New approach allowing detection of Cl using a pulsed carbon dioxide (CO\(_2\)) laser-induced breakdown spectroscopy (LIBS)

A M Sari\(^1\), K Lahna\(^2\), M Ramli\(^3\), A Miura\(^4\), K Kurihara\(^5\), Marwan\(^6\) and N Idris\(^2\)

\(^1\) Graduate School of Mathematics and Applied Sciences, Universitas Syiah Kuala, Banda Aceh 23111, Aceh, Indonesia
\(^2\) Department of Chemistry, Faculty of Mathematics and Natural Sciences, Syiah Kuala University, Jl. Syech Abdurrauf No. 3 Darussalam, 23111 Banda Aceh, Aceh, Indonesia
\(^3\) Department of Science and Mathematics Education, Science Education, Faculty of Education, University of Fukui 3-9-1, Bunkyo, Fukui 910-8507, Japan
\(^4\) Department of Physics, Faculty of Education, University of Fukui 3-9-1, Bunkyo, Fukui 910-8507, Japan
\(^5\) Department of Physics, Faculty of Education, University of Fukui 3-9-1, Bunkyo, Fukui 910-8507, Japan
\(^6\) Department of Chemical Engineering, Faculty of Engineering, Syiah Kuala University, Darussalam, Banda Aceh 23111, Indonesia

E-mail: nasrullah.idris@unsyiah.ac.id

Abstract. A new approach to allow detection of Cl emission using a transversely excited atmosphere (TEA) carbon dioxide (CO\(_2\)) laser-induced breakdown spectroscopy (LIBS), namely utilization of a metal sub-target, was introduced. The Cl sample was prepared from pure chemical powder in the form of a solution deposited on the metal sub-target. A zinc selenium lens was used to focus the CO\(_2\) laser beam (10.6\(\mu\)m, 2.5 J, 10 Hz, 200 ns) onto the deposited sample under the surrounding gas of helium (pressure of 1 atm) for generated luminous plasma. An optical multichannel analyzer (OMA) system was used for collecting plasma and acquiring the emission spectrum. It was found that luminous plasma can be produced upon focusing the laser irradiation onto the deposited layer of the sample on the sub-target metal while leaving no ablation from the sub-target metal. Many ionic emission lines from Cl can be detected in the visible region. The ionic emission lines occur with favorable spectrochemical features, namely strong emission intensity and low background level. Thus, this new approach is promising for conducting Cl analysis using a CO\(_2\) LIBS.

1. Introduction

Environmental monitoring from the excessive harmful element is crucial. Chlorine is an element that is generally contained in many materials used daily. However, Cl will be very dangerous when the concentration exceeds the standard limit. For example, concrete with high exposure to Cl may corrode steel reinforcement\([1,2]\). Also, poisoning and carcinogenesis can be caused by residual Cl in tap water \([3]\). A study about the risk of tap water containing chlorination shows that men exposed to chlorinated water pose a high risk of life-threatening diseases such as bladder cancer\([4]\). Therefore, Cl analysis is imperative and urgent in many fields of interest.
Conventional laboratory tools for analyzing Cl [5, 6], cannot achieve real-time analysis and always require complex sampling procedures. Meanwhile, rapid detection of Cl in the environment is needed. As an analytical technique with many advantages, LIBS has been developed and used for the rapid analysis of miscellaneous samples in various fields. The benefits of this technique include that it does not require complicated sample treatment and supports in-situ measurement, making this technique widely used for environmental monitoring [7], industrial applications [8], and food security [9]. Several LIBS studies have detected Cl in various samples such as concrete[10, 11, 12 13], water [14], and even exploration of Mars [15]. In the studies, multiple variations of experimental conditions and sample preparation were carried out to better LIBS performance for Cl detection.

It should be noted that Cl is a problematic element to detect by LIBS because it has a high excitation energy level. Strong Cl atomic lines are also distributed in the ultraviolet wavelength region, which requires special expensive optical devices to detect. Cl detection studies using LIBS generally use the atomic Cl emission line 837.59 nm as the analyte line. Another alternative has been carried out by Ma S, et al., who carried out Cl analysis in water using an indirect LIBS method by analyzing the excess of Ag added to the Cl sample solution to determine the amount of Cl concentration bound to Ag[14]. Analysis of Cl at the wavelength of visible light has also been successfully carried out in solid organic samples by using TEA CO2 LIBS [16, 17]. But for heterogeneous samples, even after adopting several unique approaches such as the metal mesh method and the soil mixed silicone grease (SMS) method, previously found worked well for powder samples including soil, Cl detection have been unsuccessful [18]. The two methods are unique phenomena utilizing the sub-target effect found in a TEA CO2 LIBS in the case of soft samples. A new approach utilizing the sub-target effect is introduced for the possibility of Cl. The metal sub-target was introduced for generating the plasma from soft samples in LIBS [19]. In this approach, the Cl sample is prepared by deposition on the metal sub-target's surface, leaving a thin layer on the metal surface for laser irradiation. In this work, this new approach is examined.

2. Method
The solution samples were prepared by dissolving NaCl in distillate water with Cl content variations, as illustrated in Fig. 1. Next, the Cl solution is dropped on a nickel plate's surface and dried in a microwave oven, removing the water and then leaving the salt layers deposited on the nickel sub-target plate. The nickel plate dimension is 2 cm x 2 cm, with a thickness of 1 mm. The amount of the solution dropped on the metal plate's surface is fixed, namely 3 cc, for all Cl content cases. The analysis is carried out using the TEA CO2 LIBS onto the deposited layer.

![NaCl](Image1)
![Water](Image2)
![Nickel plate](Image3)

Figure 1. Solution sample preparation.

The experimental set-up employed in this research is basically similar to that adapted in previous research [18]. Measurement was made in a chamber filled with helium as the surrounding gas at atmospheric pressure (760 torr). The laser beam of TEA CO2 with an energy of 250 mJ (10.6 μm, 10 Hz, 200 ns) was used as the plasma excitation source. The plasma has been generated by irradiating a focused laser beam onto the target using a ZnSe lens (f = 200mm). Emissions from the consequent
The plasma are collected and fed into an optical multichannel analyser (OMA) system (ATAGO Macs-320) consisting of a spectrograph equipped with a photodiode detector for acquiring the plasma emission spectrum. The OMA system is connected to a personal computer for controlling the measurement and observing as well as recording the emission spectrum. The data of spectrum emissions are then processed and matched with a database published by the National Institute of Standards and Technology (NIST), United States of America [20].

3. Result and Discussion

Visual observation during the experiment confirms that strong luminous plasma can be generated from the deposited layer on the metal sub-target using a TEA CO2 laser. The results from previous CO2 LIBS works on Cl detection in the solid organic sample, and emission spectrum wavelength database published by NIST suggest the appearance of several strong Cl emission line in the visible range, namely Cl ionic emission lines [16, 21]. It is suitable to be detected using the OMA system used in this study because it is equipped with a sensitive detector in the visible range. At first, the LIBS spectrum of the aqueous sample containing Cl at a relatively high concentration, namely 1000 ppm, was detected in the wavelength range of 460-510 nm. Then the LIBS spectrum was detected from samples with various Cl levels and recorded in the same range, as displayed in Figure 2.

![Figure 2](image_url)  
**Figure 2.** LIBS spectra from salt deposited on the surfacenickel plate.

Figure 2 shows Cl emission ionic emission lines in a sample with a Cl content of 1000 ppm is extreme and clear. All of the strong Cl emission lines listed in the NIST database for the wavelength region can be detected and identified, specifically 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, Cl II 491.77 nm. The lines appear
with strong intensity and narrow spectral width as well as relatively low background level. This result is consistent with our previous works using an organic sample of polyvinylchloride samples with Cl as host particles of more than 50% [16, 21]. This implies that Cl dissolved in the solution was deposited on the metal sub-target in the form of the thin layer. The layer is ablated upon CO₂ laser irradiation producing luminous plasma emitting Cl lines. When measurements were made on the solution sample with a lower Cl concentration of 100 ppm, only triplet lines (Cl II 479.45 nm, Cl II 481.00 nm, and Cl II 481.94 nm) around 480 nm were detected. In comparison, the other emission lines due to Cl cannot be seen anymore. These triplet lines appear at a lower intensity than the intensity of the lines on the spectrum of the sample with a higher Cl content (1000 ppm). When the solution sample contains a much lower Cl concentration of 10 ppm, no single Cl emission line can be detected. In the LIBS analysis, intensity represents the concentration of the element in a specimen; thus, it is used for quantitative analysis.

In addition to the emission lines due to Cl, an H₆ emission line at the wavelength of 486.1 nm was detected. This fact gives an advantage that the H₆ line can be used for internal standardization in quantitative analysis, promising a better estimation than the ordinary method, namely analysis directly with a single atomic line 837.5 nm [22]. Another interesting fact is that Cl ionic emission line in the visible light wavelength range can be detected with a clear and strong intensity even though the sample does not use a binder. In contrast, Ni, which is contained in the sub-target, is not detected. Based on the NIST database inspection, it is learned that the strong emission line of Ni lies in the visible range. However, none of the Ni emission lines appears in the emission spectrum. This proves that the nickel sub-target that was used in the experiment has not been ablated. The CO₂ laser beam has a much lower power density than the Nd-YAG laser beam, which is ordinarily adopted for LIBS measurement. Thus, the nickel plate is not damaged, instead of serving to generate a strong plasma from the material [19, 23].

4. Conclusion
Cl prepared in the solution sample can be deposited on the metal surface and can be detected using a TEA CO₂ LIBS utilizing the unique phenomenon of the sub-target effect. At a high concentration of Cl in solution, 1000 ppm, eight (8) Cl ionic lines with very clear, strong intensities and low background levels can be found in the visible range of 460-510 nm, namely 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. The emission lines are very sensitive to its concentration, namely in terms of intensity and the number of lines, implying a linear relationship between the LIBS emission intensity and concentration. Thus, the metal sub-target effect can be utilized to study Cl emission and carry out Cl quantitative analysis.

Acknowledgments
The authors (N. I., M. R., K. K.) thank to Research and Society Service Directorate (DP2M), Directorate General of the Research Strengthening and Developing, Ministry of Research, Technology and Higher Education, Government of Republic Indonesia, for research funding through international collaboration and publication research grant at Institute for Research and Community Service, Syiah Kuala University, Aceh, Indonesia 2016 with contract grant no. 6/UN11.2/PP/SP3/2016 and no. 6/UN11.2/PP/SP3/2017. The authors (N. I., M. R., A. M. S. and M) also thank to Syiah Kuala University, Aceh, Indonesia for financial support through Research of the Unsyiah Leading Research Program for Doctoral Acceleration (Program Riset Unggulan Unsyiah Percepatan Doktor, PRUUPD)2020 with a contract number: 318/UN11.2.1/PT.01.02/PNBP/2020 on March 26, 2020. The authors (N. I., M. R. and K. K.) appreciate University of Fukui, Fukui, Japan for financially support this research on 2017 and 2018.
References

[1] Baltazar-Zamora M A, Mendoza-Rangel J M, Croche R, Gaona-Tiburcio C, Hernández C, López L, Olguin F and Almeraya-Calderón F 2019 Corrosion Behavior of Galvanized Steel Embedded in Concrete Exposed to Soil Type MH Contaminated With Chlorides *Front. Mater.* 6 1–12

[2] Verma S K, Bhadauria S S and Akhtar S 2013 Evaluating effect of chloride attack and concrete cover on the probability of corrosion *Front. Struct. Civ. Eng.* 7 379–90

[3] Yang C-Y, Chiu H-F, Cheng M-F and Tsai S-S 1998 Chlorination of Drinking Water and Cancer Mortality in Taiwan *Environ. Res.* 78 1–6

[4] Cantor K P, Lynch C F, Hildesheim M E, Dosemeci M, Lubin J, Alavanja M and Craun G 1998 Drinking water source and chloride byproducts. I. Risk of bladder cancer. *Epidemiology* 9 21–8

[5] Nunes T S, Muller C C, Balestrin P, Muller A L H, Mesko M F, Mello P de A and Muller E I 2015 Determination of chlorine and sulfur in high purity flexible graphite using ion chromatography (IC) and inductively coupled plasma optical emission spectrometry (ICP OES) after pyrohydrolysis sample preparation *Anal. Methods* 7 2129–34

[6] Pereira J S F, Mello P A, Moraes D P, Duarte F A, Dressler V L, Knapp G and Flores É M M 2009 Chlorine and sulfur determination in extra-heavy crude oil by inductively coupled plasma optical emission spectrometry after microwave-induced combustion *Spectrochim. Acta Part B At. Spectrosc.* 64 554–8

[7] Idris N, Lahna K, Usmawanda T N, Herman, Ramli M, Hedwig R, Marpaung A M and Kurniawan K H 2018 Preliminary panoramic study of river calm muscle using neodymium:yttrium-aluminum-garnet (Nd: YAG) laser-induced breakdown spectroscopy (LIBS) *J. Phys. Conf. Ser.* 1011 012057

[8] Huber N, Eschlböck-Fuchs S, Scherndl H, Freimund A, Heitz J and Pedarnig J D 2014 In-line measurements of chlorine containing polymers in an industrial waste sorting plant by laser-induced breakdown spectroscopy *Appl. Surf. Sci.* 302 280–5

[9] Sezer B, Bilge G and Boyaci I H 2017 Capabilities and limitations of LIBS in food analysis *TrAC Trends Anal. Chem.* 97 345–53

[10] Šavija B, Schlangen E, Pacheco J, Millar S, Eichler T and Wilsch G 2014 Chloride ingress in cracked concrete: A laser induced breakdown spectroscopy (LIBS) study *J. Adv. Conc. Technol.* 12 425–42

[11] Sugiyama K, Fujii T, Matsumura T, Shiozawa Y, Yamaguchi M and Nemoto K 2010 Detection of chlorine with concentration of 0.18 kg/m^3 in concrete by laser-induced breakdown spectroscopy *Appl. Opt.* 49 C181

[12] Eto S, Matsuo T, Matsumura T, Fujii T and Tanaka M Y 2014 Quantitative estimation of carbonation and chloride penetration in reinforced concrete by laser-induced breakdown spectroscopy *Spectrochim. Acta - Part B At. Spectrosc.* 101 245–53

[13] Eto S, Tanji J, Shirai K and Fujii T 2013 Measurement of concentration of chlorine attached to a stainless-steel canister material using laser-induced breakdown spectroscopy *Spectrochim. Acta - Part B At. Spectrosc.* 87 74–80

[14] Ma S, Tang Y, Zhang S, Ma Y, Sheng Z, Wang Z, Guo L, Yao J and Lu Y 2020 Chlorine and sulfur determination in water using indirect laser-induced breakdown spectroscopy *Talanta* 214 120849

[15] Radziemski L, Cremers D A, Benelli K, Khoo C and Harris R D 2005 Use of the vacuum ultraviolet spectral region for laser-induced breakdown spectroscopy-based Martian geology and exploration *Spectrochim. Acta - Part B At. Spectrosc.* 60 237–48

[16] Sari A M, Lahna K, Ramli M, Kurihara K and Idris N 2020 Investigation into time evolution of chlorine emission in pulsed CO2 laser induced breakdown spectroscopy (LIBS) *IOP Conf. Ser. Mater. Sci. Eng.* 796 12030
[17] Sari A M, Lahna K, Idris N, Ramli M and Kurihara K 2019 Energy dependence of Cl emission lines in CO2 laser induced breakdown spectroscopy *IOP Conf. Ser. Earth Environ. Sci.* **364** 2017

[18] Sari A M, Ramli M, Kurihara K and Idris N 2018 Preliminary Study on Possibility Cl Detection in Soil by Means of the Unique Sub-target in a Transversely Excited Atmospheric Pressure (TEA) Carbon Dioxide (CO 2 ) Laser Induced Breakdown Spectroscopy *J. Phys. Conf. Ser.* **1116**

[19] Idris N, Ramli M and Kurihara K 2016 Detection of salt in soil by employing the unique sub-target effect in a pulsed carbon dioxide (CO2) laser-induced breakdown spectroscopy 2016 *International Seminar on Sensors, Instrumentation, Measurement and Metrology (ISSIMM)* (Malang: IEEE) pp 79–83

[20] Kramida, A., Ralchenko, Yu., Reader, J., and NIST ASD Team (2020). NIST Atomic Spectra Database (ver. 5.8), [Online]. Available: https://physics.nist.gov/asd [2020, October10]. National Institute of Standards and Technology, Gaithersburg, MD. DOI: https://doi.org/10.18434/T4W30F.

[21] Sari A M, Lahna K, Idris N, Ramli M and Kurihara K 2019 Energy dependence of Cl emission lines in CO2 laser induced breakdown spectroscopy *IOP Conf. Ser. Earth Environ. Sci.* **364** 2017

[22] Idris N, Kobayashi T, Sullyanti M M, Kurniawan H, Lie T J, Kagawa K and Lee Y I 2005 Confinement effect in TEA CO 2 laser-induced plasma on solid organic samples *J. Korean Phys. Soc.* **47** 256–62

[23] Idris N, Sari A M, Ramli M and Kurihara K 2018 Plasma induced by a pulsed CO2 laser from powder samples mixed with silicone on metal subtarget and its possibility for detecting difficult salts of Cl, B, and S *J. Phys. Conf. Ser.* **1120** 2019