associated emission intensity nicely fits a linear relation adequate for quantitative analysis. Further, a near zero extrapolated intercept as shown in the figure indicates the presence of background equivalent concentration of only 50 ppm. For an estimation of the detection limit, the emission spectrum of a concrete sample containing 0.04% of Cl was measured. The LOD was obtained following the conventional criterium for estimating the detection limit as a ratio of the signal to three times the noise level. The estimated LOD for Cl obtained according to this rule was found to be around 80 ppm, which is much lower than the 5000 ppm LOD reported before from the concrete sample using the standard LIBS measurement [37,38].

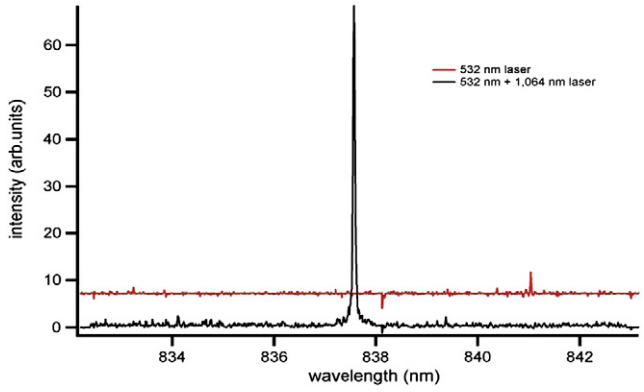

Fig. 5. Black plastic spectrum showing Cl I 837.5 nm line in the wavelength region from 833 nm till 842 nm at ablation laser energy of 2.5 mJ in the presence and absence of cooled helium plasma. The gate delay and width of the OMA system was set at 50 ns and 30 μs, respectively after the laser-target ablation.

4. Conclusion

We have performed in this work the measurement of single pulse (SP) and double pulse (DP) LIBS spectra of Ca and Cl using two lasers in orthogonal geometry and He ambient gas. It is shown that the remarkable intensity enhancement much like the effect reported previously from other analytes observed with 37 mJ ablation energy is also observed in this experiment. It is especially noteworthy that the result shown in this work is achieved with much lower ablation energy of 2.5 mJ, resulting in much smaller crater size of about 10 μm, which promises its application for practically non-destructive analysis. Further, a linear concentration–intensity relation is also found for Cl emission in alumina samples. Using concrete sample, we obtained an LOD of 80 ppm, which offers its potential application to highly sensitive and quantitative spectrochemical analysis, particularly for the much needed regular and early chlorination inspection of concrete.

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