Energy dependence of Cl emission lines in CO₂ laser induced breakdown spectroscopy

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Abstract. Chlorine (Cl) detection using laser induced breakdown spectroscopy (LIBS) techniques in geology and environment samples is still challenging since the experimental conditions greatly influence the analytical performance of LIBS. Cl emission in LIBS must be studied carefully to find the optimum condition to allow Cl detection. In the present study, Cl emission was studied from polyvinyl chloride (PVC) sample containing Cl as major element. A Transversely Excited Atmosphere (TEA) carbon dioxide (CO₂) laser was used for inducing plasma from the sample. Cl emission was investigated by varying the experimental conditions, especially energy of the laser pulse. The emission spectrum from the consequent plasma was detected using an Optical Multichannel Analyzer (OMA) system. It was found that Cl emission lines only can be obtained when helium was used as the surrounding gas. The strongest emission line of Cl I 837.59 nm in the infrared region cannot be detected even under helium surrounding gas. Instead, many ionic emission lines of Cl in ultraviolet regions including the strong ionic lines (Cl II 479.45 nm, Cl II 481.00 nm, Cl II 481.94 nm and the weak lines (Cl II 476.86 nm, Cl II 478.13 nm, Cl II 489.67 nm, Cl II 490.47 nm and Cl II 491.77 nm) can unequivocally be detected. It was also found that the intensity of Cl emission lines critically depends on the energy of the laser pulse, namely the emission intensity of Cl lines increases sharply with energy. In present work, the highest intensity of Cl emission lines was obtained when the energy of the laser pulse was about 2500 mJ, giving strong and clear Cl emission lines with low background and relatively high signal to background ratio of more than 3.

1. Introduction
Laser Induced Breakdown Spectroscopy (LIBS) is a rapidly developing spectroscopic technique. LIBS has become very popular analytical tool and has been applied in various fields [1-3]. This is because this technique has many advantages in terms of rapid detection of chemical elements in a quested

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sample and minimal sample treatment. In addition, the LIBS technique is able to detect almost all elements simultaneously in single measurement [4-6]. Although LIBS has gained such strong popularity in recent decades as emerging analytical tool, however, some chemical elements are still very difficult to analyse using LIBS. Chlorine (Cl) is one difficult element to detect using LIBS due to its specific physical and chemical properties.

Cl causes corrosion of steel bones in civil structures and buildings [7], thus, analysis of chlorine in environmental samples is very important and being always hot environmental issues. Actually LIBS is promising analytical tool for fast environmental screening, thus many works have been devoted to application of LIBS to detection of chlorine in various samples. In several studies, chlorine content has been detected in building samples using the LIBS technique [8-13], especially ultraviolet (UV) and infrared (IR) wavelength regions. However, detection at these regions is limited to certain detectors. The detector system with an Intensified Charge Couple Device (ICCD) camera is difficult to use because it tends to be less sensitive in the wavelength ranges.

It is not only in UV and in IR wavelength ranges, but strong Cl emission line can also be detected at visible wavelength region. Cl in rocks was successfully detected in environmental conditions simulated like environmental conditions on Mars [14]. However, detection of Cl in environmental samples at a pressure of 1 atm is still very difficult. This is because environmental samples are basically very complex samples where Cl is just a trace in the sample [15]. On the other hand, a Cl emission line in visible regions was succeeded to detect from PVC sample using a TEA CO$_2$ laser in a helium environment [16]. Thus, prior to complex samples, Cl emission dynamic in laser induced plasma can be studied using the PVC sample. In this study, the effect of experimental conditions especially laser pulse energy for detection of Cl using TEA CO$_2$ LIBS in PVC samples was evaluated.

2. Experimental procedure
The experimental setup adopted in this study is illustrated in Figure 1. The beam of TEA CO$_2$ laser operating at a wavelength of 10.6 µm was focused on the sample placed in a chamber using a zinc selenide (ZnSe) lens (f = +200 mm). The spectrum was acquired using the OMA system, consisting of a 0.32-m-focal-length spectrograph with a 1200 groves/mm grating and a detector array of 1024-channel photodiodes.

![Figure 1. Experimental setup of LIBS using the TEA CO$_2$ laser.](image-url)
Figure 2. Photograph of PVC sample after laser irradiation.

In this study the sample used was plastics polyvinyl chloride (PVC) plat. PVC was cut into small pieces with a dimension of 15 × 15 mm and the thickness of 0.73 mm. Figure 2 shows PVC sample after laser beam irradiation. The energy of the laser pulse was varied from 360 to 2500 mJ. Delay and width of the detector gate was set at 2 µs and 50 µs, respectively during experiment. The plasma was produced under different surrounding gas at a pressure of 1 atmosphere. For plasma generation, the PVC sample was attached to a nickel metal plate, which functions as a sub-target. The metal sub-target is never damage by laser irradiation because of low energy density of CO2 laser. The metal sub-target serves to forward momentum of the radiating atom which enhanced by the repulsion force supported by the sub-target so that atoms from the sample are excited effectively [17].

3. Result and discussion
At first, the experiment was made under air as surrounding gas at pressure of 1 atm. It was found that no any Cl emission lines could not be detected even though the laser energy has been increased to 2500 mJ.

When air has been replaced by helium as surrounding gas, the emission lines of Cl appear clearly. Figure 3 shows emission spectrum detected from plasma produced on PVC sample using the TEA CO2
laser at different laser pulse energies of 360, 515, 750, 1500, and 2500 mJ, respectively. The spectrum was detected in a visible region centred at wavelength of 480 nm. The emission intensity of chlorine lines increase critically with energy of the laser pulse. This shows that the use of helium as environmental gas is crucial for detection of Cl using the TEA CO₂ LIBS. It was proved in several studies that excited helium metastable state produced after helium gas breakdown plays very important role, providing a delayed excitation mechanism, resulting in effective excitation of ablated atoms in the long life breakdown plasma. The delayed excitation mechanism produces a strong emission line with narrow spectral width and low background intensity [18-20]. From the emission spectrum, Cl emission line is confirmed by fitting the measured wavelength to the atomic spectrum database published by the National Institute of Standard and Technology (NIST) [21]. Based on NIST atomic spectrum database, strong Cl emission lines in the visible region is listed in Table 1. It was found that the detected wavelength of Cl is fit well with wavelength in the database.

### Table 1. Strong emission line of Cl in visible region based on NIST atomic spectrum database [21].

| Wavelength (nm) | Relative Intensity (arb. Unit) | \(A_{ii}\) \((\text{S}^2)\) | \(E_i\) \((\text{cm}^{-1})\) | \(E_k\) \((\text{cm}^{-1})\) | Lower Configuration | Upper Configuration |
|-----------------|--------------------------------|-------------------------|-----------------|-----------------|-------------------|-------------------|
| Cl II 476.86    | 4300                           | 7.7e+07                 | 137806.15      | 158770.6        | \(3s^23p(\text{p})4s\) \(P^0\) 2 | \(3s^23p(\text{p})4p\) \(D^2\) 2 |
| Cl II 478.13    | 13000                          | 1.0e+08                 | 137879.37      | 158788.3        | \(3s^23p(\text{p})4s\) \(P^0\) 2 | \(3s^23p(\text{p})4p\) \(D^2\) 2 |
| Cl II 479.45    | 99000                          | 1.0e+08                 | 107879.66      | 128730.8        | \(3s^23p(\text{s})4s\) \(P^0\) 2 | \(3s^23p(\text{s})4p\) \(P^2\) 2 |
| Cl II 481.00    | 29000                          | 9.9e+07                 | 107879.66      | 128663.6        | \(3s^23p(\text{s})4s\) \(P^0\) 2 | \(3s^23p(\text{s})4p\) \(P^2\) 2 |
| Cl II 481.94    | 16000                          | 1.0e+08                 | 107879.66      | 128623          | \(3s^23p(\text{s})4s\) \(P^0\) 2 | \(3s^23p(\text{s})4p\) \(P^2\) 2 |
| Cl II 489.67    | 81000                          | 8.8e+07                 | 126784.37      | 147200.2        | \(3s^23p(\text{d})4s\) \(P^0\) 2 | \(3s^23p(\text{d})4p\) \(F^2\) 4 |
| Cl II 490.47    | 47000                          | 8.1e+07                 | 126744.97      | 147127.6        | \(3s^23p(\text{d})4s\) \(P^0\) 2 | \(3s^23p(\text{d})4p\) \(F^2\) 4 |
| Cl II 491.77    | 26000                          | 7.5e+07                 | 126726.70      | 147055.6        | \(3s^23p(\text{d})4s\) \(P^0\) 2 | \(3s^23p(\text{d})4p\) \(F^2\) 2 |

**Figure 4.** Emission lines of Cl at visible region when laser energy of (a) 360 mJ and (b) 2500 mJ.

For detailed evaluation and wavelength assignment, several spectra exhibited in Figure 3, particularly the lowest and the highest energy cases, 360 mJ and 2500 mJ, respectively, were separated. Figure 4(a) displays emission spectrum taken when the laser energy used was 360 mJ. The emission intensity of the spectral lines of Cl obtained is very low with noisy spectrum, thus the emission lines obtained cannot clearly be seen. Figure 4(b) shows the emission spectrum taken when the laser energy used was increased up to 2500 mJ, around 7 times higher. As shown in Figure 4(b), the emission intensity increases very significantly, in overall more than 7 folds. Intensity of emission lines due to Cl, namely ionic emission lines, become very strong, thus the lines can clearly be distinguished. All Cl ionic lines listed in Table 1 can undoubtedly be identified and assigned, especially the strongest Cl ionic triplet emission lines, namely Cl II 479.45 nm, Cl II 481.00 nm and Cl II 481.94 nm and followed by another
weaker Cl ionic triplet emission lines, namely Cl II 489.67 nm, Cl II 490.47 nm and Cl II 491.77 nm. It is interesting that even the relatively weaker lines as compared to Cl II 479.45 nm, namely Cl II 476.86 nm and Cl II 478.13 nm, can surely be recognized and assigned in case of high pulse energy. This confirm the essential role of the laser energy for allowing Cl detection, namely high laser energy is necessary for effective excitation of Cl. On the other hand, this also means that PVC is actually very good sample for studying Cl emission dynamic using TEA CO$_2$ laser induced breakdown plasma, since all Cl emission lines can be observed particularly in this visible region. As mentioned in the introduction, most LIBS study on Cl detection so far is using Neodymium Yttrium Aluminum Garnet (Nd-YAG) laser as excitation source and emission lines detected normally is in UV or IR regions. Cl ionic emission lines in the visible region could not be detected. However, as just observed above the use of TEA CO$_2$ laser as excitation source allow us to detect clearly Cl ionic lines, and it is not only one line but also many Cl ionic lines in the visible regions.

![Figure 5. Emission intensity of Cl ionic line versus laser energy.](image)

![Figure 6. Signal to background ratio for all lines versus laser energy.](image)
The last results lead to a conclusion that laser energy is one of the most important parameter in detection Cl using LIBS. Figure 5 shows detailed plot of the emission intensity of each Cl lines versus laser energy. The emission lines examined are Cl II 476.86 nm and Cl II 478.13 nm, Cl II 479.45 nm, Cl II 481.00 nm and Cl II 481.94 nm, Cl II 489.67 nm, Cl II 490.47 nm and Cl II 491.77 nm. It can be seen that although the emission intensity differs, however all emission lines share the same tendency for energy dependence, namely increases with energy and then get saturated at higher energy regions. It is considered greater the energy used, the more mass that is ablated, thus affecting the emission intensity.

Figure 6 shows the emission line intensity to the background ratio versus energy for each line. The highest ratio is for the laser energy of 2500 mJ, namely more than 3 times. In case of 360 mJ, the ratio is also more than 3 times for Cl II 479.45 nm, however, as explained earlier, the line obtained is distortedly severely by noise.

4. Conclusion
It was found that strong emission lines of chlorine from PVC sample can be observed using the TEA CO₂ LIBS. The chlorine ionic lines can clearly be detected and identified in visible region (Cl II 476.86 nm, Cl II 478.13 nm, Cl II 479.45 nm, Cl II 481.00 nm, Cl II 481.94 nm, Cl II 489.67 nm, Cl II 490.47 nm and Cl II 491.77 nm). In present experimental parameter, the ionic Cl emission lines can only be detected when using helium as the surrounding gas. The appearance of the emission lines strongly depends on the energy of laser pulse and the kind of surrounding gas used. The emission intensity of Cl increase with energy of laser pulse. The Cl emission lines feature a strong intensity with relatively high signal to background ratio, especially when the energy of laser pulse of 2500 mJ used.

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