The 1064 nm laser-induced breakdown spectroscopy (LIBS) inspection to detect the nutrient elements in freshly cut carrot samples

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Abstract. The laser-induced breakdown spectroscopy (LIBS) technique was applied to detect the nutrient elements contained in fresh carrot. Nd:YAG laser the wavelength of 1064 nm was employed in the experiments for ablation. Employing simple set-up of LIBS and preparing the sample with less step method, we are able to detect 18 chemical elements including some fundamental element of carrot, i.e Mg, Al, Fe, Mn, Ti, Ca, and Mn. By applying normalized profiles calculation on some of the element, we are able to compare the concentration level of each element of the outer and inner part of carrot.

1. Introduction
Elemental detection and analysis has played very important role for agricultural product examination. Hence we will be able to determine the nutritional and harmful element for human body. Detecting nutritional element is very useful to ensuring that our body will not be lacked of nutrient consisted on agricultural product or food that we consume [1]. For the plant itself, nutritional detection is also good to observe whether the plant gains sufficient inputs of macro-nutrients and/or micronutrients. It was reported that the deficiency of some elements could adversely give the bad effect of growth process. For example, the plant which is lack of Mg can lead to chlorosis and impair shoot and root growth. Another case, Ca has role to deliver nutrients into the plant, therefore Ca deficiency gives effect in deformation and chlorosis of leave [2]. In the other hand harmful elements such as toxic or heavy metals inside the food and agricultural product has also become urgent need to be detected. The accumulated amount of armful element may lead to intoxication for human health [3].

A lot research has been developed such that the examination of the food and agricultural product sample could be conducted with fast analysis and less preparation step. Some worked has been done by employing chemical method which need multistep of sample preparation, whilst the data acquisition and analysis took a long time [4]. The laser-induced breakdown spectroscopy (LIBS) offers more promising technique to detect the nutritional and harmful element in the agricultural product. This technique has basic rule on laser-induced material ablation (vaporization and ionization of a minute amount of sample materials) and on spectral analysis of the plasma emission [3]. The plasma emission is captured by fiber optic and translated into emission spectra data. The spectra
consist of some lines and they were identified as element consisted in the sample. This measurement technique is relatively simple and fast, and we do not need much sample preparation step.

In this study, we use carrot as our experimental sample. We choose carrot because this vegetable grew as root in the ground. This will be good sample to detect if there are some contaminant elements inside the carrot, because the root is the main part of the plant to absorb water and element in soil. Once the soil was contaminated by harmful elements, it is highly possible that the carrot was polluted as well. Some of the work has been done by employing LIBS technique to determine the chemical element inside of the agricultural product [1, 2, 4]. On 2008, a research has been done on using the LIBS technique to determine chemical element on freshly cut potato and carrot, this study used 266 nm wavelength and Echelle spectrometer, hence it was able to detect 27 elements inside the potato [5]. In this work, we have demonstrated a simple LIBS set-up and less preparation step of sample. We are able to detect 18 chemical elements including some fundamental element of carrot, i.e Mg, Al, Fe, Mn, Ti, Ca, and Mn.

2. Methodology

The schematic diagram of this experiment is shown in figure 1a. The LIBS system consists of Nd-YAG laser (Q-Smart 850mJ, Quantel) with the wavelength of 1064 nm, energy of 80 mJ and frequency of 10 Hz. The laser beam was focused to sample by a 150 mm focal length plano-convex lens. The sample was attached into a rotation holder inside the vacuum chamber which was operated on the pressure of 6.9 torr. The generated plasma was then collected by using collimating lens and focused into fiber optics. The fiber optic was connected to Ocean Optics Spectra Suite MAYA2000 Pro measuring emission lines from 200 to 1200 nm with a spectral resolution of 0.25 nm.

![Figure 1. (a) LIBS experiment set-up and (b) carrot samples used in this experiment.](image)

The carrot used in this experiment was randomly bought from traditional market. As we shown in figure 1b, the carrot sample was prepared by simply cutting it into horizontal and vertical cutting, hence we can obtain a slice with center part (A) and a slice with external part (B). The thickness of both samples was around 5 mm. Data acquisition process was done using Spectra Suit software. The data was taken five times to ensure and validate the real spectrum and peaks observed in the experiment. The peak appeared in the spectrum was identified as chemical elements inside the sample. The NIST database was used in this study to identify the chemical element of the carrot sample.

3. Results and discussion

Figure 2 gives an overview of the typical LIBS spectra of the carrot sample, the black and red data was respectively the center and external part of the carrot sample. The plasma was induced on the carrot sample. The spectra from the plasma was captured using spectrometer fiber in the dark room and by eliminating the background spectra.
Figure 2 shows the LIBS spectra of the carrot sample. According to the spectra, we could identify some high peaks as well as the low peaks at some point of wavelength. The two high peaks have been identified as H and O. Because we use the freshly cute carrot, and it has high water composition. Therefore, it is most likely dominated by H and O element. Also, because we use organic sample another element that expected to be appeared is C, or carbon. To see more detail spectra, we chop the graph on figure 3 into several some particular wavelength range. On figure 3, we could see a spectrum with quite large number of lines with quite acceptable background signal. For the data analysis, we use the NIST spectral database [6] to identify line by line of the spectrum. In total we have distinguished around 35 lines, which consist of 17 chemical elements.

The detail spectra of carrot sample could be seen in figure 3. There are 18 chemical elements could be identified in the spectrum of carrot sample. For species that emit a large number of lines in the observed spectral range, only the most intense lines are presented. Apart from organic elements (H, C, N, O), we can see a large number of inorganic elements including metals (Fe, Cu, Ti, Mn, Th, Zr, W, Ne) and nonmetals (Mg, K, P, S, Cl, Ca). These elements were detected for both the external and the center part of the carrot. The intensity of each element on the external part differs from the central part. For comparing and calculating the amount level of each element we will need quantitative analysis, which require more complex instrument to trace and ultra-trace elements in vegetables. This information is important for the improvement of the detection sensitivity by using a dedicated narrow bandwidth, high resolution and high throughput spectrometer Echelle spectrometer or (Czerny-Turner spectrometer for example) instead. Such dedicated detection system can be optimized for one or several elements in order to get higher sensitivity and lower limit of detection for targeted elements.

In this study we might still be able to see rough calculation to compare the element intensity on the central and external part of the carrot. For this investigation, we chose some elements as examples, which are K, Mn, Fe, and Cu. The normalization was made for a given spectrum by dividing the line intensity of each element by the highest among the two data, external and central element in intensity. Figure 4 shows the normalized profile of K, Fe, Mn, and Cu element level inside the carrot sample. By applying this method the concentration level of each element could be compared between the outer and inner part of carrot. In the center part Fe level was higher than in the external part, while K, Mn, and Cu were more dominant in the external part than in center one.
Figure 3. LIBS spectra of carrot samples, the black and red data was for the center and external part respectively.
Some other works have been done in the same field to detect the chemical elements of vegetables. Some of the works have demonstrated the measurement with more complex sample preparation [1, 7], while some other did experiment with different laser type [3, 11], laser wavelength [5, 8, 9], and spectrometer tool [5, 10]. Juve et al. [5] conduct the same experiment with UV laser (the wavelength of 266 nm) and Echelle spectrometer which has much more sophisticated technology than common spectrometer used in this experiment, which is able to detect some of the major element such as Mg, Al, Fe, Mn, Ti, Ca, and Mn.

The study in this paper employed a simple LIBS set-up and the least step of sample preparation, but the result is quite promising. Using our simple LIBS system, the number of element detected is indeed less than the previous work but we are able to detect the same main elements as the previous work did. Hence, in the future work we would be able to apply these methods on some other organic sample with very simple preparation step. By adding and replacing some of the instruments, i.e using Echelle spectrometer and delay stage generator, more detail analysis could be conducted on determining the element level, including determining limit of detection of each elements.

4. Conclusion

The chemical element detection on freshly cut carrot sample has been done in this study. By employing simple set-up of LIBS and preparing the sample with less step method, we are able to detect 18 chemical elements including some fundamental element of carrot, i.e Mg, Al, Fe, Mn, Ti, Ca and Mn. By applying normalized profiles calculation on some of the element, we are able to compare the concentration level of each element of the outer and inner part of carrot. By adding and replacing some of the instruments, i.e using Echelle spectrometer and delay stage generator, we expect to have more detail analysis on determining the element level, including determining limit of detection of each elements.

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