

## Mesh-Assisted Laser-Induced Plasma Spectroscopy Using Pulse Carbon Dioxide Laser for Analysis of Powder Material by Confining the Powder in a Hole and Employing a Condensation Technique

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**Abstract:** Analysis of impurity in powder samples has been made by using metal-assisted laser-induced plasma spectroscopy utilizing a pulsed CO<sub>2</sub> laser. Various powders including food powder, supplement powder, baby powder, and medicine powder were employed as sample materials. Experimentally, the powder sample was tightly put in a hole made on a metal plate and a metal mesh was placed on the powder surface. A pulse CO<sub>2</sub> laser (10.6 μm, 1500 mJ) was irradiated on the powder surface passing through the metal mesh. Luminous plasma was induced by mesh just above the mesh when a part of laser energy attacked the mesh. The other part of laser energy impinged the powders and ablated fine particles of powder to the plasma to be atomized and excited. Identification and analysis of elements in powder were successfully conducted. A linear calibration curve of Cu in baby powder has been demonstrated with an intercept zero, certifying that the present technique was a high possibility to be employed for semi-quantitative analysis of elements in powder material. It was proved that by applying the present technique and employing a condensation technique, the detection sensitivity of Cr impurity in the powder sample increased about twenty times compared to the case without condensation. The limit of detection of Cr in rice powder sample was 25 mg/kg. The proposed method was very convenient for the identification and analysis of elements in the powder sample.

**Keywords:** laser-induced breakdown spectroscopy; mesh-assisted laser-induced plasma spectroscopy; pulse carbon dioxide laser; analysis of powder sample

### ■ INTRODUCTION

Atomic Emission spectroscopy using pulse laser, which most scientists call laser-induced plasma spectroscopy (LIPS) or laser-induced breakdown spectroscopy (LIBS), has been receiving a good popularity as a spectrochemical method for the elemental analyses due to the simplicity and the capability of rapid identification of elements in target as well as the feasibility of in-situ analysis [1-2]. By comparing with the other conventional analytical methods such as X-ray Fluorescence Spectroscopy (XRF), the LIBS has stronger points for powder analysis, namely onsite multi-elemental

detection can be carried out simultaneously and the sample pretreatment is not necessary. Furthermore, the analytical results show the much better accuracy of analysis for LIBS and the detection of light elements such as carbon (C) and hydrogen (H) can successfully be conducted using LIBS [3].

In standard LIBS, a high energy pulsed Nd:YAG laser is irradiated on/in the target surface to induce a luminous plasma [4-7]. The method has benefit for rapid identification of elements in materials including solids [8-9] and liquids [10]. However, it is known that the powder sample is delicate to be analyzed by LIBS

because the blow-off of powder happens when the pulse laser is irradiated directly on the powder target. Therefore, the powder is usually compressed to make a pellet sample for identification of elements in the powder sample. However, based on our experiments, even though the powder was pressed in the form of a pellet, the pellet of powder material is not as hard as the solid sample such as ceramic. Thus, a strong shock wave, which is imperative to produce high-temperature plasma [11-12], cannot be induced because of low repulsion force on the surface of the sample, resulting in weak atomic emission intensity of the plasma. In order to increase the hardness of the powder pellet, material binders like potassium bromide, polyvinyl, starch, aluminum, and silver were employed as reported in this paper [13]. However, those binding materials disturbed the analytical lines and therefore they retarded the analytical results.

In other direction, we have successfully demonstrated analysis of powder material without pellet preparation using LIBS method utilizing a pulsed CO<sub>2</sub> laser [14]. Compared to ordinary Nd:YAG laser (1.064 μm, 10 ns), a pulse CO<sub>2</sub> laser (10.64 μm, 200 ns) is much suitable for powder analysis because of high-absorbance characteristics in powder material. The results show that a tiny amount of powder including soil, chemical powder, and high-purity gold can qualitatively be analyzed. However, in the report, a silicon grease binder was used to attach the powder on a metal subtarget for assisting the plasma production. Therefore, in the reported technique, a delicate sample pretreatment was still needed and the analytical results were still disturbed by the material binder.

In this work, an analysis of powder sample was carried out using the LIBS method utilizing a pulse transversely excited atmospheric (TEA) CO<sub>2</sub> laser without material binder. A unique technique was devised and applied to the analysis of elements in powder. Namely, the powder material was confined in a hole made on a metal and then covered by a metal mesh, which functions to assist the plasma production; the plasma produced by using this present technique is then called "mesh-assisted laser-induced plasma". It is assumed that the confinement of powder in a hole can control the amount of ablated powder entering into the plasma region. For sensitive

analysis of elements in powder material containing low-concentration, a condensation technique was also introduced via combustion of powder material in a small chamber. This present technique offers a sensitive analysis of impurity in powder material.

## ■ EXPERIMENTAL SECTION

An experimental arrangement used in this research is shown in Fig. 1. A pulse TEA CO<sub>2</sub> laser (200 ns, 10.64 μm, 1500 mJ) was irradiated on powder material by ZnSe lens (200 mm in focal length) via a metal mesh to produce a luminous plasma. The power density of the laser beam on the sample surface was 0.75 GW/cm<sup>2</sup>. An emission spectrum was gained from the plasma emission by using an optical multichannel analyzer system (OMA ATAGO Macs-320). The plasma emission was collected by the fiber system connected to OMA.

The sample materials used were rice powder, supplement powder, medicine powder, and milk powder containing Ca of 5600 mg/kg, which are available in the local market. The sample was set in the chamber (12 x 12 x 12 cm<sup>3</sup>). The pressure in the chamber was 1 atm. The sample was prepared in two conditions as shown in Fig. 2. First, the powder was placed in a small plastic bucket with a diameter and a depth of 40 and 11 mm, respectively (Fig. 2(a)).

A Cu metal mesh (0.3 mm in lattice constant and 0.4 mm wire diameter) was applied to case the materials from the blow-off of powder and to assist a plasma production. It should be mentioned that no mark of

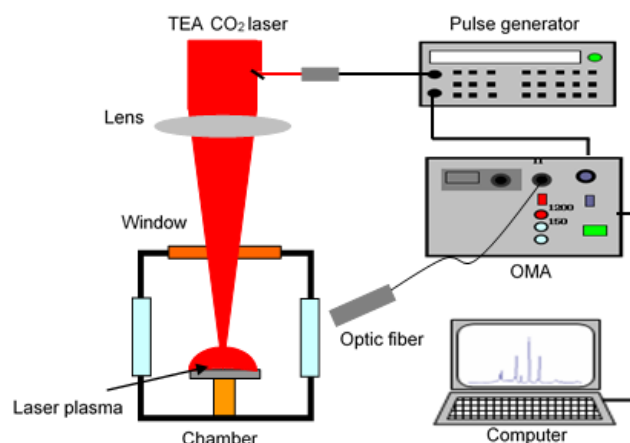


Fig 1. Experimental setup used in this work

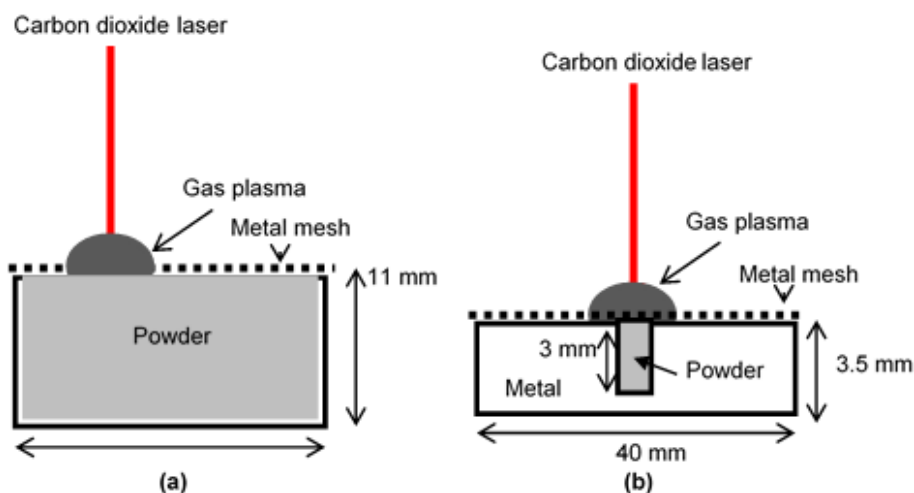
irradiation damage was found on the surface of the mesh. This is because the power density of the laser is much lower than the ablated mesh threshold [15]. To improve the accuracy of analytical emission spectra, a newly devised sampling technique was proposed as displayed in Fig. 2(b). Namely, the material powder was confined tightly in a hole made in the center of the aluminum plate and finally covered by a metal mesh.

## RESULTS AND DISCUSSION

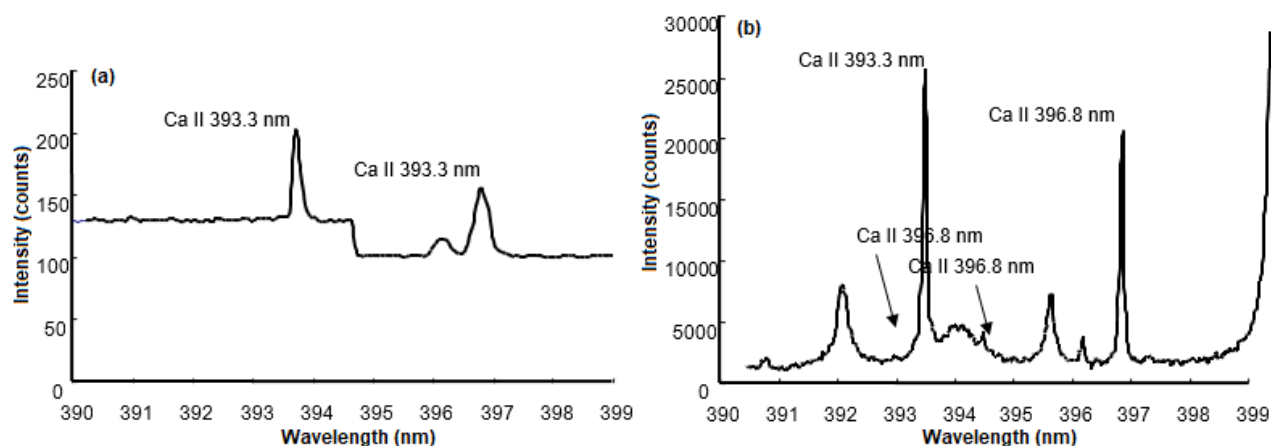
In this present study, the metal mesh was applied to cover the analyzed powder samples. As explained above, the use of the metal mesh in the analysis of the powder samples plays some important roles. First, it suppresses

the severe blowing-off effect that commonly takes place in the powder sample bombarded by using high-power laser due to reducing the power density of laser energy impinging on the sample surface. Second, the metal mesh placed in tight contact on the front side of the powder sample induces strong gas breakdown plasma. Therefore, it is expected that the enhanced intensity of emission lines from the samples are produced because the atomization and excitation of ablated particles of the sample run well in the hot gas breakdown plasma induced by the metal mesh.

At initial, a comparative study on elemental identification of herbal medicine has been performed using a standard LIBS employing an Nd:YAG laser and



**Fig 2.** Illustration of the powder container by using (a) a plastic vessel, (b) a hole made in the center of the aluminum plate. The powder was covered by a metal mesh to avoid the blow-off of powder



**Fig 3.** Emission spectra obtained from the herb medicine using (a) commercial LIBS system using Nd:YAG laser, and (b) mesh-assisted laser-induced plasma utilizing TEA CO<sub>2</sub> laser

present devised technique utilizing a mesh-assisted laser-induced plasma employing a pulsed CO<sub>2</sub> laser. The herbal medicine contains calcium (Ca) and aluminum (Al) with a concentration of several hundred mg/kg and several tens mg/kg, respectively. Fig. 3(a) shows the emission spectrum obtained from the herb medicine sample using standard LIBS. Prior to laser irradiation, the herb sample was formed as a pellet by compressing the herb powder using a pressing machine with a pressure of 200 atm for 15 min. It should be mentioned that no material binder was added to the pellet of powder. A fundamental Nd:YAG laser 1064 nm with an energy of 140 mJ was employed as an irradiation source. As shown in Fig. 3(a) that the ionic Ca lines at 393.3 and 396.8 nm were detected with rather a weak emission intensity and quiet high background emission. Also, no neutral Al lines at 394.4 and 396.1 nm occurred. As mentioned in the introduction, the powder sample is basically cannot be made a hard pellet without adding a binder. Therefore, when the Nd:YAG laser was bombarded on the surface of the soft pellet, the powder particles having micro sizes were ablated and thus complete dissociation of particles cannot take place well. Those particles contribute to the continuous emission spectrum as the blackbody radiation, resulting in high background emission as shown in the figure.

On the other hand, when the present devised technique utilizing a mesh-assisted laser-induced plasma employing a pulse CO<sub>2</sub> laser without pellet pretreatment was used, high-intensity emission lines of Ca at 393.3 and 396.8 nm were clearly detected with low background emission as shown in Fig. 3(b). Furthermore, emission lines of Al at 394.4 and 396.1 nm clearly occurred; it has been confirmed that the Al lines were also detected by using scanning electron microscope-energy dispersive X-ray (SEM-EDX). This emission spectrum has much better in emission intensity and analytical line profiles compared to that of standard LIBS case. It is considered using this present devised technique (Fig. 2(a)) that the metal mesh plays a very important role in plasma generation. It is assumed that when the TEA CO<sub>2</sub> laser beam is focused on powder material via a metal mesh, part of laser beam is used to induce a breakdown plasma just

in the surface of mesh and the other part of laser beam is applied to ablate the powder material to enter into the gas breakdown plasma to be dissociated and excited. It should be mentioned that no ablation of metal mesh is found proved by the absence of analytical lines contributed to the metal in the emission spectrum (Fig. 3(b)). Based on this result, the present devised technique of mesh-assisted laser-induced plasma spectroscopy employing a pulsed TEA CO<sub>2</sub> laser is much better for identification and analysis of elements in powder material compared to the case of standard LIBS technique using a pulsed Nd:YAG laser. The devised technique was then used for identification and analysis of elements in powder material.

First, a commercial chemical powder of ZnS powder was employed as a sample. Fig. 4 shows the spectrum obtained from the ZnS powder. A typical doublet of ionic Ca lines at 393.3 and 396.8 nm can clearly be seen. The Ca is an impurity contained in the ZnS powder. Another sample, namely powdered commercial medicine supplement (containing 1.5% of Zn), was also employed. High-signal emission lines of neutral Zn at 328.2, 330.2, and 334.5 nm from the powdered commercial supplement can be clearly observed (Fig. 5(a)). Furthermore, the group of Si emission lines, namely neutral Si at 250.7, 251.6, and 252.9 nm appear together with neutral C at 247.8 nm as shown in Fig. 5(b). The supplement was also contained a few percent's of Si. From these experiments, it is proved that the present method can be employed for the detection of elements in the powder sample.

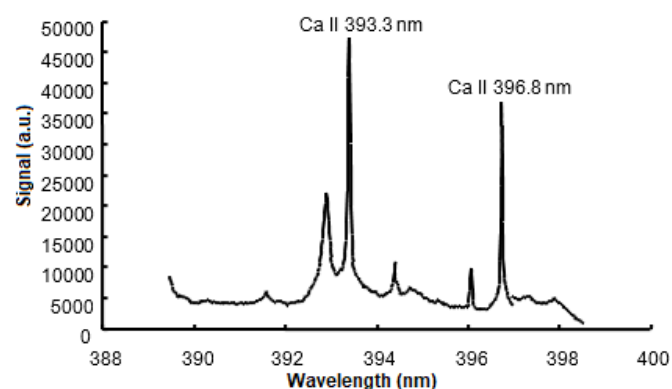
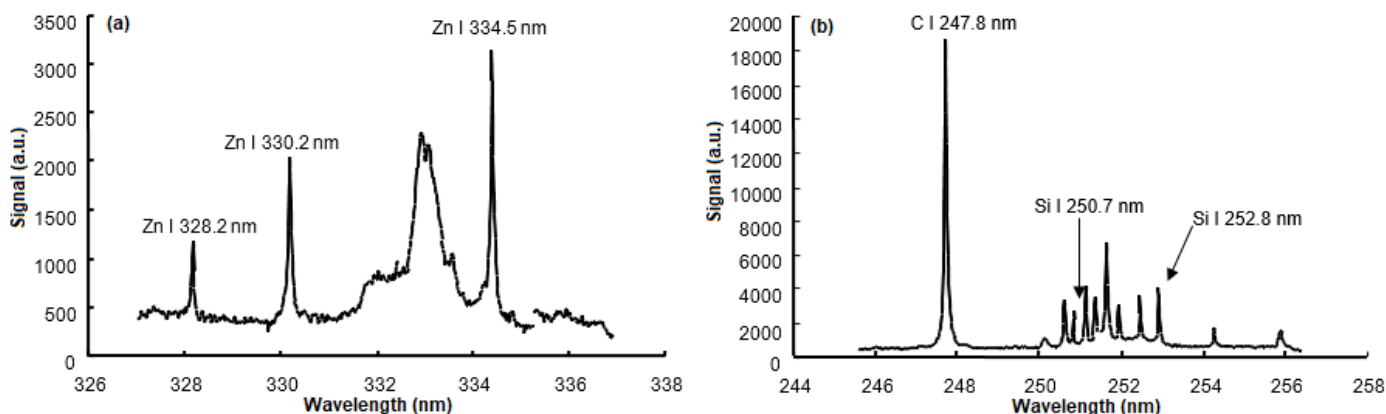
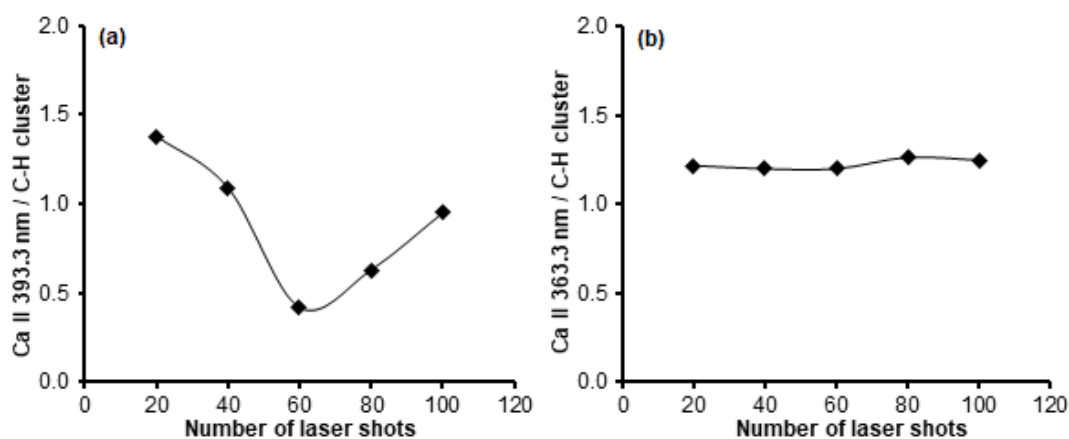


Fig 4. Emission spectrum taken from the zinc sulfide powder



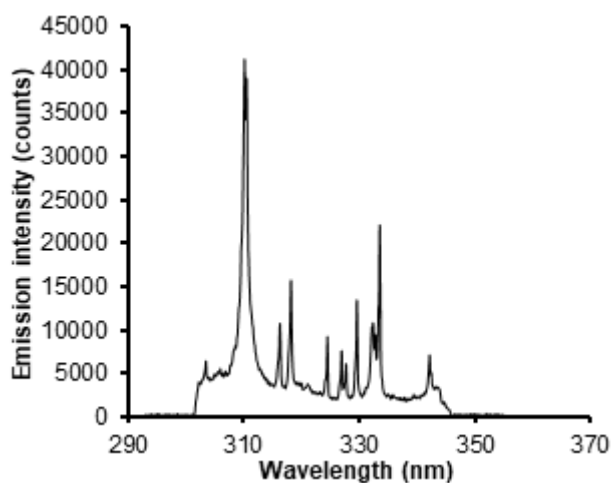
**Fig 5.** Emission spectra taken from the powdered commercial tablet containing zinc of 1.5% in the wavelength region of (a) 326–338 nm, (b) 244–256 nm



**Fig 6.** Ratio of emission signal between ionic calcium 393.3 nm and carbon-hydrogen cluster taken from the milk powder sample using mesh-assisted laser-induced plasma spectroscopy (a) without powder confinement, and (b) with powder confinement

To test the capability of the present technique for analysis of other powder material, a reproducibility of the emission spectrum is very important. To this end, Ca emission signal relative to C-H cluster from the milk powder sample was used. However, good reproducibility of the emission signal cannot be made by using the present technique (Fig. 2(a)), namely, the emission signal of the ionic Ca at 393.3 nm to C-H cluster fluctuates so much with a standard deviation of 0.38 as depicted in Fig. 6(a). It should be understood that the characteristic of the sample plays an important role. In the case of the powder sample, soon after laser attacks on the sample surface, the large amount of fine particles ablate to enter in plasma by creating the crater in the sample surfaces. The crater produced in the varied positions had varied sizes. From

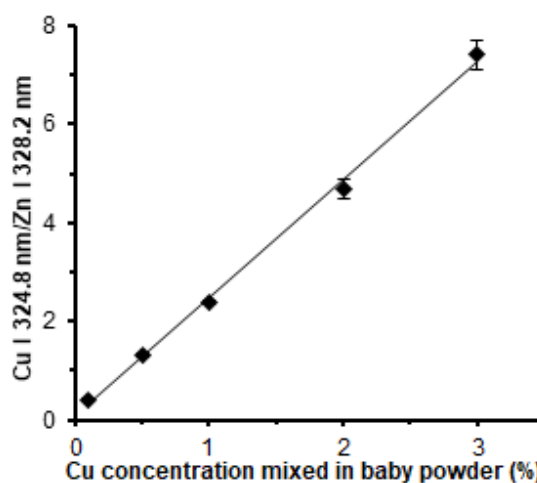
this fact, the crater was considered to directly influence the plasma generation and composition. To make plasma with a good stability, in which the emission signal was stable, the plasma temperature needs to be constant; as reported in our previous work, we confirmed that in order to make a good stability of laser plasma emission, the temperature of the produced plasma should be constant [16]. In fact, when the bombardment position on the powder sample was changed, the amount of fine particle powder entering into the plasma region also changes proved by the different crater size. The amount of fine particles influences the plasma temperature. If the amount of fine particles enter the plasma so much, the temperature will be down influencing the dissociation and excitation process.



**Fig 7.** Emission spectrum obtained from the baby powder containing 1% Cu using the mesh-assisted laser-induced plasma spectroscopy employing confinement technique

To solve the problem, a newly devised technique was employed as displayed in Fig. 2(b). In this device, the powder target was confined tightly in a hole. The metal mesh was used as a cover to avoid blow-off of powder and produce a luminous plasma. Fig. 6(b) exhibits the emission signal ratio between ionic Ca II 393.3 nm and C-H cluster obtained from the same milk powder used in Fig. 6(a) with the number of laser shots. It is seen the signal almost constant from 20 shots to 100 shots with a standard deviation of 0.03 (ten times lower than the case of results shown in Fig. 6(a)). This result indicated that the hole effectively confines the powder and controls the amount of powder particles moving into the plasma region due to the laser bombardment.

The newly devised technique was then examined for quantitative analysis of baby powder. To this end, a baby powder containing a various concentration of Cu was employed as samples. Prior to this examination, emission spectrum obtained from a baby powder containing 1% Cu taken by using this present technique utilizing a pulsed TEA CO<sub>2</sub> laser was shown as in Fig. 7. It can be seen that high emission lines of neutral Zn at 328.2, 330.2, and 334.5 nm are clearly observed in the emission spectrum. Furthermore, Cu line as an impurity in the baby powder also clearly detected at the wavelength of 324.7 and 327.4 nm. Some other lines, including the broadened emission lines at around 310 nm, are unidentified. It is



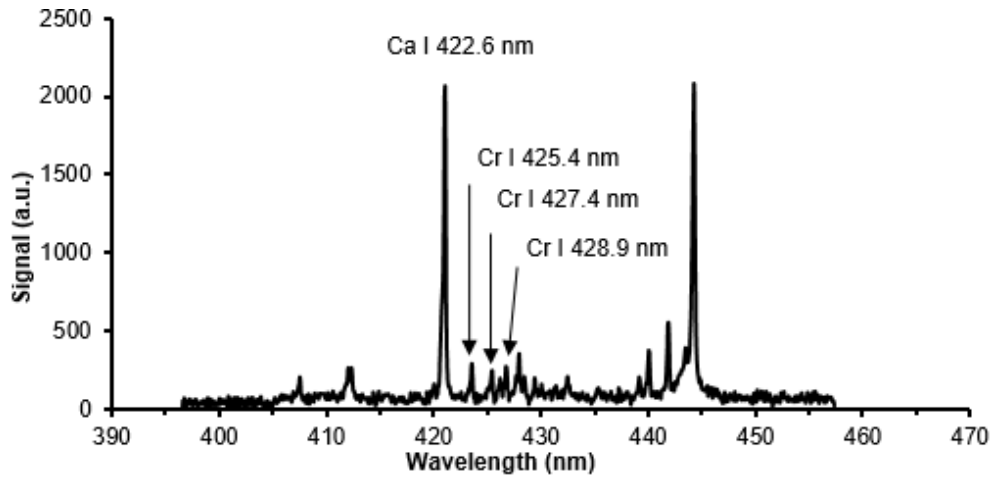
**Fig 8.** Calibration curve of Cu in baby powder material using the mesh-assisted laser-induced plasma spectroscopy employing confinement technique

also clearly observed that the spectrum produces high background emission contributed to the stark effect due to the high electrons and ions density at the initial stage of laser plasma. For a quantitative analysis of powder material, baby powders containing different concentrations of Cu (0.1, 0.5, 1, 2, and 3%) was applied as samples. Fig. 8 presents a calibration curve obtained from the samples having different concentrations of Cu. The linear relationship between the concentration of Cu in the powder and the ratio intensity of Cu to Zn with zero intercepts can clearly be observed. As well known, the reason to use The Zinc (Zn) to make calibration is that the Zn is a major constituent in baby powder. The error bars in this figure represents the standard deviations deduced from 5 data taken on different positions at each concentration. This result stated that the present technique can be used for quantitative analysis of powder material.

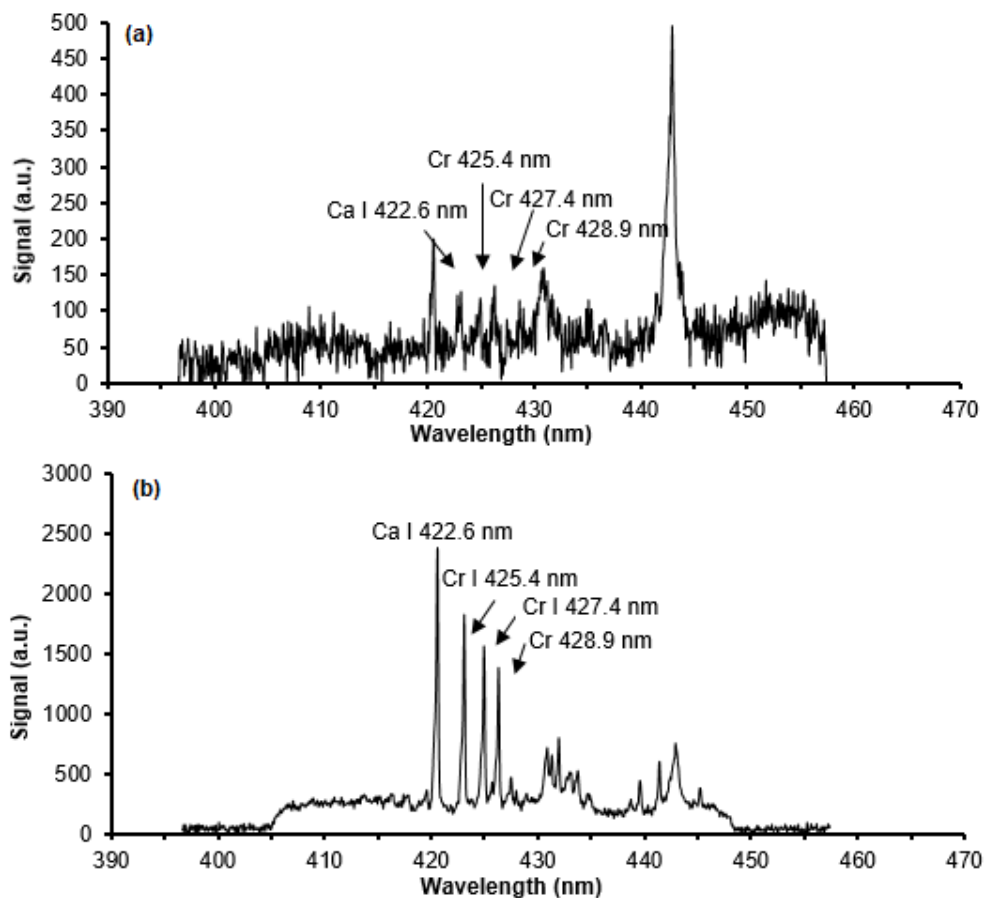
The devised sampling technique was then employed to perform impurity analysis in powder material. For this purpose, a heavy metal element of Cr, which is the type of Cr(VI) and is dangerous for human health, is used as the impurity. The emission spectrum of Cr obtained from the agar powder containing 0.1% Cr was displayed in Fig. 9. Typical triplet neutral Cr (I) at 425.4, 427.4, Cr I 428.9 nm are clearly observed. The method was also employed to detect Cr lines in

powdered rice containing 0.1% Cr as shown in Fig. 10(a). However, the analytical lines of neutral Cr at 425.4, 427.4, and 428.9 nm are only slightly detected. Furthermore, the

noise of emission spectrum on Fig. 9 and 10(a) is quite high. Thus, the detection sensitivity by using this present technique is low. To solve this problem, a condensation



**Fig 9.** Emission spectrum taken from the agar powder containing 1% Cr using the mesh-assisted laser-induced plasma spectroscopy employing confinement technique



**Fig 10.** Emission spectrum taken from the rice containing 0.1% of chrome, (a) without condensation, and (b) with condensation technique

method was employed, namely, the powdered rice sample containing 0.1% Cr was shaped like a ball shape with a diameter of 30 mm by adding little amount of water of around 10 mL. Afterward, the sample was directly dried by using a commercial microwave oven for around 1 min and finally, a combustion process of powder in a closed chamber was carried out. The powder material obtained from the combustion process was then used as a sample and put it into the hole of the sample holder. This pretreatment was intended to make a condensation process inside the sample. As reported by Senior et al. [17], the combustion process of powder like coal powder results in vaporization of powder particle followed by condensation. The results showed that the emission signal lines of Cr increase sharply about twenty times compared to the sample without the combustion process as shown in Fig. 10(b). For quantitative analysis of Cr impurity in powder material, following equation was used to estimate the limit of detection (LoD),

$$\text{LoD} = \frac{3 \times \text{Noise intensity}}{\text{known line intensity}} \times \text{impurity conc. in sample (mg/kg)} \quad (1)$$

Based on the literature [18], the detection limit was calculated by multiplying three times noise intensity to the impurity concentration in the sample divided by known analytical lines as in Eq. 1. The LoD of Cr in rice powder using Cr line at 422.6 nm was 25 mg/kg; The Cr I 425.4 nm line was used as a representative for quantitative measurement because this line has the highest sensitivity compared to other Cr lines at 427.4 and 428.9 nm. This LoD is much lower compared to the result as described in the report [19], namely the LoD of Cr in powder material is 43 mg/kg. In the report, a standard LIBS using pulse Nd:YAG laser was employed and the powder material was prepared in the pellet form. Therefore, this method promises to be applied to the identification of impurity elements in the powder sample with high precision and sensitivity.

## ■ CONCLUSION

Identification and analysis of powder material have been successfully demonstrated using the newly devised technique of mesh-assisted laser-induced plasma spectroscopy utilizing pulse CO<sub>2</sub> laser. In this study, the

powder target was put tightly in a hole and covered by metal mesh. Using this devised technique, rapid identification of major elements in powder can successfully be demonstrated with a good precision. Furthermore, the result confirmed that the present technique is much better in accuracy and sensitivity compared to conventional LIBS using Nd:YAG laser. By employing a condensation technique proposed in this study, the detection sensitivity of Cr impurity in powder material was improved of about twenty times compared to that of without condensation process of powder material. The limit of detection of Cr in powdered rice was 25 mg/kg. This present devised technique is very useful for rapid analysis of powder material in the production factory.

## ■ ACKNOWLEDGMENTS

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