Food powder analysis by using transversely excited atmospheric CO\textsubscript{2} laser-induced plasma spectroscopy

Ali Khumaeni,\textsuperscript{1*} Zener Sukra Lie,\textsuperscript{2} Wahyu Setiabudi,\textsuperscript{1} Koo Hendrik Kurniawan,\textsuperscript{2} and Kiichiro Kagawa\textsuperscript{3}

\textsuperscript{1}Department of Physics, Diponegoro University, Semarang, Indonesia
\textsuperscript{2}Maju Makmur Mandiri Research Center, Kembangan, Jakarta, Indonesia
\textsuperscript{3}Research Institute of Nuclear Engineering, University of Fukui, Fukui, Japan

*Email: khumaeni@fisika.undip.ac.id

Abstract. A direct and sensitive analysis of food powder sample has successfully been carried out by utilizing the special characteristics of pulsed transversely excited atmospheric (TEA) CO\textsubscript{2} laser. In this study, a food powder was placed in a container made of copper plate and covered by a metal mesh. The container was perpendicularly attached on a metal surface. A high-temperature luminous plasma was induced on a metal surface 5 mm above the mesh. Once the plasma was produced, a strong shock wave was induced, blowing-off of the powder from the container to enter into the plasma to be dissociated and excited. By using this method, a semi-quantitative analysis of food powder was made. The detection limits of Cr in the powdered agar and Cd in the powdered rice were 9 mg/kg and 50 mg/kg, respectively.

1. Introduction
Analysis of food powder sample has become an interesting subject. This is due to the fact that the food materials contain the important nutrition for human being such as calcium, sodium, and potassium. Thus, the development of the technique for rapid quantitative analysis with high precision to measure the concentration of essential elements for nutritional purpose is urgently necessary\textsuperscript{[1]}. Beside that, it is also necessary to examine the existence of heavy elements such as chromium (Cr) and cadmium (Cd), which are hazardous for human health and might be accidentally contained in the powder food material during the growth of the food plant and industrial process.

Generally, the method applied for food powder analysis is Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) or Inductively Coupled Plasma Mass Spectrometry (ICP-MS)\textsuperscript{[2]}. Those methods perform high precision and sensitivity in elemental analysis. However, in those methods, the samples must first be liquid often being prepared by either wet digestion or dry ashing. Thus, the analysis requires delicate sample preparation, labor intensive and expensive equipment.

Recently, laser-induced breakdown spectroscopy (LIBS) has become a tremendous method for rapid qualitative and quantitative analysis\textsuperscript{[3-4]}. In conventional LIBS technique, a pulsed laser with high peak power and short pulse duration such as Nd: YAG laser is mostly employed to induce laser plasma at atmospheric pressure. In this method, the vaporization, atomization, and excitation processes take place at the same time due to a single treatment of laser irradiation. However, due to the short pulse duration (8 ns) and high power density (about 10\textsuperscript{10}-10\textsuperscript{11} W/cm\textsuperscript{2}) of the Nd: YAG laser, the blowing-off of powder occurs when the laser is directly irradiated onto the powder sample. Therefore, in this technique, analysis is mostly made after pressing the powder sample into a pellet\textsuperscript{[5]}. 

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We found that a direct analysis of a powder sample can be made by utilizing the specific characteristics of a TEA CO\(_2\) laser [6]. The TEA CO\(_2\) laser is longer in wavelength (10.64 µm) and in pulse duration (200 ns) compared to the Nd:YAG laser. Thus, the TEA CO\(_2\) laser is suitable to the analysis of powder samples. In the study, a powder sample was placed into a small hole in a metal plate and covered with a metal mesh. The TEA CO\(_2\) laser was then focused on the powder surfaces through the metal mesh. However, the sensitivity of the elemental result was rather low. Therefore, this technique cannot be employed for a quantitative analysis of minerals and hazard materials at low concentration in the organic powder samples.

To solve this problem, we propose a unique method by utilizing the specific characteristics of TEA CO\(_2\) laser. In this method, a powder sample was placed into a container and covered by a metal mesh. The container was then perpendicularly attached on an iron metal surface. The fine powder particles are dissociated and excited in the gas plasma induced by a TEA CO\(_2\) laser on metal surface. Compared to our previous method [6], the present method is much superior. Namely, the luminous plasma has higher temperature and larger diameter because the plasma was induced on metal surface, while in the previous method, the plasma was induced by assisting a metal mesh, resulting in lower temperature. Therefore, the dissociation and excitation processes can effectively takes place in the plasma induced by using our present method.

2. Experimental setup

The basic experimental setup applied in this work is the same as the one used in previous research [5]. A TEA CO\(_2\) laser (Shibuya SQ 2000, pulse energy of 3 J, wavelength of 10.6 µm, pulse duration of 200 ns in full width of half maximum, beam cross section of 3 mm x 3 mm), which was constructed by Shibuya Company for laser marking, was employed in this study. The laser beam was focused by a ZnSe lens (f = 200 mm) onto a target sample through a ZnSe window. The laser energy was set at 1.5 J by inserting an aperture in the front of the focusing lens. The spot size of the laser beam on the sample surface was 2 x 2 mm\(^2\), which results in an irradiance of 0.19 GW/cm\(^2\) for an energy of 1.5 J.

The sample was placed in a metal chamber with dimensions of 12 cm x 12 cm x 12 cm. During the experiment, nitrogen gas was flowed into the metal chamber, in which the pressure of the surrounding gas was kept constant at 1 atmosphere. The flow rate of the gas was 4 liters per minute (Lpm).

![Figure 1. Illustration of the sample holder used in this study.](image)

The samples used in this study were a powdered agar, a herb medicine (Tsumura Kackontou) and a standard polished rice (NIES certified reference material, produced by Environment Agency National Institute for Environmental Studies, Japan) containing mineral and hazardous impurity. Prior to the analysis, 0.5 g powder sample was placed into a container made of copper plate with a dimension of 15 x 22 x 6 mm\(^3\) and covered by a metal mesh made of stainless steel wires (lattice constant of 0.2 mm and wire diameter of 0.1 mm). The mesh functions to control the blowing-off of the powder particles caused by the plasma shock wave. The container was then perpendicularly attached on an iron metal surface as shown in Fig. 1. The sample preparation and data acquisition were made at the University of Fukui, while the data processing and analytical study were carried out at Diponegoro University.
The plasma emission spectrum was obtained by detecting laser plasma radiation using optical multi-channel analyzer (OMA) system (ATAGO Macs-320) consisting of a 0.32 m focal-length spectrograph with a grating of 1200 groves/mm, a 1024-channel photodiode detector array, and a micro-channel plate image intensifier. The spectral resolution of the OMA system is 0.2 nm. The light emitted from the laser plasma was collected by an optical fiber (θ= 27° in solid angle) and fed into the OMA system. One end of the fiber was placed at 15 cm distance from the focusing point of the laser light and set perpendicularly to the path of laser beam. Another OMA system with an intensified charge-coupled device (CCD) (Lambda vision LVICCD 1012), was also used in this experiment. This OMA has higher spectral resolution of 0.02 nm. We use the OMA system with an ICCD having higher resolution because we will improve the sensitivity of analytical detection for impurity analysis. By using the higher resolution spectrometer, the background emission and the noise can be suppressed and the analytical lines can clearly be identified with an adjacent lines. Thus, the detection sensitivity of analyte can be improved. This OMA will be used to detect poisonous heavy metals contained in the food powder at low concentration.

3. Results and discussion

Initially, the study was addressed to search the optimum experimental condition. First, we examined the distance (D) between the focusing point of laser beam on a metal surface and the metal mesh used to cover the powder in the container (Fig. 1). Figure 2 shows the emission spectra taken from the herb medicine powder using the present technique with the D of (a) 10 mm (red line), and (b) 5 mm (blue line). The herb medicine contains Ca of approximately 400 mg/kg. In this experiment, the TEA CO₂ laser energy was set at 1500 mJ. The lattice constant and the wire diameter of mesh used to control the blowing-off of the powder were 0.2 mm and 0.1 mm, respectively. During the experiment, the nitrogen gas was flowed in the chamber in order to avoid gas breakdown taking place in front of the metal due to the interaction between dust and TEA CO₂ laser beam. It is seen in the figure that the emission intensities of ionic Ca lines at 393.3 nm and 396.8 nm for the case of D of 5 mm is much higher than that of 10 mm. The Ca has a specific doublet ionic lines at 393.3 nm and 396.8 nm with the excitation energies of approximately 3 eV from the ground state of ionic energy level. It is assumed that the amount of powder particles entering into the gas plasma region is much larger for the case of 5 mm of D. Therefore, we chose the D of 5 mm for further practical applications.

Another experiment was also made in order to get the best experimental circumstances. To this end, the same technique as used in Fig. 2 (D = 5 mm) with a different lattice constant of mesh, namely 0.2 mm and 0.4 mm, was employed. The sample used in this experiment is the same as in Fig. 2. The results certified that the lattice constant of 0.2 mm is much more effective to result in higher intensity than that of 0.4 mm. This is probably that for the case of mesh with the lattice constant of 0.2 mm, the powder particles entering into the gas plasma can be suppressed and controlled, so that the amount of evaporated powder particles entering into the gas plasma region is suitable. While, in case of lattice
constant of 0.4 mm, the amount of evaporated powder particles are too much, lowering the
temperature of gas plasma. Detail mechanism of plasma generation and dissociation and excitation
processes of atoms in the powder sample was shown in the previous work [7]. From this point, we
assumed that the control of the blowing-off of the powder being sent into the gas breakdown plasma is
crucial issue.

To estimate the temperature of plasma induced by using the present technique, a Boltzmann
method was employed. To this end, the emission spectrum of copper (Cu) taken from the CuSO₄⋅5H₂O
powder was used. Figure 3(a) shows how the emission intensities of Cu I 510.5 nm and Cu I 521.8 nm
change with time. It is seen in the figure that the emission intensity of Cu I 510.5 nm and Cu I 521.8
nm (blue and red curves, respectively) is rather high at the initial stage. With increasing the time, the
Cu intensities slowly decrease and last very long time up to around 60 µs. Figure 3(a) also presents
how the plasma temperature changes with time (green curve); the plasma temperature can readily be
derived by the ratio of the emission intensity of Cu I 521.8 nm (excitation energy of 6.2 eV) to that of
Cu I 510.5 nm (excitation energy of 3.8 eV), with the assumption of Boltzmann’s distribution [10]. It
is seen that at the initial stage, the plasma temperature is approximately 5750 K. The plasma
temperature keeps almost constant up to 20 µs and finally slowly decreases up to 60 µs.

Figure 3. (a) Time profiles of emission intensities of Cu lines and plasma temperature taken
from the CuSO₄⋅5H₂O powder sample using the metal-induced plasma technique.
(b) Emission spectrum of magnesium taken from the powdered rice.

At initial, the present technique was employed to perform the direct analyses of food powder
samples. It is well known that food powders contain the primary source of nutrition for human being
such as magnesium (Mg). Figure 3(b) shows the emission spectrum of magnesium taken from the
powdered rice. Two specific ionic emission lines of Mg II at 279.5 nm and 280.2 nm were strongly
detected. The ordinary powdered rice sample contains magnesium of around 400 mg/kg. This result
certified that the present method can be used to detect the nutrition elements such as Mg in the food
powder.

For further exploration of the capability of this technique, an analysis of poisonous-heavy-metals in
the powdered agar and the powdered rice was made. This analysis is necessary because the heavy
metals are hazardous elements for human health. Figure 4(a) shows the emission spectrum of Cr taken
from the powdered agar. The powdered agar contains Cr of approximately 1000 mg/kg. It can be seen
that the strong emission lines of Cr I 425.4 nm and Cr I 427.4 nm clearly appear. It should be
mentioned that Cr I 428.9 nm cannot clearly be seen in this spectrum because it overlaps with Fe I
428.8 nm. Other strong emission lines of Fe also occur in the spectrum. By using Cr I 425.4 nm line,
the signal to background (S/B) ratio and the detection limit were estimated. The S/B ratio of Cr line
was approximately 10 and the detection limit of Cr in powdered agar was approximately 9 mg/kg; the
detection limit was derived by calculating what concentration of the signal yielded 3 times of the noise
level is because the 3 times of the noise is clearly identified as a signal that can be distinguished from
the noise. It should be noted that the detection limit of Cr produced by using the present method is much lower compared to the case of X-ray fluorescence spectroscopy (XRF) method (detection limit of Cr in the powdered agar is approximately 170 mg/kg). The other heavy metal was also detected from the powdered rice containing 1000 mg/kg of Cd. The Cd is poisonous heavy metals usually contained in the rice during the growing process due to the environment pollution. Figure 4(b) shows the emission spectrum of Cd taken from the powdered rice. It is seen that strong emission lines of Cd neutral at 346.6 nm and 361.0 nm can clearly be observed. Compared to the Cr lines, the efficiency of the Cd atomic excitation is much lower. Thus, total emission intensity of Cd lines is much lower than that of Cr lines. By using Cd I 361.0 nm line, the S/B ratio and the detection limit of Cd in the powdered rice were approximately 7 and 50 ppm, respectively. The results certified that this present technique has high possibility to be applied to the practical quantitative analysis of powders.

4. Conclusion
The direct analysis of powder sample has been demonstrated by using the specific characteristics of a TEA CO₂ laser. In this study, a powder was placed in a container, equipped with a metal mesh, perpendicularly attached on a metal surface. High-temperature and large-size luminous plasma was induced when a TEA CO₂ laser was focused on the metal surface just 5 mm above the mesh. Due to strong shock wave induced by the plasma, a lot of fine powder particles were blown-off and finally entered into the gas plasma region to be dissociated and excited. By using this present technique, a semi quantitative analysis of food powder sample can successfully be carried out. The detection limit of Cr in the powdered agar and Cd in the powdered rice was approximately 9 mg/kg and 50 mg/kg, respectively. This technique can potentially be used to be applied to checking the powder containing low concentration elements such as heavy metals in the food powder.

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