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To cite this article: N Idris et al 2018 J. Phys.: Conf. Ser. 1120 012019

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Plasma induced by a pulsed CO\textsubscript{2} laser from powder samples mixed with silicone on metal subtarget and its possibility for detecting difficult salts of Cl, B, and S

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Abstract. Emission spectrum from plasma produced by a transversely excited atmosphere (TEA) carbon dioxide (CO\textsubscript{2}) laser from pure powder samples mixed with silicone grease attached to a nickel plate was studied. The pulsed CO\textsubscript{2} laser operating at wavelength of 10.6 μm with energy and duration of the laser pulse is 2.5 J and 200 ns, respectively. The plasma was produced by focusing the laser beam onto the sample using a focusing lens (f = +200 mm) under air and helium surrounding gas at atmospheric pressure alternatively. The plasma emission spectrum was detected using an optical multichannel analyser (OMA) system equipped with a 0.32-m-focal length spectrograph. The spectrograph consists of a grating of 1200 grooves/mm and a 1024-channel photodiode detector array with a micro-channel plate intensifier.

The samples used this work are pure chemical powder samples. This technique was used to investigate emission spectral lines due to important salts but difficult to detect such as boron (B), chlorine (Cl) and sulphur (S) from powder samples. It was found that emission intensity detected from the produced plasma is remarkably higher in case using He as ambient gas compared with that using air. It was found that emission spectral lines due to B, Cl, and S can clearly be detected. Even though concentration of the salts (B, Cl, S) is very high since the samples used are pure chemical powder, however several emission spectral lines theoretically expected to appear with strong relative intensity displays relatively low intensity in the detected spectrum. This result confirms the difficulty for detecting the salts, especially chlorine (Cl) and sulphur (S). This technique basically promises a potential application for direct detection of B, Cl and S from powder samples, however new approaches must be developed to realise a high sensitive detection especially for Cl and S.

1. Introduction
Laser induced breakdown spectroscopy (LIBS) technique is a rapidly growing analytical spectroscopy technique. This technique has been widely used for detection of elemental content in various samples. This technique has many unique advantages including simple sample preparation, able to detect many elements in one measurement, both qualitative and quantitative detection, supports in situ
measurements, and allows for elemental detection of various types of samples such as solids, liquids and gases [1]. It has also been used for the analysis of geological samples, environmental samples, and even has been used for analysis of food samples [2-4].

One widely used application of this technique is for environmental monitoring, namely for monitoring pollution of organic and inorganic chemicals including heavy metals and salts in soil. Soil, as already well known, is a kind of powder sample, thus analysis of soil samples using LIBS is limited by certain constraints such as blowing off of the sample upon laser irradiation. This causes a difficulty for generating the plasma and reproducing the plasma emission during spectrum acquisition, resulting in difficulty for detecting constituent elements. This is complicated by the fact that several elements are basically difficult to detect due to its chemical properties, such as boron (B), chloride (Cl) and sulphur (S). Nevertheless, detection of the salt content in soil samples and other environmental samples is very important because the salts are very crucial elements promoting the corrosion of the civil structures [5-6]. Therefore, basis study of pure powder sample using LIBS is very important to know and identify emission spectral lines due to the difficult salts that can be detected from the pure powder samples.

In most works applying LIBS for analysis of powder samples, the powder samples were made in pellet form to avoid blowing off effect [7-8]. Also, a Nd-YAG laser operating at a fundamental wavelength of 1064 nm is commonly used as an excitation source in the works using LIBS for studying powder samples. In some previous studies, detection of salts, Cl and S, using LIBS was performed in vacuum ultraviolet and infrared wavelength regions, requiring special optical fibres in the experiments [9-11]. In previous study of powder sample using LIBS, it was found that the analytical performance of LIBS could significantly be improved by using TEA or pulsed CO$_2$ lasers as excitation source. This is because the much longer wavelength and pulse duration of a pulsed CO$_2$ laser beam as compared to that of a Nd-YAG laser beam. Soil sample and other environmental samples display a much stronger absorption in the wavelength of CO$_2$ laser. Several methods were studied to allow direct analysis of powder samples including soil using CO$_2$ LIBS avoiding blowing off effect, such as mixing the powder sample with silicone grease and then attached to a nickel plate [12]. It was found in the study that strong plasma can be induced and emission spectral lines due to powder sample constituents can be detected with strong emission intensity. In this study we will use this technique to study emission spectral lines due to the difficult salts (B, Cl and S) from pure chemical powder sample binding to a nickel plate subtarget using a pulsed CO$_2$ laser.

2. Experimental Procedure

The experimental settings of LIBS apparatus used in this study are similar to those used in the previous study [12]. The laser used is a TEA or pulsed CO$_2$ laser with wavelength of $\lambda = 10.6$ $\mu$m with energy and duration of the laser pulse is 2.5 J and 200 ns, respectively. The laser pulse was focused onto the sample surface using a lens (zinc selenium, Zn Se) with a focal length of 200 mm. The pure powder samples used were potassium chloride (KCl) powder, boric acid (H$_3$BO$_3$) powder and aluminium sulphate (Al$_2$SO$_4$) powder for detecting emission spectral of Cl, B, and S, respectively. The powder sample was mixed uniformly with silicone grease in a ratio of 1:1. The mixture of the powder sample with silicone grease was put over the nickel subtarget resulting in a layer with a thickness of about 0.5 mm. The sample was then placed in the chamber for laser irradiation. Fig. 1 illustrate the sample preparation process and the LIBS setup for acquiring emission spectrum from the sample. Fig. 2(a) and (b) displays selected photographs of the prepared powder sample of the pure boric acid powder ($H_3BO_3$) mixed with silicone grease placed on the subtarget, before and after laser irradiation. Fig. 3(a) and (b) shows the photographs show pure potassium chloride (KCl) powder sample mixed with silicone grease placed on the metal subtarget before and after the CO$_2$ laser beam bombardment. The plasma generation was made under two different kind of ambient gas alternately, namely air and helium, at atmospheric pressure. In case using helium ambient, helium gas was flown into the sample chamber at a controlled rate of about 5 liter per minute (LPM).
Figure 1. Illustration of (a) process of the powder sample preparation and (b) LIBS experimental setup for acquiring emission spectral lines.

Figure 2 Photographs of pure boric acid powder (H₃BO₃) mixed with silicon grease placed on a nickel metal plate, (a) before laser irradiation, and (b) after laser irradiation.
Figure 3 Photographs of the pure potassium chloride powder (KCl) mixed with silicon grease placed on a nickel metal plate, (a) before laser irradiation, and (b) after laser irradiation.

The resulting plasma emissions are collected by an optical fibre bundle place at a distance of 7.5 cm from the centre of the generated plasma in inclined direction of 45° to the incoming laser beam and the surface of the sample. The OMA system used in this work comprises of a spectrograph with a focal length and a grating of 0.32 m and 1200 graves/mm, respectively. Optical signal output from the spectrograph was detected by a photodiode array of 1024 channels for acquiring emission spectrum from the produced plasma. Operation the OMA system was controlled by a computer using software of SpectraView. The acquired emission spectrum is displayed on the computer screen and it can be stored in the computer memory or other devices for the further processing and analysis of the emission spectra. Identification and confirmation of the emission spectral lines due to Cl, B and S were made using atomic spectral database, published by NIST (National Institute of Standards and Technology), United States of America (USA) [13].

3. Results and discussion
As shown in Figs. 2(a) and (b) and also Figs. 3(a) and (b) the pure powder sample mixed with silicone grease is strongly bounded on the nickel subtarget and even after focusing the CO₂ laser beam (Figs. 2(b) and 3(b)), the pure powder sample remains bounded on the nickel subtarget without blowing off. It can clearly be seen in the photographs (Figs. 2(b) and 3(b)) the powder sample on the laser spot was ablated leaving a trace of the laser spot. Careful visual inspection on the laser spot traced on the metal plate surface found that the metal subtarget was never damaged upon focusing the pulsed CO₂ laser beam. This was again confirmed from assessing the detected emission spectra, as will be shown shortly, revealing that there are no any emission spectral lines due to the nickel subtarget. This unique phenomenon happens because the power density of the CO₂ laser beam is far lower than that of a Nd YAG laser beam commonly used as LIBS excitation source. Since the optical detector of the OMA system has good sensitivity only in the wavelength region ranging from 200 nm to 800 nm, emission spectral lines due to the salts of B, Cl and S in the wavelength region was carefully examined from NIST atomic spectra database to easy acquisition and identification of the emission spectral lines. The emission spectral lines with well isolated wavelength and strong relative intensity were selected from the database for each element of B, Cl and S and tabulated in Table 1. Table 1 displays the selected emission spectral lines for B, Cl and S together with their spectroscopic data including relative
intensity, transition probability, level energy of the emission and the level configuration. The relative
intensity scale differs for each element, the spectral lines with respective high relative intensity was
selected.

Table 1. List of the strong emission spectral lines of B, Cl and S based on NIST database [13].

| Wavelength (nm) | Relative Intensity | $A_{Ki}$ (s$^{-1}$) | $E_i$ (cm$^{-1}$) | $E_k$ (cm$^{-1}$) | Lower level configuration | Upper level configuration |
|----------------|------------------|-------------------|----------------|----------------|-------------------------|-------------------------|
| **Boron**      |                  |                   |                |                |                         |                         |
| B II 239.50    | 520              | 7.56e+07          | 102362.770     | 144102.94      | 1s$^2$2p$^2$ '1'D 2     | 1s$^2$2s3p '1'D 2       |
| B II 249.67    | 110              | 8.40e+07          | 0.0000         | 40039.6907     | 2s$^2$2p '2'S$^1/2$      | 2s$^2$3s '2'S$^1/2$     |
| B II 249.77    | 210              | 1.68e+08          | 15.287         | 40039.6907     | 2s$^2$2p '2'S$^3/2$      | 2s$^2$3s '2'S$^1/2$     |
| B II 332.35    | 780              | 1.15e+08          | 143994.11      | 174073.33      | 1s$^2$2s3p '2'D 2       | 1s$^2$s$^4$4d '1'D 3   |
| B II 345.13    | 7400             | 5.42e+07          | 73396.510      | 102362.770     | 1s$^2$2s2p '2'D 2       | 1s$^2$p$^2$ '2'D 2     |
| **Chlorine**   |                  |                   |                |                |                         |                         |
| Cl II 476.86   | 4300             | 7.7e+07           | 137806.15      | 158770.6       | 3s$^3$p$^-(p^3) 4$p^s$ '1'D 1| 3s$^3$p$^-(p^3) 4$p^s$ '1'D 2|
| Cl II 478.12   | 13000            | 1.0e+08           | 137879.37      | 158788.3       | 3s$^3$p$^-(p^3) 4$p^s$ '1'D 2| 3s$^3$p$^-(p^3) 4$p^s$ '1'D 3|
| Cl II 479.45   | 99000            | 1.04e+08          | 107879.66      | 128730.8       | 3s$^3$p$^-(p^3) 4$p^s$ '1'D 2| 3s$^3$p$^-(p^3) 4$p^s$ '1'D 3|
| Cl II 481.00   | 29000            | 9.9e+07           | 107879.66      | 128663.6       | 3s$^3$p$^-(p^3) 4$p^s$ '1'D 2| 3s$^3$p$^-(p^3) 4$p^s$ '1'D 3|
| Cl II 481.94   | 16000            | 1.00e+08          | 107879.66      | 128623         | 3s$^3$p$^-(p^3) 4$p^s$ '1'D 2| 3s$^3$p$^-(p^3) 4$p^s$ '1'D 3|
| Cl II 489.67   | 81000            | 8.8e+07           | 126784.37      | 147200.2       | 3s$^3$p$^-(p^3) 4$p^s$ '1'D 2| 3s$^3$p$^-(p^3) 4$p^s$ '1'D 3|
| Cl II 490.47   | 47000            | 8.1e+07           | 126744.97      | 147127.6       | 3s$^3$p$^-(p^3) 4$p^s$ '1'D 2| 3s$^3$p$^-(p^3) 4$p^s$ '1'D 3|
| Cl II 491.77   | 26000            | 7.5e+07           | 126726.70      | 147055.6       | 3s$^3$p$^-(p^3) 4$p^s$ '1'D 2| 3s$^3$p$^-(p^3) 4$p^s$ '1'D 3|
| **Sulphur**    |                  |                   |                |                |                         |                         |
| S I 415.26     | 50               | 1.48e+06          | 55330.811      | 55330.811      | 3s$^3$p$^-(4S^0) 4$p^s$ '1'S 1| 3s$^3$p$^-(4D^0) 4$p^s$ '1'D 2|
| S II 542.86    | 23               | 3.77e+07          | 109560.69      | 127976.34      | 3s$^3$p$^-(3P) 4$p^s$ '1'P 1/2| 3s$^3$p$^-(3P) 4$p^s$ '1'P 3/2|
| S II 543.28    | 25               | 6.04e+07          | 109831.59      | 128233.20      | 3s$^3$p$^-(3P) 4$p^s$ '1'P 1/2| 3s$^3$p$^-(3P) 4$p^s$ '1'P 3/2|
| S II 545.38    | 27               | 7.75e+07          | 110268.60      | 128599.16      | 3s$^3$p$^-(3P) 4$p^s$ '1'P 1/2| 3s$^3$p$^-(3P) 4$p^s$ '1'P 3/2|
| S II 547.36    | 23               | 6.61e+07          | 109560.69      | 127825.08      | 3s$^3$p$^-(3P) 4$p^s$ '1'P 1/2| 3s$^3$p$^-(3P) 4$p^s$ '1'P 3/2|
| S II 563.99    | 23               | 6.33e+07          | 113461.54      | 131187.19      | 3s$^3$p$^-(3P) 4$p^s$ '1'P 1/2| 3s$^3$p$^-(3P) 4$p^s$ '1'P 3/2|
| S II 628.69    | 33               | 1.96e+07          | 115285.61      | 131187.19      | 3s$^3$p$^-(3P) 4$p^s$ '1'P 1/2| 3s$^3$p$^-(3P) 4$p^s$ '1'P 3/2|
| S II 630.54    | 33               | 2.02e+07          | 114279.33      | 130134.16      | 3s$^3$p$^-(3P) 4$p^s$ '1'P 1/2| 3s$^3$p$^-(3P) 4$p^s$ '1'P 3/2|

**Figure 4** Boron emission spectral lines detected from the pure powder sample of boric acid ($\text{H}_3\text{BO}_3$)
under air environment after (a) 10 shots and (b) 50 shots of laser irradiation

Figure 4 shows boron emission spectral lines detected from the pure powder sample of boric acid (H$_3$BO$_3$) under air environment detected at beginning of 10 laser shots (a) and after 50 laser shots (b) laser irradiation. It can be seen that at the beginning laser shots, boron emission spectral lines (B II 345.13 nm) can clearly be detected together with silicone emission spectral line. However, the spectral lines feature a relatively weak emission intensity and high background. After irradiation of 50 shots, the emission intensity of the boron ionic spectral line increases largely but the background is still relatively high. The strong emission intensity is kept the same for many laser shots after the 50 shots. The large increment in the emission intensity of the boron ionic spectral line is interpreted by shockwave mechanism in plasma generation process. It is considered that hardness of sample is crucial for inducing strong shockwave moving at supersonic speed, compressing the surrounding gas creating a high temperature region just behind the shock front, generating luminous plasma. Hard sample gives off strong repulsion force to the ablated atoms creating strong shockwave, resulting in strong plasma. Whereas a soft sample gives not sufficient repulsion force to the ablated atoms, resulting in difficulty to initiate a shockwave, producing very weak plasma and even no plasma from the soft sample. This explains the weak emission intensity obtained at the beginning laser shots in case the soft sample put on the hard metal subtarget as shown in Fig. 4(a). After many laser shots, the laser beam arrived on the hard surface of the metal subtarget, giving off strong repulsive force to the ablated atoms of the soft sample. This yields to generation strong plasma from the soft sample bounded on the hard metal subtarget, resulting in high emission intensity of the spectral lines as observed in Fig. 4(b).

![Figure 4 Emission spectra detected from (a) silicone grease only and (b) the pure powder sample of boric acid (H$_3$BO$_3$) mixed with silicone grease placed on the nickel subtarget after 50 shots of laser irradiation under helium ambient](image)

**Figure 4** Emission spectra detected from (a) silicone grease only and (b) the pure powder sample of boric acid (H$_3$BO$_3$) mixed with silicone grease placed on the nickel subtarget after 50 shots of laser irradiation under helium ambient

Figure 5 shows emission spectral lines measured from (a) silicone grease only and (b) the pure powder sample of boric acid (H$_3$BO$_3$) mixed with silicone grease placed on the nickel subtarget under helium ambient. The emission spectra were detected after irradiation 50 laser shots. It can surely be seen in Figure 5(a) there are strong emission spectral line due to silicone, namely Si II 333.98 nm with relatively simple emission spectra appearance. It is interesting to note that the simple emission spectrum implies the high purity of silicone grease used this study. There are no appreciable emission spectral lines arising from any impurities in the silicone grease. Figure 5(b) shows the emission spectral line of boron ionic emission spectral lines, B II 345.13 nm detected under helium surrounding. In general, the emission intensity extremely increases in this helium ambient case in comparison with
the case of air surrounding. The emission intensity of the spectral line of B II 345.13 nm is very high with very low background while the emission intensity of Si spectral lines due to silicone grease becomes significantly weak as compared to in case silicone grease only. This means the presence of the pure powder sample in the silicone grease suppresses the excitation of silicone grease. This results basically is very good for analytical purposes, namely the silicone grease basically works only as binding material, thus it is expected that the emission spectral lines due to silicone grease would not disturb the analytical spectral lines. The boron ionic spectral line of B II 345.13 nm is well isolated, free from any interfering spectral lines due to silicone and other possible constituents of the pure powder and the silicone grease. The large enhancement of boron ionic emission line (B II 345.13 nm) is attributed to chemical and physical properties of the helium ambient. There is actually another boron ionic emission spectral line (B II 332.35 nm) expected to arise in the wavelength region near the silicone spectral lines of Si II 333.9 nm. However, the relative intensity of the boron ionic emission line (B II 332.35 nm), based on NIST database presented in Table 1, is much lower, about 10 tens lower than that of the boron ionic emission spectral line, B II 345.13 nm. Thus it is probably reasonable the boron ionic spectral line (B II 332.35 nm) cannot be seen in the same emission spectrum.

![Emission spectra detected under helium surrounding from (a) silicon grease only on the nickel subtarget, (b) silicon grease mixed the pure powder sample of boric acid (H₃BO₃) on the nickel subtarget](image)

**Figure 6** Emission spectra detected under helium surrounding from (a) silicon grease only on the nickel subtarget, (b) silicon grease mixed the pure powder sample of boric acid (H₃BO₃) on the nickel subtarget

Besides the boron ionic emission spectral line at 345.13 nm, there are also several boron atomic emission spectral lines with relatively high intensity expected to appear at wavelength of 249.67 nm and 249.77 nm. Fig. 6(a) exhibited the emission spectrum taken from silicone grease only in wavelength region centered at 255 nm under helium surrounding. The emission spectra also were collected after irradiation of 50 laser shots. As it can surely be seen in Fig. 6(a) there are many emission spectral lines due to Si can certainly be found in the region. There are two most strong atomic spectral lines of Si in this region, namely Si I 250.68 nm and Si I 251.61 nm. Fig. 6(b) shows the emission spectrum taken after mixing the silicone grease with the pure powder sample of boric acid (H₃BO₃). The emission spectral lines of B I 249.67 nm and B I 249.77 nm can be identified among the high density of Si emission spectral lines. Even though after careful examination on the emission spectra it is found that the emission intensity of silicone emission lines is lower than that in case of silicone grease only, similar to that observed in the region centered at wavelength of 345.0 nm shown above in Fig. 5(b), however the spectral lines of B I 249.67 nm and B I 249.77 nm are not well
isolated. The spectral lines of B I 249.67 nm and B I 249.77 nm are heavily overlapped the silicone spectral lines. Although the spectral lines of B I 249.67 nm and B I 249.77 nm feature a high emission intensity but the background of the emission spectrum is also high. The features of the emission spectral lines are actually not favorable for realizing a high sensitive spectrochemical analysis. Therefore, considering the emission spectral line obtained in the other region centered at wavelength of 345.0 nm (Fig. 5(b)) showing the best features of the emission spectral line of boron ionic emission line (B II 345.13 nm), thus the spectral line of B II 345.13 nm is the best analytical line for detecting B using pulsed CO₂ LIBS. The boron ionic emission spectral line of B II 345.13 nm detected under helium ambient demonstrates a well isolated spectral line with very strong emission intensity and very low background.

Figure 7 Emission spectrum taken in the region centred at wavelength of 479.00 nm from (a) silicon grease sample only (b) the pure powder sample of potassium chloride (KCl) mixed with silicon grease after irradiation 10 laser shots (c) after irradiation 50 laser shots, (d) emission spectral line centred at 770 nm for potassium line detection.
Similar experiment was carried out for the pure powder sample of potassium chloride (KCl) mixed with silicone grease. The emission spectrum acquisition was made under helium environment at atmospheric pressure. Figure 7(a) shows emission spectrum in the region centered at a wavelength of 479.00 nm taken from silicon grease only before mixing with the pure powder. It is theoretically expected that many strong emission lines due to chlorine to occur in this wavelength region from a sample containing Cl. Fig. 7(a) confirms there is only very weak spectral lines due to silicone from the silicone grease appearing in the center of this wavelength region when the sample is silicone grease only. When experiment was conducted for the pure powder sample of potassium chloride (KCl) mixed with silicon grease, the chlorine ionic emission spectral lines namely Cl II 476.86 nm, Cl II 478.13 nm, Cl II 479.45 nm, Cl II 480.0 nm, Cl II 489.67 nm, Cl II 490.47 nm and Cl II 491.77 nm are readily started to occur after irradiation of 10 laser shots (Fig. 7(b)), even though the emission intensity actually is still very weak. The intensity of the chlorine ionic emission spectral lines increases significantly when measured after irradiation of 50 laser shots onto the sample (Fig. 7(c)). The chlorine ionic emission spectral lines occur clearly with relatively strong emission intensity. Cl is actually a difficult element to analyze with LIBS techniques, because of its high thermal conductivity and high lying excitation level. However, in this study it is found that Cl emission spectral lines can unequivocally be detected from the pure powder sample in the visible wavelength region. Fig. 7(d) exhibits emission spectral lines of potassium detected under helium environment at wavelength of K I 766.49 nm and K I 769.90 nm. The intensity of the potassium atomic emission spectral lines, since K is host of the pure powder of potassium chloride (KCl). Comparing this results to the emission intensity of Cl spectral lines from the same sample found that the intensity of Cl emission spectral lines is far lower than of K emission spectral lines, nevertheless it was detected from the same pure powder samples prepared in the same manner containing only Cl and K at almost same amount. This indicates a much difficulty for detecting Cl than K using LIBS.

The same sample preparation and emission spectral acquisition adopted for the other pure powder samples above were also made for the pure powder sample of aluminum sulphate (Al₂SO₄) for studying sulphur emission spectral lines. Fig. 8(a) displays the emission spectral lines of Al I 394.4 nm and Al I 396.15 nm coming from aluminum of the pure aluminum sulphate (Al₂SO₄) powder sample, confirming that actually the pure powder sample was ablated and atomized, resulting in the aluminum
emission spectral lines. Therefore, it is considered that the sulphur emission spectral lines can also be detected from the pure powder sample. Fig. 8(b) shows emission spectrum centered at a wavelength of 415.00 nm where strong sulphur atomic emission spectral line (S I 415.26 nm) is theoretically expected to appear. As it can be seen in the figure, sulphur atomic emission spectral line (S I 415.26 nm) cannot be detected. Nevertheless, the powder sample is a pure chemical powder containing only Al, S and O and the detected sulphur atomic emission spectral line (S I 415.26 nm) is the strongest spectral line as shown in Table 1. This result implies the difficulty for detecting sulphur emission spectral lines in laser induced breakdown spectroscopy. It is learned that even though the sample actually contains sulphur at very large amount, however it cannot easily be detected. In this wavelength region, there is actually a very strong emission spectral line of silicone (Si II 413.09 nm) certainly due to silicone grease just near the sulphur atomic spectral line (S I 415.26 nm).

Figure 9 Spectrum emission lines taken under helium surrounding from (a) silicone grease only and (b) the pure powder sample of aluminium sulphate (Al₂SO₄) sample in the region with wavelength centred at 550.00 nm

The sulphur emission spectral lines were also detected in other region centered at a wavelength of 550.00 nm. It is supposed that in this region many sulphur emission spectral lines will appear, namely S II 542.7 nm, S II 544.9 nm, S II 545.3 nm, S II 547.3 nm, and S II 563.99 nm with strong relative intensity as listed in Table 1. Figure 9(a) show the emission spectrum taken from the silicone grease only in the wavelength region. It can be seen that there are silicone emission spectral lines due to silicone grease with strongest spectral line of Si II 566.95 nm. Though the background of the emission spectrum is also relatively high, the profile of the emission spectrum is relatively simple, consisting of only several silicone emission spectral lines. Figure 9(b) displays emission spectrum taken from the pure aluminum sulphate powder sample (Al₂SO₄) mixed with silicone grease. Now, it can be found that there are many spectral lines in the acquired emission spectrum. It is considered these spectral lines appear from the pure powder sample (Al₂SO₄) indicated by their absence when the sample was only silicon grease. Moreover, there is aluminum ionic spectral line (Al II 559.3 nm) in the spectrum. This leads to a conclusion that the appeared spectral lines come from the pure powder sample. Many of the spectral lines was assigned to sulphur, namely S II 542.7 nm, S II 544.9 nm, S II 545.3 nm, S II 547.3 nm, and S II 563.99 nm. Next measurement of the sulphur emission spectral lines was made in other region centered at a wavelength of 630.00 nm. Fig. 9 shows emission spectrum detected in the region. In this region, it is theoretically expected that several strong sulphur emission spectral lines will occur namely S II 628.69 nm and S II 630.54 nm as listed in Table 1. Although the background of
the emission spectrum is significantly high, it can clearly be observed in Fig. 9 that the strong silicon atomic emission spectral lines of Si I 634.71 nm and Si I 637.14 nm coming from silicone grease can surely be detected. However, there are no any emission spectral lines due to S found in the emission spectrum. Nevertheless, as depicted in Table 1, the relative intensity of the emission spectral lines of S II 628.69 nm and S II 630.54 nm are relatively strong, and the pure powder sample contains sulphur at very high concentration. This result is just similar to that found in the wavelength region centered at wavelength of 415.00 nm as displayed in Fig. 8(b), namely the strongest sulphur emission spectral line (S I 415.26 nm) cannot be found in the region.

Figure 10 Emission spectrum taken under helium surrounding from the pure powder sample of aluminium sulphate (Al₂SO₄) sample in the region with wavelength centred at 385.00 nm and 630.00 nm, consecutively.

4. Conclusion
It was found that the pure powder samples can be mixed well with silicone grease and bound well on the nickel subtarget. There is no blowing sample off upon laser irradiation except that on the laser spot. Strong plasma can be produced from the pure powder sample mixed with silicone grease placed on the metal subtarget, indicated by appearance of strong emission spectral lines due to host element in each pure powder sample, such as B (H₃BO₃), Cl and K (KCl), Al (Al₂SO₄). For this kind of sample, namely mixture of the powder sample and silicone grease, the useful emission spectrum can be obtained after several tens of laser irradiation shots, namely after the laser beam reaches the hard surface of the metal subtarget. The features of the emission spectrum in terms of intensity and background improved remarkably when using helium as ambient gas. Several emission spectral lines due to boron, chlorine and sulphur can surely be detected from each pure powder sample at different wavelength regions. The best wavelength region for detecting boron is the region centered at wavelength of 345.00 nm with the best analytical spectral line is boron ionic spectral line of B II 345.13 nm. The best wavelength region for detecting chlorine is the wavelength region centered at 479.00 nm, since there are many chlorine ionic emission spectral lines occurs simultaneously in the visible region, namely Cl II 476. 86 nm, Cl II 478. 13 nm, Cl II 479.45 nm, Cl II 480. 0 nm, Cl II 489. 67 nm, Cl II 490. 47 nm and Cl II 491. 77 nm. The most difficult element to detect at this stage is sulphur. The strongest sulphur atomic emission spectral line of S I 415.26 nm cannot be detected from the pure powder sample of the aluminum sulphate (Al₂SO₄). The most probable wavelength region for
detecting sulphur found is the region centered at wavelength of 550.00 nm, because several sulphur emission spectral lines can be observed in this region, namely S II 542.7 nm, S II 544.9 nm, S II 545.3 nm, S II 547.3 nm, and S II 563.99 nm. Paying close attention to the obtained emission intensity of the spectral lines of Cl and S, it is basically rather weak considering that each pure powder (KCl and Al2SO4) contains the elements at very large amount. These results again confirm the difficulty of Cl and S detection using laser-induced breakdown spectroscopy, even the sample contain the elements as host constituent. Thus, new approaches must be devised to allow high sensitive detection of these element in various samples using CO2 LIBS.

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