A new method of detecting heavy metal in vegetable based on LIBS system

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ABSTRACT

The LIBS detection experiments of the quantitative measurement of heavy metal Pb in the vegetables were reported. The samples pretreatment method and standard operating procedures for quickly detecting heavy metal elements in vegetable by LIBS detection technique are summarized. The calibration curve of Pb in Chinese cabbage has been made, which linearity is 0.99962. The limit of detection 2.39 mg/kg for Pb in Chinese cabbage has been obtained, which is the Pb concentration in the fresh Chinese cabbage.

Keywords: Laser Induced Breakdown Spectroscopy (LIBS), heavy metal in vegetable, qualitatively detecting, quantitatively detecting.

INTRODUCTION

The quality of agriculture products has become the focus of the government and the citizen these years; it affects everybody’s health and safety directly. Heavy metal is a main pollutant which imperils the food safety. It comes from industrial manufacture and automobile exhaust etc., pollutes the soil and irrigative water and enters human body through alimentary crop. Heavy metal has extremely harm to health and not easy to be eliminated. In recent years, lots of tragedies which were caused by heavy meal pollution of food were reported on news, such as “Cd Rice” and “Excessive levels of lead in children's blood”. It is not hard to find that most of them are reported after the damages have influenced the health of people. How about identify problems before loss? Absolutely, it is better to keep all the processes of food production safe and healthy, and also the hardest way. Therefore, we need to have an effective way to detect quickly if our food has excess heavy metal, which keeps the food safe and healthy before going onto our table. Here, we will introduce a method of detecting heavy metal in vegetable quickly based on Laser Induced Breakdown Spectroscopy (LIBS) system. We attempt to take the advantages of LIBS technology and apply them into quantity detection of heavy metal in vegetable.

Laser Induced Breakdown Spectroscopy (LIBS), an element detection technique based on atom emission spectrum analysis, use focused high power narrow pulse width laser beam to create instant high temperature on sample surface and produce plasma. Element under test can be detected qualitatively and quantitatively by analyzing emission light spectrum information from the plasma (Leon and David, 2013).

Compared to the popular chemical analysis methods such as AAS and ICP, LIBS may be the fastest detection technique because other techniques are very strict about the state of samples. Most of the samples have to be dissolved by chemical reagents before being detected in AAS or ICP system. Usually, it takes days to get the useful information, meanwhile only minutes to hours by LIBS. LIBS technique is not only attractive in simple sample preparation and rapid response but also a cheaper method for elements detection and analysis compared to traditional ones. For now, LIBS was mainly applied in metallurgy, biomedicine, environmental surveillance, archaeology etc (Kuwako et al, 2003; Kiefer et al, 2011; Chen et al, 2012; Zheng et al, 2009). Many methods were applied in order to get more accurate result and lower limit of detection of concentration (Kuwako et al, 2003; Scaffidì et al, 2006; Bogaert et al, 2008; Shen et al, 2007).

The research of heavy metal in vegetable has just started and only a few experiments about the qualitative detection, not quantitative yet (Vincent et al, 2008). The procedure
of detecting heavy metal element concentration in vegetable was established in this article. At the beginning, we will introduce our LIBS system set-up, the basic methods about preparing vegetable samples and other protocol, then, the experiment analyzing heavy metal in vegetable quantitatively, getting the system detection limit of 2.3 mg/kg for Pb in Chinese cabbage.

LIBS SYSTEM SET-UP AND DETECTION METHOD

According to the theory of atomic radiation, the wavelength of emission spectrum depends on atomic energy level structure of different elements and the intensity of emission spectrum is given by formula (1). Suppose the particles jump from energy level α to energy level β, N is stimulated emission particles number; v is emission photon frequency, h Planck constant, g is the statistical weight of energy level α, A is transition probability, Z is partition function, E is energy of emission state; k is the Boltzmann constant and T is temperature of the plasma.

For a specific emission spectrum line, we can get to know which element comes out and then check out all the quantities but N and T in the physical handbook. As for the temperature of plasma, T, we can eliminate its influence by internal standard method. Now, simplify formula (1) to formula (2). C represents the concentration of specific element which is determined by the number of stimulated particles, N. Formula (2) shows the relationship between concentration of the element under test and the spectrum intensity of the element. That is so-called calibration curve.

In summary, testing the characteristic spectral line exist or not can analyze the element under test qualitatively. Intensity of characteristic spectral line is proportional to the element content.

\[
I_{\alpha\beta} = N \cdot v_{\alpha\beta} \cdot \frac{h \cdot 2 \cdot \lambda_{\alpha\beta}^2}{4 \pi} \cdot e^{-E_\alpha / kT}
\]  

(1)

\[
I = \alpha \cdot C
\]  

(2)

The LIBS system set-up is fabricated including laser, spectroscopy, sample stage and data processing software (Figure 1). The output beam of Nd: YAG solid laser, which has 8 ns pulse width, 100 mJ light pulse energy and 1064 nm wavelength was focused on the sample surface by a lens, thereafter, plasma is stimulated at that focused point. Fiber coupled grating spectrometer was used to probe spectrum with the range of 200 and 400 nm, respectively. The software completes the controlling of the system and the spectrum data processing. This set-up was used to carry on the experiments about the detection of heavy metal concentration in vegetable.

EXPERIMENTS

In the experiments, the Chinese cabbage from the market was bought and the fresh cabbage divided into 5 groups, soaked in different concentrations of lead acetate (CH₃COO)₂Pb·3H₂O solution for 48 h, taken out, washed clean and natural air drying carried out. This method compared with earth planting and water planting of preparation can save 3 to 6 months and easier to get sample in concentration gradient distribution. There is need for further research on the molecular conformation of heavy metal in such kind of samples which is same or not as that in earth planting Chinese cabbage. Now, we used such soaked samples temporarily in the experiment. Furthermore, three steps were in progress, such as sample treatment, spectral acquisition and data processing.

Fresh Chinese cabbage contains much water, so as to influence spectrum’s production and measurement. Figure 2 shows that it is certified by experimental results. Spectrum intensity has negative correlation with water content. So in the experiment, Chinese cabbage needs to be dehydrated before the test and numerate dehydration rate. After dehydration dry cabbage is put in the grinder and powder is then pressed into tablet with presser machine. The sample is placed on sample stage of LIBS system; 8 to 10 different points on the pill is chosen and 3 to 5 spectrums are gathered on each point so as to get about 30 spectrum data. Processing software is used to get one spectrum data that fits the request of the internal standard method, the wavelength of characteristic spectral line is therefore compared and the data in standard library (NIST) used to distinguish the type of element using different samples of different concentration gradient distributions to fit calibration curve can get the result of quantitatively test.

Our experimental result verified Pb element existence in Chinese cabbage. In the quantitative experiment, first of all, the rule of determination of analytical spectral line and reference spectral line should be made (Figure 3). 1) Priority to choose atom spectral line; 2) There is no strong interferential line aside; 3) The concentration of reference element is constant; 4) Analytical spectral line and reference spectral are as close as possible in the premise of non-overlap. For Pb, 283.3 nm is selected as analytical line and Mg 285.2 nm as reference line (Figure 3). The concentrations of the five samples were measured by ICP-MES in Analyzing Center on Tsinghua University, which are 12.5, 18.75, 37.5, 57.5 and 72.5 mg/kg respectively. In the meantime, the content of Mg was measured in the five samples and the relative content of Pb/Mg in the calibration curve used (Figure 4). We measured the spectrum relative intensity of five samples as 0.1051, 0.1297, 0.1845, 0.2436 and 0.2700. So, we obtained the calibration curve of spectrum strength and element concentration with linearity of 0.99962 (Figure 4). Therefore, the limit of detection is 2.39 mg/kg for Pb in Chinese cabbage.
Figure 1: LIBS detection system set-up.

Figure 2: Spectrum line intensity vs. dehydration of Chinese cabbage.

Conclusions

By means of repeated experiments, we summarized the method and standard operating procedures for quickly detecting heavy metal elements in vegetable by LIBS detection technique. Due to the high water content, the dehydration pretreatment was necessary. As a result, the calibration curve of Pb in Chinese cabbage has been made, which linearity is 0.99962. Therefore, we have got the limit of detection as 2.39 mg/kg for Pb in Chinese cabbage. That is the Pb concentration in the fresh Chinese cabbage. Up to now, the limit of detection of Pb in Chinese cabbage is much higher than the national standard, which is 0.3 mg/kg, not satisfied to be used into detection in food safety. The reason is complex, probably relevant to the system hardware with sensitivity and heavy metal elements’ molecular conformation in the plant. Subsequently, we will improve the LIBS hardware system and research the property that Pb combine with big molecular when vegetable absorb it, so as to get lower detection limit. Furthermore, the
Figure 3: Analytical spectral line Pb 283.31 nm and reference spectral line Mg 285.21 nm of five content samples under test.

Figure 4: Calibration curve of Pb/Mg in Chinese cabbage.

Calibration curve of Pb in Chinese cabbage

\[ Y = 0.19513x + 0.05433, \quad R^2 = 0.99962 \]

LOD = 2.3916 ppm

Relative content Pb/Mg (Mg = 85.29 ppm)

Instrumentation of LIBS system was pushed to realize better accuracy and stability, to achieve on site, real time,
quickly detecting of heavy metal element and make it possible for detecting heavy metal in other agriculture products.

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REFERENCES


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