

Rapid Detection of Heavy Metal Contents in Fruits by Laser Induced Breakdown Spectroscopy

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Abstract—To detect heavy metal contents in fruits rapidly, the Citrus Nanfeng tangerines pericarp and flesh have been analyzed by laser induced breakdown spectroscopy. Line emissions from five heavy metal elements, Pb, Cd, Hg, Cr and As, have been clearly extracted. Their intensities correspond to relative concentrations of these elements contained in the analyzed samples. The results demonstrated that the species and contents of heavy metal in fruits can be identified by their LIBS spectra, and the heavy metal contents in the inner of fruits are more than the outer. This analysis showed efficient discrimination between heavy metals from different parts of a single fruit by laser induced breakdown spectroscopy spectra.

Index Terms—fruits, heavy metal contents, rapid detection, LIBS

I. INTRODUCTION

In recent years heavy metals elements contained in fertilizer and environment contamination have been used in agriculture widely. Some deleterious heavy metals elements, such as plumbum (Pb), cadmium (Cd), hydrargyrum (Hg), chromium (Cr) and arsenic (As), are transmitted into fruits and other farm produces. Some of them are transited into high toxic compound going with food in body. Most of them have the characteristic of accumulation and longer half life, which brings acute or chronic toxicity reaction so that teratogenicity, cancer-causing and mutagenicity come into being [1, 2]. So, the detection and identification of heavy metals elements in foods, such as fruits, has been an important problem around the world.

The traditional means of detecting the heavy metal contents in fruits has been used by inductively coupled plasma atomic emission spectrometry (ICP-AES), flame atomic absorption spectrometry (FAAS), and so on[3, 4]. But the samples need to be digested by concentrated acid in the above ways. The pre-treatment processing is complicated and time-consuming, the real-time detection can not be implemented, and the secondary contamination appears easily.

Laser-induced breakdown spectroscopy (LIBS) is

basically an emission spectroscopy technique where atoms and ions are primarily formed in their excited states as a result of interaction between a tightly focused pulse-laser beam and the material sample [5]. One of the important features of this technique is that it does not require any sample preparation, unlike conventional spectroscopic analytical techniques. Samples in the form of solids, liquids, gels, gases, plasmas and biological materials [6-10] can be studied with almost equal ease. LIBS has rapidly developed into a major analytical technology with the capability of detecting all chemical elements in a sample, of real-time response, and of close-contact or stand-off analysis of targets.

In this paper, the characteristic spectrum of elements Pb, Cd, Hg, Cr and As in orange pericarp and flesh were collected by laser-induced breakdown spectroscopy. Based on our results we propose an innovative strategy to detect heavy metal contents in fruits rapidly.

II. MATERIALS AND METHODS

A. Experimental samples

Fifty Citrus Nanfeng tangerines from Jiangxi province were chosen as experimental objectives. Each orange was divided into pericarp and flesh at the same dimensions. That is, the total number of samples is 100. The pericarp and flesh have 50 samples respectively.

B. Experimental Setup

Experimental setup sees Fig.1. The Nd:YAG (yttrium-aluminum-garnet) nanosecond laser (BeamTech, Nimma-200) provides pulses of 10 ns duration at 1064 nm and a repetition rate of 10 HZ. The laser beam is focused on the surface of a sample using a single lens of 200 mm focal length. Typical maximum pulse energies at the ablation surface were 200 mJ/pulse. To have a fresh spot for each laser shot, the sample is fixed on a move platform. Optical emission from the LIBS plasma was collected by a 2 m steel encased multimode fiber (core diameter=400 um). This fiber was coupled to an eight-channel AvaSpec spectrometer equipped with a 2048 pixel CCD (charge coupled device) detector (AVANTES B.V., 2048-USB2-RM) which provided complete spectra coverage from 200 to 1100 nm with a resolution of 0.07 nm at 315 to 417nm. The AvaSpec spectrometer was controlled by personal computer (PC)

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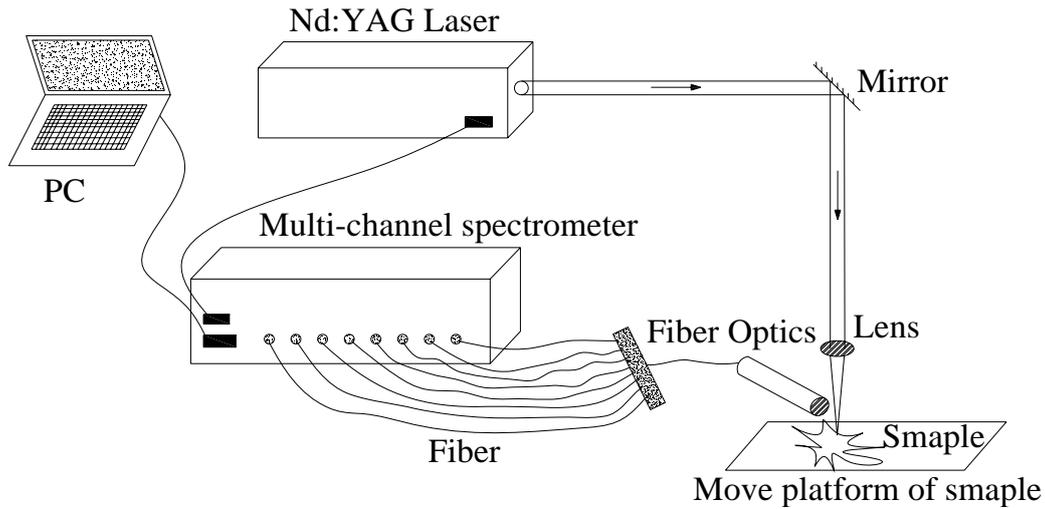


Figure 1. The experimental setup of LIBS

running manufacturer-provided software. LIBS spectra were acquired at a delay time of 1.28 μs after the ablation pulse. For each pericarp or flesh sample 20 spectra were taken. Each individual spectrum was accumulated over 100 laser shots. Spectra were recorded continuously in order to keep the experimental conditions as identical as possible for all samples.

For each individual spectrum, the line intensity was extracted for each of elements Pb, Cd, Hg, Cr and As. For given experimental conditions, we can consider the line intensity of an element is proportional to the relative concentration of the element. The average of 20 spectra of individual sample was extracted as the line intensity of the element. Line intensities of elements in sample provide a profile of relative concentrations of the elements.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

Fig.2 and Fig.3 show a typical LIBS spectrum from Citrus Nanfeng tangerines pericarp and flesh respectively. Five elements have been included in our consideration: Pb, Cd, Hg, Cr and As. From each individual spectrum, line intensity was extracted for each of the five elements. Look first at Fig.2, the spectrum is dominated by emission from Cr and Pb. To a lesser extent, emission from Cd, As and Hg is visible. For the same experimental conditions, continuous emission is much more obvious in the pericarp spectrum than the flesh spectrum. That can be clearly seen by comparing Fig.2 and Fig.3.

The 238.12 nm As line, 247.77 nm Cr line, 274.85 nm Cd line, 280.20 nm Pb line and 302.15 nm Hg line

were chosen as the characteristic spectra. Each line was collected for 20 spectra, and each spectrum was accumulated for 100 laser shots. For the data processing, I_{ij}^k is used to represent a specific raw line

intensity, where k represents different samples ($k=1, \dots, 100$), j refers to an individual spectrum ($j=1, \dots, 20$), and i refers to a specific element ($i=1, \dots, 5$). In order to present a relative

concentration of the element. The mean value \bar{I}_i^k of line intensities of an element are calculated for 20 spectra of a given sample.

$$\bar{I}_i^k = \frac{1}{N} \sum_{j=1}^N I_{ij}^k$$

The average intensity of emission line is given in Table 1.

In Table 1, for the same element, the mean values of LIBS relative line intensity is more in pericarp than in flesh. That indicates the relative contents of elements are more in pericarp than in flesh. This result fits well with the property of heavy metals in fruits, in which heavy metals accumulate in outer of the fruits more than the inner. The contents of heavy metals are less in inner of the fruits. So, line intensities associated to the elements for a given fruit samples provide a profile of relative concentrations of the elements. Further studies are underway to detect the heavy metal contents from outer to inner in fruits by LIBS spectra.

TABLE I.
MEAN VALUES OF LIBS RELATIVE LINE INTENSITY OF ELEMENTS

Samples	Relative line intensity (dimensionless)				
	As238.12nm	Cr247.77nm	Cd274.85nm	Pb280.20nm	Hg302.15nm
Pericarp	35.222	220.391	40.522	242.915	20.935
Flesh	3.491	64.705	5.413	46.731	5.123

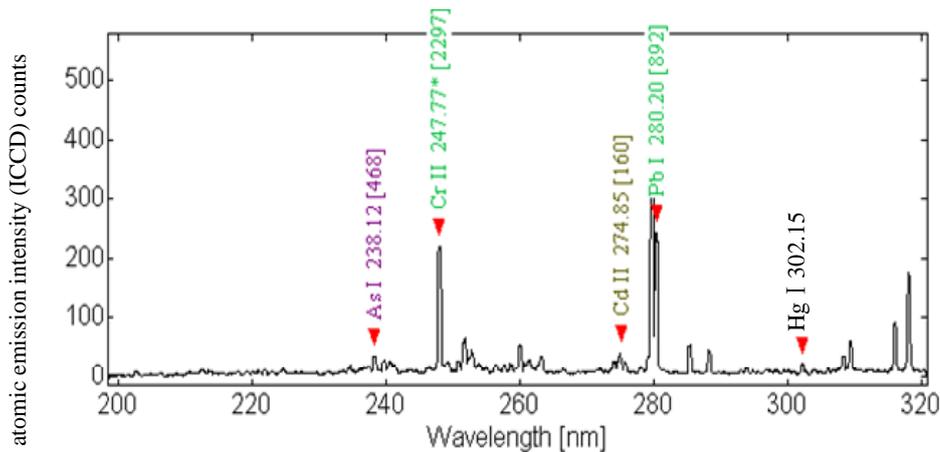


Figure 2. LIBS spectrum of Citrus Nanfeng tangerines pericarp with the Pb, Cd, Hg, Cr and As emissions identified

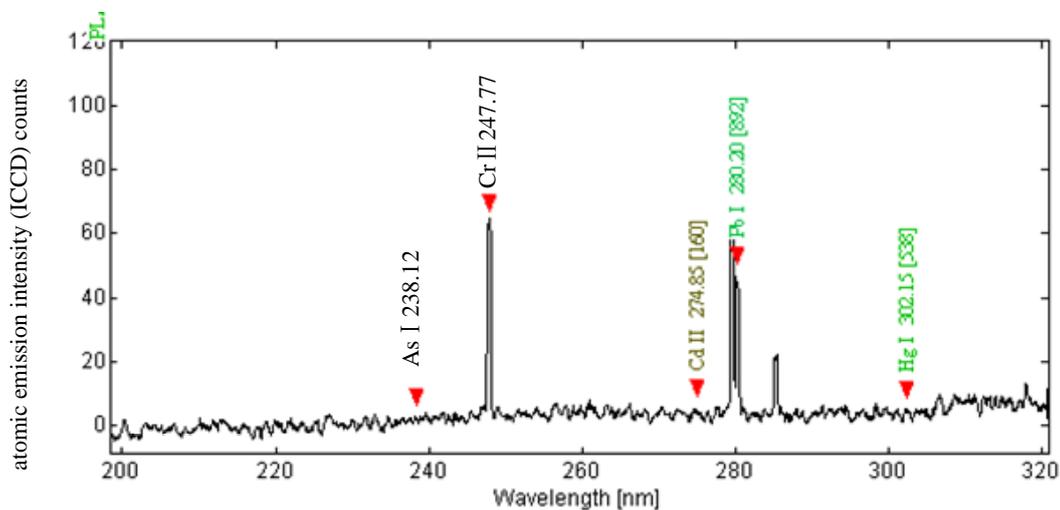


Figure 3. LIBS spectrum of Citrus Nanfeng tangerines flesh with the Pb, Cd, Hg, Cr and As emissions identified

IV. CONCLUSIONS

In this paper, we have extracted the characteristic spectra of Pb, Cd, Hg, Cr and As in Citrus Nanfeng tangerines pericarp and flesh by LIBS. The results demonstrated that the species and contents of heavy metal in fruits can be identified by their LIBS spectra, and the heavy metal contents in the inner of fruits are more than the outer. The profile of relative concentrations of the elements can be associated with their LIBS spectra. Such relative concentrations can be precisely determined by LIBS. However, much progress needs to be achieved before LIBS can be considered as a practical application. Experiments are currently underway in our laboratory utilizing several different samples of fruits to address these problems.

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