Investigation into time evolution of chlorine emission in pulsed CO$_2$ laser induced breakdown spectroscopy (LIBS)

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Abstract. Detection of chlorine (Cl) using LIBS technique is greatly influenced by experimental conditions including the delay time of the detecting device. Time evolution of Cl emission in plasma produced on polyvinyl chloride (PVC) sample using CO$_2$ laser with variation of delay time has been carried out. The plasma was produced at atmospheric pressure under different environment of helium and air, respectively. It was found that when using the pulse energy of 750 mJ under helium surrounding, strong emission line of Cl at 479.45 nm can be observed until 4 µs of delay time, while when using laser energy 2500 mJ strong Cl emission line can be observed until 7 µs. The higher signal to background ratio was observed at delay time of 1 µs. However, Cl emission line cannot be detected under air environment.

1. Introduction

LIBS is a technique for analyzing various samples, both solid, gas and even liquid samples. In general, LIBS is an atomic emission spectroscopic technique, which qualitative and quantitative analysis are made by monitoring the intensity and wavelength of emission lines from the consequent breakdown. LIBS is a powerful analytical tool for analysis of environmental samples. This is because LIBS has many advantages including being able to detect many elements in one measurement, minimal sample preparation and only requires a small sample size [1-2], thus capable to fast monitoring of harmful elements in the environment [3-5].

Cl is a dangerous element at high concentration and it can promote corrosion in steel bones of buildings [6]. Cl content in the environment can increase through industrial waste and natural disasters. Cl detection in environment especially soil samples by LIBS is still a big challenge. Environmental samples have very complex matrices, while Cl generally present as a trace element. Therefore, before carrying out Cl detection in the actual environmental samples, Cl emission dynamic in LIBS was studied using PVC sample, containing Cl as host element.

It was reported detection of Cl with LIBS using a fundamental Nd-YAG laser of 1064 nm, the Cl atomic emission line at 837.5 nm and 134.72 nm is commonly used [7-11]. However, detector system
with ICCD camera is less sensitive for infrared (IR) region and expensive, while a special optical fibre is required for detection at ultraviolet (UV) wavelengths [12-13]. In other study, Cl detection using a transversely excited atmosphere (TEA) carbon dioxide (CO\textsubscript{2}) laser has successfully detected ionic Cl at visible wavelength from plastic sample [14]. However, Cl cannot be detected in soil sample even though the soil sample have intentionally been added by Cl as much as 1000 ppm [15]. This is because the soil sample has a very complex matrix and Cl is one of the elements difficult to detect because its high excitation energy. Experimental conditions such as laser pulse energy, delay time of the detector and ambient gas greatly affect LIBS measurement. This study was conducted to investigate Cl emission in the CO\textsubscript{2} laser induced breakdown from a PVC sample since Cl is the main constituent in the sample. To search for the optimum conditions, the experimental parameters namely delay time of detection and pulse energy were varied.

2. Experimental procedure
LIBS experiment setup used in this study is similar to the previous research [15]. Lasers used to generate plasma is the TEA CO\textsubscript{2} laser with different pulse energy of 750 mJ and 2500 mJ, respectively. PVC samples have been cut to slide with a dimension of 15 mm x 15 mm and a thickness of 0.73 mm. The sample was attached to the metal plate sample holder and placed in the chamber. Emission spectra from the plasma was recorded by varying the gate delay of the optical multichannel analyser (OMA) system ranging from 0.1 to 10 µs. Measurements was carried out in helium and air environments at a pressure of 1 atm. For Cl detection, the wavelength of each emission line will be fitted to database published by national institute of standard and technology (NIST), United State of America (USA) [16].

3. Result and discussion
The problem in selecting ionic emission lines for carrying out a qualitative and quantitative analysis is that ions only form at the beginning of plasma formation and then decay due to the effects of recombination and cooling of the plasma. Thus, variations in delay time are needed to determine the optimum spectrum recording time.

![Figure 1](image1.png)

**Figure 1.** Spectrum emission of PVC samples in (a) air and (b) helium environments with variation of delay time.

Figure 1 shows emission spectrum detected from plasma produced on PVC sample using the TEA CO\textsubscript{2} laser at different delay time under (a) air and (b) helium surrounding gas, respectively. In case air surrounding gas, Cl ionic emission line cannot be detected. While in the previous work, it was confirmed that Cl emission lines, namely ionic emission lines can clearly detected in this wavelength
region [14-15]. When air was replaced by helium, Cl ionic emission lines in the visible region appear clearly started since the delay time of 0.1 µs. However, at early regime the emission spectra are suppressed by high background. Cl emission line still can be observed after delay time of 7 µs. At the early stages of plasma formation, signal emissions from governing species are still covered by continuum emission with very high background. Continuous emission is caused by two possible processes, namely recombination radiation and bremsstrahlung [17]. Over time, both continuum and signal emissions will decay, however continuum emissions decay faster than signal emissions [18]. It takes the right delay to produce optimum spectrum with high signal intensity and low background. At the beginning of the nanosecond regime, plasma has not yet been formed and the emission lines of all species cannot be observed.

![Figure 2. Spectrum Emission of PVC samples in (a) air and (b) helium environments.](image)

Figure 2 shows the spectrum obtained in the air and helium gas environments using laser pulse energy of 2500 mJ and a delay time of 2 µs. It can be seen that there is no any Cl emission line can be detected when measurement was made under air environment. Nevertheless, the laser pulse energy was increased largely. Meanwhile, when measurements is made under helium environment, Cl emissions line can be detected with strong and clear intensity. The emission lines are ionic Cl lines, namely Cl II 476.86 nm, Cl II 478.13 nm, Cl II 479.45 nm, Cl II 481.0 nm, Cl II 481.94 nm, Cl II 489.67 nm, Cl II 490.47 nm and Cl II 491.77 nm. The Cl II 479.45 nm emission line is the strongest line that can be observed.

Figure 3 is the signal and background emission intensity of emission line Cl II 479.45 nm with variations of delay time at energies of 750 mJ and 2500 mJ, respectively. It can be seen that the signal intensity once increases and decay at later time. When measurement was made using laser pulse energy of 750 mJ laser energy, the signal and background emission are very high at 1 µs delay time. After 1 µs, the emission intensity continues to decrease and it cannot be detected after 5 µs. While when using a 2500 mJ laser, the highest intensity of the emission and background lines is achieved after a 0.25 µs delay time. However, with 2500 mJ of energy, the emission intensity can be observed longer, up to 7 µs and after approximately 10 µs, the Cl signal becomes undetectable.
To obtain the optimum measurement results, it is necessary to calibrate the intensity of the emission signal against the background. From Figure 4 it can be seen from the two laser energy conditions, having the same graph pattern. The signal intensity ratio continues to increase and reaches the highest intensity at a delay of 1 µs, then continues to decrease to 5 µs and 10 µs with laser energy 750 mJ and 250 mJ, respectively. In measurements with a delay time of 0.1 µs, even though the signal emission is high, the background signal emission is still very high so that in this situation the measurement results are not optimum. In the experimental conditions with a delay of 1 µs with 750 mJ laser energy, the signal emission intensity ratio reaches 2.5. while for the use of laser energy 2500 mJ the ratio of signal emission intensity to the background is higher, which is almost reaching 3.

4. Conclusion
Cl measurements using the TEA CO₂ LIBS technique has produced optimum measurements at 1 µs delay in helium environment. As for measurements in air environment, Cl emission line can not
detected. Cl signal emission can be observed longer with 2500 mJ laser energy compared to using a laser with a lower energy of 750 mJ.

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