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# Discrimination of Ca,Cu,Fe and Na in Gannan Navel Orange by Laser Induced Breakdown Spectroscopy

Mingyin Yao<sup>1</sup>, Jinlong Lin<sup>1</sup>, Long Xue<sup>2</sup>, Muhua Liu<sup>\*1</sup>, Qiulian Li<sup>1</sup>, Zejian Lei<sup>1</sup>

<sup>1</sup>Optics-Electrics Application of Biomaterials Lab, College of Engineering,  
Jiangxi Agricultural University, Nanchang, P. R. China

<sup>2</sup>School of Mechanical and Electronical Engineering, East China Jiaotong  
University, Nanchang, P. R. China

E-mail:mingyin800@126.com,\*Corresponding author E-mail:suikelmh@sohu.com

**Abstract.** Laser induced breakdown spectroscopy (LIBS) has become a powerful tool for the direct analysis of a large variety of materials in order to provide qualitative and/or quantitative information. However, there is a lack of information for LIBS analysis of agricultural products. In this work a LIBS system has been designed for the discrimination of Ca, Cu, Fe, and Na elements in Gannan Navel orange. An experimental setup was established by using a Nd:YAG laser operating at 1064 nm and a grating spectrometer with CCD detector. The LIBS spectra of pericarps and fleshes of Gannan Navel orange were collected. The typical spectrum lines of mineral elements Ca,Cu,Fe,and Na were chosen and identified, and the relative content of four elements in pericarps and fleshes were compared and analyzed respectively. The results showed that the relative content of elements Ca,Cu,Fe,and Na in pericarps was more than in fleshes. The LIBS relative intensity of Na、Fe、Ca、Cu elements in pericarps decreased in turn, while the LIBS relative intensity of Na、Cu、Ca、Fe elements in fleshes increased in turn. The experimental results also showed that the relative content of mineral elements in farm product may be analyzed fast by LIBS, and the LIBS technique is a novel means for rapid detection the quality of farm product.

**Keywords:** LIBS, Gannan Navel orange, Mineral elements, Discrimination

## 1 Introduction

There are plentiful nutrient elements in fruits. The intake of trace mineral elements from fruits is one of the most important pathways for the human body to absorb dietary minerals necessary for the healthy development. Detection and analysis of trace mineral elements in fruits, and more generally in food, can provide useful assessment and control for safe and healthy alimentation. However, detection and analysis of trace and ultra-trace elements in these substances need highly sensitive detection technique.

Usually, the conventional nutrient elements analysis methods, such as ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer), AFS (Atomic Fluorescence Spectrometry), AAS (Atomic Absorption Spectrometry)<sup>[1-3]</sup>, are comprised by

the following steps: taking a sample from the substance or from a processing product line to be inspected; transporting it to an inspection device or to a laboratory; preparing it for chemical analysis; and for determination. The sample preparation for chemical analysis is a required stage for many analytical techniques, which consists in transforming the sample into an appropriate form for the analysis. For the elemental analysis, the solid samples are usually changed to solutions, which carry the analytes free of organic matter. This step is usually the most time consuming analytical procedure, in addition to generating toxic residues and increasing the probability of sample contamination.

Laser Induced Breakdown Spectroscopy (LIBS) is an emission spectroscopy technique that makes use of a high energy laser pulse to simultaneously prepare the sample and excite the species. LIBS is employed to determine the elemental composition of a sample, regardless of whether the sample is a solid, liquid or gas, with no or little sample pretreatment procedures. Due to its instrumental features, LIBS is a promising technique for in situ analysis, including direct analysis at the processing line. During solid sample analysis, its surface is irradiated by a high energy laser pulse, immediately giving rise to material ablation. The sample ablated generates a high temperature plasma plume. As a result of the temperature, the ablated material breaks down into excited ionic and atomic species. The excited species usually return to their fundamental states, emitting characteristic radiation, consequently the qualitative analysis of the emission spectrum provides the sample's "fingerprint" regarding its elemental composition<sup>[4-5]</sup>.

However, performing a quantitative analysis is no simple matter, as the element emission lines in the LIBS spectrum are closely related with the matrix in which they are embedded. The matrix effects occur in the LIBS spectra for several reasons, however the major cause of them is the change of temperature and electron density of the plasma induced on different matrix targets. This is due to variations in both the ablation and laser plasma interaction processes, resulting also in possible variations of plume expansion in the background gas. As a result, different excitation and ionization levels of plasma species are achieved. This signal feature makes it difficult to find the appropriate calibration standards for the LIBS methods. In some cases the appearance of the so-called matrix effects can be reduced by using a multivariate calibration, internal standard or calibration free method<sup>[6-7]</sup>, however significant efforts have been made to adapt conventional calibration to LIBS methods. Vincent Juvé<sup>[8]</sup> analyzed fresh vegetables using ultraviolet nanosecond LIBS. Lilian Cristina Trevizan<sup>[9,10]</sup> evaluated the macronutrients and micronutrients in plant materials by a Q-switched Nd:YAG laser. Edilene C. Ferreira<sup>[11]</sup> detected Ca in breakfast cereals by LIBS.

In this paper, a new proposal for Ca, Cu, Fe, and Na semi-quantitative and qualitative determination in the pericarps and fleshes of Gannan Navel orange using LIBS was evaluated. The method will provide easy sample preparation and fast measurement for agricultural food products, botanical materials and material of similar matrix.

## **2 Materials and Methods**

## 2.1 LIBS Experimental Setup

The experimental setup sees Figure 1. A Q-switched Nd:YAG laser (BeamTech, Nimma-200, China) operating at the fundamental wavelength (1064 nm) was employed. Laser pulses with  $(200 \pm 2)$  mJ, 8 ns pulse width at 10 Hz repetition rate were generated with a 6 mm beam diameter. The laser pulse was focused on the sample pellet by a convergent lens with 30 mm diameter and 200 mm focal length (China Optical Coating Laboratory, Inc). The 35 mm diameter pellet was placed into a plastic sample holder in single axis automatic controlled rotation stage that moved in the plane orthogonal to the laser direction.

The plasma emission was collected by the spectrometer fiber (1.5 m length, 400  $\mu$ m core diameter) matching its numerical aperture. The optical axis of the collecting system was approximately  $45^\circ$  from the laser axis. An eight-channel model AVS-Rackmount-USB2 spectrometer (Avantes, France) equipped with echelle optics was used, which provides the wavelength range between 200 and 1100 nm with a resolution of 0.09 nm at 200 to 317 nm, 0.07 nm at 315 to 417 nm, 0.06 nm at 415-499 nm, 0.08 nm at 497-565 nm, 0.08 nm at 563-673 nm, 0.12 nm at 671-750 nm, 0.13 nm at 748-931 nm, and 0.11 nm at 929-1050 nm. The detector is a 2048 pixel ICCD camera. The dark current of the ICCD was automatically subtracted from the measured spectral data. The integration time and the delay time were fixed at 2 ms and 1.28  $\mu$ s respectively for all measurements presented in this work.

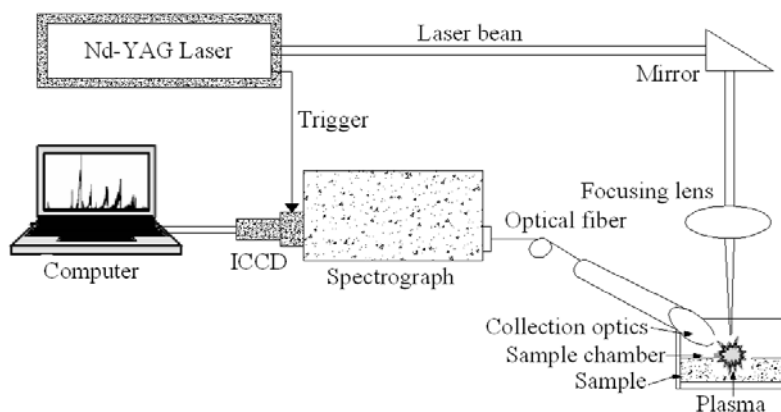


Fig. 1. LIBS experimental setup

## 2.2 Samples and Materials

Twenty fresh Gannan Navel oranges were chosen to perform preliminary experiments. The fruits were washed separately with running tap water and further rinsed twice with distilled water. After washing and natural air drying, the fruits were divided into pericarps and fleshes samples. The samples were chopped and placed in sample chamber with diameter 35 mm. Ten spectra of each sample were collected from different positions. In order to take in account the fluctuations of the laser, the average of 10 spectra in each sample was considered as a single measurement.

### 3 Results and Discussions

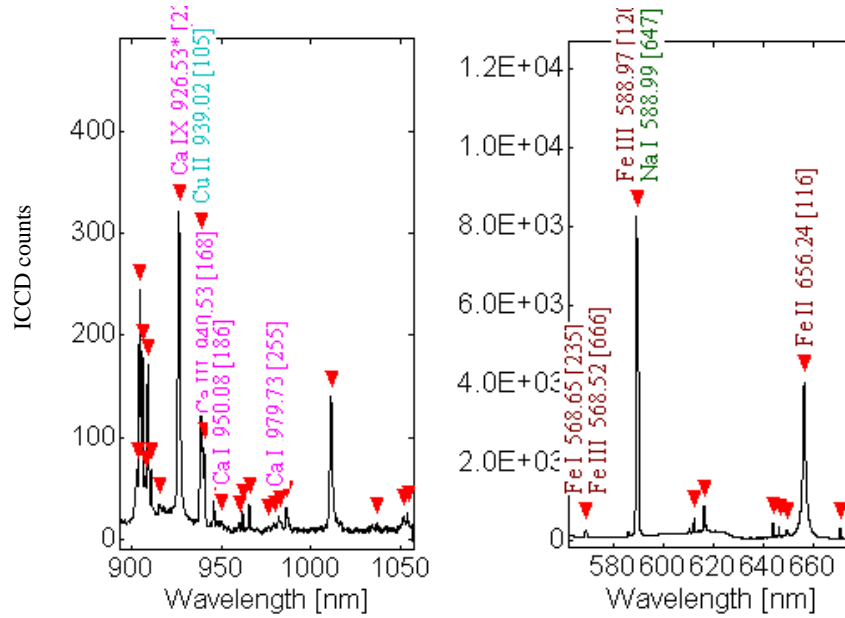


Fig. 2. Typical LIBS spectra of Ca, Cu, Fe, Na in pericarps

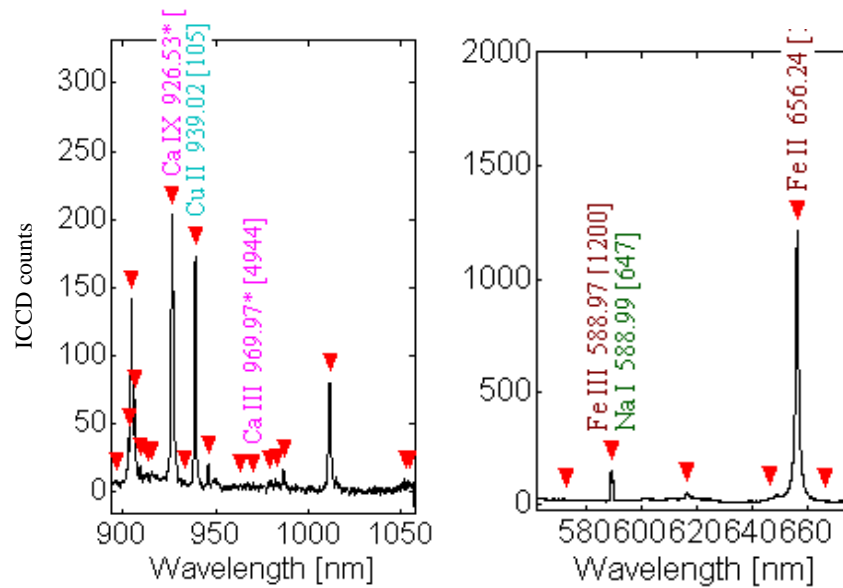


Fig. 3. Typical LIBS spectra of Ca, Cu, Fe, Na in flesh

**Table1.** LIBS relative intensity of elements Ca、Cu、Fe、Na in samples

SampleNo.	Cu939.0176nm		Ca926.5298nm		Line intensity/Counts			
					Fe656.2375nm		Na588.995nm	
	Pericarps	fleshes	pericarps	fleshes	pericarps	fleshes	pericarps	fleshes
1	246.36	3.80	287.16	4.15	1641.16	39.38	3825.61	4.63
2	156.53	1.82	177.63	3.43	790.50	12.10	2501.94	0.16
3	259.15	32.46	283.74	38.57	1569.98	228.26	2998.77	75.80
4	251.37	23.24	280.93	26.84	1213.13	63.20	4250.79	6.43
5	316.43	5.13	347.54	7.53	1328.67	58.77	2545.45	14.58
6	217.34	136.04	240.56	160.89	1238.56	1334.13	1866.93	75.24
7	352.93	28.45	392.28	35.42	1929.40	301.64	2420.07	51.18
8	294.21	182.69	315.07	217.40	1697.47	2029.83	3442.79	53.91
9	349.78	99.17	381.74	121.68	1934.49	966.53	3340.14	134.21
10	241.35	125.41	264.24	148.06	1405.67	1479.70	3217.03	40.91
11	278.20	130.75	306.24	153.07	1425.14	891.03	2323.60	82.52
12	274.79	178.92	301.39	211.28	1821.67	2421.02	3589.79	69.62
13	281.24	102.46	309.96	120.43	1907.14	734.30	4333.74	135.00
14	196.65	161.30	213.45	193.51	1003.34	2659.31	1257.58	99.60
15	354.59	135.46	392.45	161.87	2122.61	1090.93	2797.61	66.46
16	231.98	204.62	252.44	247.40	2080.04	204.62	3461.32	247.40
17	340.15	155.16	372.02	188.40	2398.25	1256.42	4298.56	49.59
18	160.05	196.61	175.11	231.49	863.38	2910.38	962.67	106.76
19	310.61	77.22	344.12	93.88	1635.43	766.21	3174.70	50.01
20	238.73	262.34	260.64	317.32	1641.44	4582.29	2906.45	100.86
Mean	535.24	224.30	589.88	268.26	3164.75	2403.00	5951.55	146.45

The plasma was induced on the surface of the pericarps and fleshes in fresh Gannan Navel orange. To represent the relative concentrations of the analyzed elements, the intensity of Cu at 939.0176nm, Ca at 926.5298nm, Fe at 656.2375nm and Na at 588.995nm were considered for the proposed LIBS method. These lines are chosen for their high intensities and low fluctuations from a spectrum to another. Typical spectra of pericarps and fleshes are shown in Figure 2 and Figure 3. Table 1 provides detailed information of Cu 939.0176nm, Ca 926.5298nm, Fe 656.2375nm and Na 588.995nm in the spectrum of fresh Gannan Navel orange.

From Figure 2, Figure 3 and Table 1, the relative intensity of Ca,Cu,Fe and Na was higher in pericarps than in fleshes. As for same or similar matrix, the relative intensity of elements LIBS is proportional to their concentration, so, the accumulation of Ca,Cu,Fe and Na was obvious in pericarps than in fleshes. Moreover, the relative intensity of elements Cu and Ca was twice in pericarps than in fleshes, and the intensity of Na was far higher in pericarps than in fleshes. The observation and statistics showed that the difference of concentration of mineral elements in pericarps and fleshes.

#### 4 Conclusions

In this work, mineral elements detection, qualitative analysis and semi-quantitative analysis have been demonstrated in fresh Gannan Navel orange using LIBS technique. However, works are still needed to be accomplished in order to understand in detail the plasma generation in a complex matrix such as pericarps and fleshes tissue. Such a detailed understanding would allow a quantitative analysis of trace elements in fruits. The results obtained in this work show the potential of the

LIBS technique to provide an interesting tool for detection and analysis of trace elements in fresh fruits and more generally in food. Trace element detection and analysis in fruits represent important issues for the assessment and the control of food quality and safety, as well as for the detection and the monitoring of the environment pollutions including heavy metal charges in soil, water and air.

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