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Detection of Pesticide Residues on Fruit Surfaces Using Laser Induced Breakdown Spectroscopy

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The detection of pesticide residues on fruits surface is closely related to people's life. Based on our previous research, we further explored the detection of chlorpyrifos residue on apple surface by laser induced breakdown spectroscopy (LIBS) in the paper. We observed the characteristic peaks of P at 213.62 nm, 214.91 nm, 253.56 nm, and 255.33 nm and the characteristic peak of Cl at 837.59 nm. We studied the influences of pesticide concentration and argon on the intensity of LIBS signals. The intensity of LIBS signal showed the linear relationship with the pesticide concentration, and argon could enhance the intensity of LIBS signal. In the case of purging argon, the characteristic peak of P was observed in the LIBS spectrum of chlorpyrifos solution of 1:1000. Then we studied the difference of the LIBS signals of pesticide residues among different matrixes and pesticides. Finally, we performed the quantitative detection of the pesticide residues with LIBS, which will provide a reference for the quantitative detection. Our work gives a new method for the fast detction of pesticide residues on fruits.

Introduction

With the development in modern agriculture, more and more chemicals and fertilizers are widely used in agricultural production and the phenomenon of pesticide residues on the surfaces of agricultural products is serious. Pesticide residues have threatened the health of human beings. Therefore, the detection of pesticide residues on the surfaces of agricultural products is becoming a hot spot.

Conventional detection methods of pesticide residues on the surfaces of agricultural products including gas chromatography, high performance liquid chromatography, gas chromatography coupled with mass spectroscopy, and high-performance liquid chromatography coupled with mass spectroscopy[1-3] are time-consuming and laborious and can hardly achieve real-time detection[2,3]. Moreover, some organic solvents used in these methods are toxic and unfriendly to the environment[1]. Considering the above shortcomings of traditional methods, some scholars studied the optical methods to analyze agricultural products, such as surface-enhanced Raman spectroscopy[4-6]. Shende et al. studied the detection of chlorpyrifos-methyl solution of the orange juice using the surface-enhanced Raman spectroscopy coupled with solid-phase extraction and realized the detection of the chlorpyrifos-methyl at 50 ppb[4]. Shende et al. studied the detection of organophosphorus pesticides on fruits surface by the surface-enhanced Raman spectroscopy and successfully detected 0.1% fonofos on apple surfaces within approximately 5 min with a sensitivity of 10 ppm[5]. Liu et al. studied the detection of pesticide residues on fruit surface by surface-enhanced Raman spectroscopy coupled with gold nanostructures and achieved the limits of detection (LODs) for carbaryl, phosmet, and azinphos-methyl (4.51 ppm, 6.51 ppm, and 6.66 ppm on apple surface and 5.35 ppm, 2,91 ppm, and 2.94 ppm on tomato surface)[6]. Although the limit of detection (LOD) of surface-enhanced Raman spectroscopy is low, it cannot realize the quick online detection.

Since the method using ruby maser-induced plasma has been proposed by Brech in 1962[7,8], LIBS has been applied in solid, liquid, and gas fields[9,10]. Moreover, LIBS can realize fast real-time detection of multiple components without the sample preparation procedure and LIBS is developing rapidly [11-13]. Kim et al. studied the detection method of nutrient elements and agricultural products contaminated by pesticides with LIBS and quantitatively analyzed the nutrient elements in rice and spinach[12]. The LODs of Mg, Ca, Na, and K were 29.63 mg/kg, 102.65 mg/kg, 36.36 mg/kg, and 44.46 mg/kg in spinach, respectively. The LODs of Mg, Ca, Na, and K were 7.54 mg/kg, 1.76 mg/kg, 4.19 mg/kg, and 6.70 mg/kg in unpolished rice, respectively. They also distinguished the samples contaminated by pesticides from uncontaminated samples and the mistaken determination percentage was less than 2%. Multari et al. studied the method of LIBS to distinguish the samples contaminated by different pesticides in complex matrixes (tissue fats and fatty oils)[14]. The detection concentration of pesticides ranged from 0.005 to 0.100 μg/g. The detection method distinguished not only the samples of

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different pesticides, but also the samples of different concentrations. Our previous study described the detection of chlorpyrifos residues on apple surfaces by LIBS[15]. We distinguished the high concentration samples (1:1 and 1:20) accurately. However, it was difficult to distinguish the samples in the lower concentrations (1:100 and 1:1000).

In this paper, based on previous study, we further studied the precise detection method of pesticide residues on fruit surfaces with LIBS in three aspects. Firstly, we explored the influences of the concentration of pesticides and purging argon on the intensity of LIBS signal. Secondly, we studied the differences of LIBS signal among different matrixes and pesticides, respectively. Thirdly, we quantitatively analyzed the pesticide residues on apple surfaces. This paper provides the technical support for the application and development of LIBS in the detection of pesticide residues on agricultural products.

Materials and Methods

Preparation of Samples

Preparation of pesticide samples. The chemical name of chlorpyrifos is O,O-Diethyl-O-(3,5,6-trichloro-2-pyridyl) phosphorothioate (C9H11Cl3NO3PS). Chlorpyrifos was from Dow AgroScience Company and the content of active ingredients was 480 g/L. We dissolved chlorpyrifos in deionized water according to 9 dilution ratios (1:50, 1:80, 1:90, 1:100, 1:110, 1:120, 1:130, 1:500, and 1:1000).

The chemical name of omethoate is O,O-Dimethyl S-methylcarbamoylmethyl phosphorothioate (C5H12NO4PS). Omethoate was produced by Zhengzhou Labor Agrochemicals CO.LTD and the content of active ingredients was 40%. We dissolved omethoate in deionized water according to the dilution ratio of 1:100.

Preparation of fruit samples. Red Fuji apples and Housui pears were bought from GuoXiangSiYi Supermarket. We cleaned the fruits with water firstly and then dried them in the natural environment. Then we cut the fruits into small pieces with a weight of each pieces about 100 g and an area of each pieces about 4cm^2. We smeared 100 μL pesticide solution of each concentration on the surface of fruit pieces as homogeneous as possible and dried them in the natural environment for about 30 mins. Therefore, the samples can be considered as fresh but the pesticide solution had been dried. For the laser spot size was only 100 μm, the apples surface can be considered as flat. So, if the pesicide were 1000 times diluted, its average concentraion in a 100g sample is about 1 mg/kg.

Experimental Devices

Fig. 1 shows the schematic diagram of the LIBS system. Nd:YAG Laser induces a beam laser, which is reflected by the mirror. Then the laser is collimated by the lens and focused on sample surfaces. The materials on sample surfaces are ionized and vaporized by the high-power laser. Then the high-temperature plasma is formed on sample surfaces. The vaporized materials will be broken down into atoms and ions. At the end of laser pulse, the plasma will be cooled and spread to the surrounding environment. The atoms and ions in the excited state will relax from high energy level to low energy level and the optical radiation of specific wavelength will be released[16,17]. A quartz fiber is used to collect the spectrum signal and transmit it to the spectrometer.

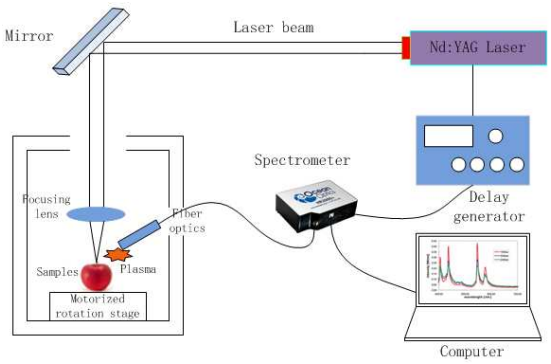


Fig. 1 The schematic diagram of the LIBS system.

The delay generator (Fig.1) is integrated into the equipment to produce the delay time from laser emission to spectrometer collection. Motorized rotation stage is used to adjust the position of samples. Through the adjustment, the focus of the lens just falls on the sample surfaces. The laser generator produced by Beamtech Optronics Co., Ltd. can deliver the monochromatic light at 1064 nm. The maximum energy of the laser beam is 200 mJ and the frequency is 20 Hz. The laser energy was set as 160 mJ in the experiment. The spectrometer (HR2000+) is produced by Ocean Optics Company. The spectral range of the spectrometer is from 200 nm to1000 nm. The resolution is 0.2 nm and the signal-to-noise ratio is 250:1.

The delay time was set as 2 μs, which was the optimal value obtained in the experiment. Compared with our previous studies, this study optimized the focusing lens group used to collect the plasma signal. We also optimized the focusing system of the laser and enhanced the laser energy. All these optimization have improved the detection performance of the system that will present in the part of Results and Analysis .

Experimental Design

We used the LIBS system to collect the signal of the samples, including the apple samples contaminated with chlorpyrifos solutions of 9 dilution ratios (1:50, 1:80, 1:90, 1:100, 1:110, 1:120, 1:130, 1:500, and 1:1000), the clean apple sample, the apple sample contaminated with the omethoate solution of the dilution ratio of 1:100, the pear sample contaminated with the chlorpyrifos solution of the dilution ratio of 1:100, and the apple sample contaminated with the chlorpyrifos solution of the dilution ratio of 1:1000 and purged with argon. We

collected 12 data for each sample and averaged 12 data of each sample to reduce the errors. The influence of heterogeneity of pesticide on samples can also be reduced.

Then, we analyzed the pesticide LIBS signal from four aspects. Table 1 shows the experimental design.

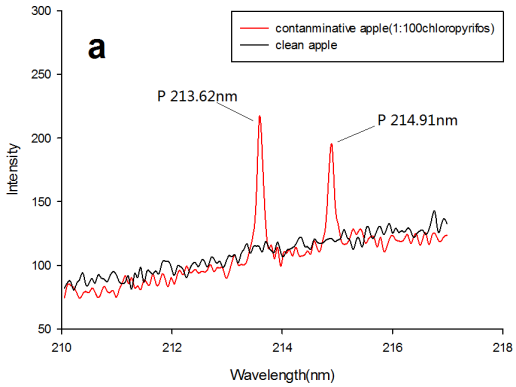
Table 1 The design of the experiments

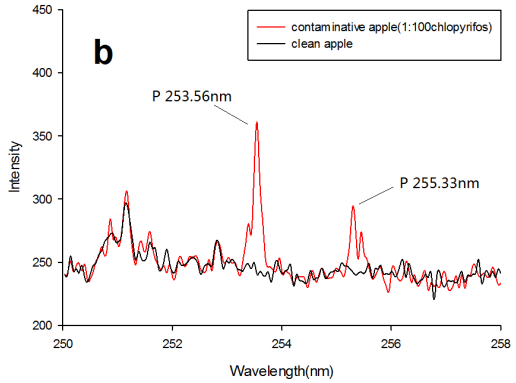
Experiments		Matrix	Pesticide	Concentration
The characteristic of pesticide LIBS signal		Apple	Chlorpyrifos	1:100, clean apple
The influence factors of pesticide LIBS signal	Pesticide Concentration	Apple	Chlorpyrifos	1:50,1:100, 1:500,1:1000
	Purge argon	Apple	Chlorpyrifos	1:1000
Different matrix		Apple	Chlorpyrifos	1:100
		Pear	Chlorpyrifos	1:100
Different pesticide		Apple	Chlorpyrifos	1:100
		Apple	Omethoate	1:100
The quantify analysis of pesticide LIBS signal		Apple	Chlorpyrifos	1:80,1:90,1:100 1:110,1:120,1:130

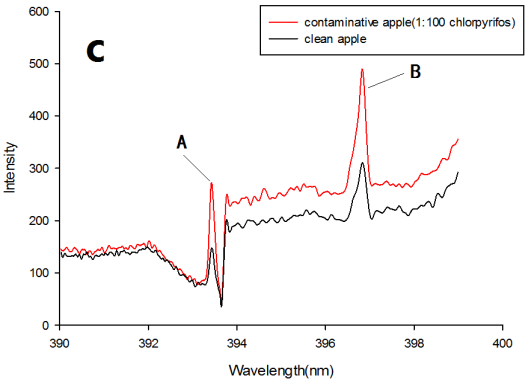
Results and Analysis

LIBS Signal Analysis of Chlorpyrifos

From the molecular formula of chlorpyrifos, we can know that chlorpyrifos include 7 kinds of elements: C, H, O, N, P, S, and Cl. Because the elements of C, H, O and N in air, which will interfere with the LIBS signal analysis of chlorpyrifos, so we chose the characteristic peaks of LIBS signal of P, S, and Cl to analyze the chlorpyrifos residues on apple surfaces.







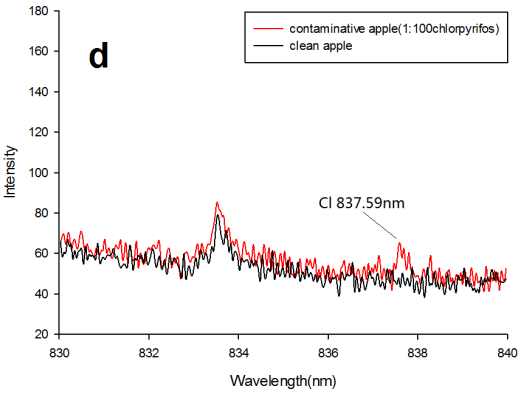
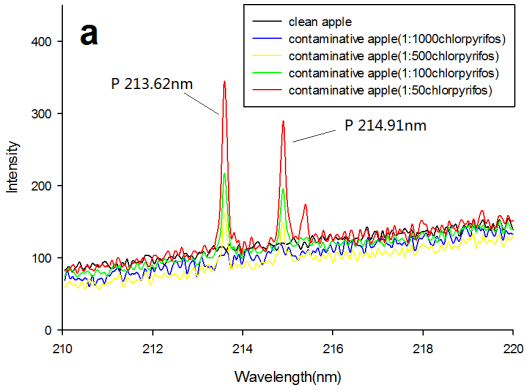


Fig. 2 The LIBS spectra of apple sample contaminated with the chlorpyrifos solution(1:100) and clean apple:**(a)** the characteristic peaks of P element at 213.62 nm and 214.91 nm; **(b)** the characteristic peaks of P element at 253.56 nm and 255.33 nm; **(c)** the characteristic peaks, A and B; **(d)** the characteristic peak of Cl element at 837.59 nm.

Fig. 2 shows the LIBS spectra of P and Cl. The red line represents the spectrum of apple sample contaminated with the chlorpyrifos solution (1:100). The black line represents the spectrum of the clean apple. We observed the characteristic peaks of P at 213.62 nm and 214.91 nm (Fig. 2a), which was the same to our previous results. In addition, we found the others characteristic peaks of P at 253.56 nm and 255.33 nm (Fig. 2b), which was not found in our previous study. As the Fig.2c shown, our previous study presented that the peak A was located at 393.33 nm and the peak B was located at 396.89 nm which were regarded as the characteristic peaks of S. After carefully analysis, we found that the peaks of A and B were not the characteristic peaks of S. We also found the characteristic of Cl element at 837.59 nm (Fig. 2d), which was also observed in our previous study.

Influencing Factors of the LIBS Signal of Chloripyrifos

Different solution concentrations. Fig. 3 shows the LIBS signal spectra of Cl and P, which contaminated with chlorpyrifos solution at different concentrations (1:50, 1:100, 1:500, and 1:1000). As shown in Fig. 3a,



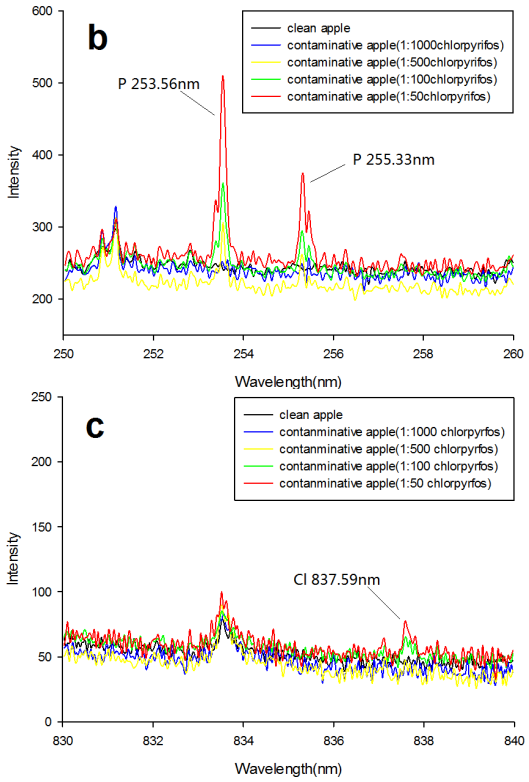


Fig. 3 The LIBS spectra of apple sample contaminated with chlorpyrifos solution of different dilution ratio(1:50, 1:100,1:500,1:1000) and clean apple: **(a)**the characteristic peaks of P element at 213.62 nm and 214.91 nm; **(b)** the characteristic peaks of P element at 253.56 nm and 255.33 nm; **(c)** the characteristic peak of Cl element at 837.59 nm.

we can see that the intensity of the LIBS characteristic peaks shows the stepped change. In addition, with the increase of the solution concentration ,the intensity of the LIBS signal increased as well. Figs. 3b and 3c show the same tendency. Therefore, we concluded that the intensity of LIBS signal of chlorpyrifos apple sample showed a linear relationship with the concentration of the chlorpyrifos solution.

In addition, we found the LIBS characteristic peaks of P in apple sample which contaminated with the chlorpyrifos solution of 1:500 (Figs. 3a and 3b). However, in the previous study, the libs characteristic peaks of P were found in the apple samples which contaminated by the chlorpyrifos solution that the concentration higher than 1:100. We also found the LIBS characteristic peak of Cl in apple sample which contaminated with the chlorpyrifos solution of 1:100 (Fig. 3c), while the characteristic peak of Cl was only found in the apple sample which contaminated with the chlorpyrifos solution of 1:1 in the previous study. We attributed the change to the optimization in the laser energy and the focusing lens group.

Purging argon. Fig. 4 shows the spectra of apple sample contaminated with the chlorpyrifos solution of 1:1000 and the chlorpyrifos solution of 1:1000 purged with argon. As shown in Fig. 4, we could not find the characteristic peaks of P and Cl in apple sample which contaminated by the chlorpyrifos solution of 1:1000. After purging with argon, the characteristic peaks of P (213.62 nm,

214.91 nm, 253.56 nm, and 255.33 nm) were observed clearly. However, the intensity of the characteristic peak of Cl showed a slight change, because it was difficult to excite that the peak of Cl element at 837.59 nm. Therefore, we concluded that the argon could enhance the LIBS signal. This conclusion was also mentioned in previous studies by some scholars[18, 19]. Ref.18 present that the argon gas could provide the best environment which could enhance the intensity of the LIBS signal and minish the interface. In our study, the characteristic peaks of P were found in apple sample contaminated with the chlorpyrifos solution of 1:1000 purged with argon, which was not mentioned in our previous study.

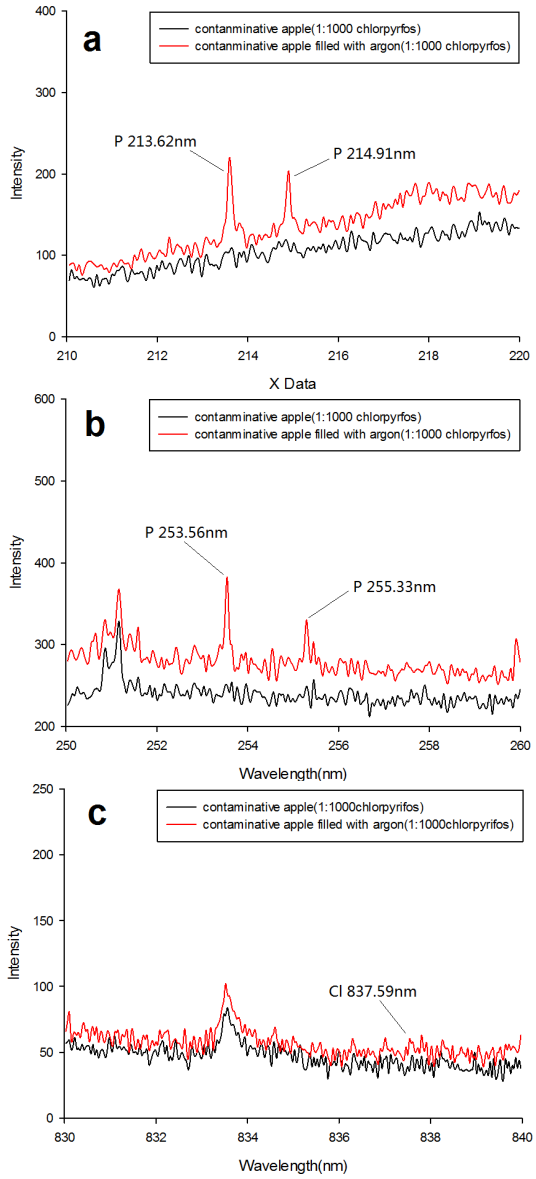


Fig. 4 The LIBS spectra of apple sample contaminated with chlorpyrifos solution of 1:1000 in the case of purging with argon and not purging. **(a)**the characteristic peaks of P element at 213.62 nm and 214.91 nm; **(b)** the characteristic peaks of P element at 253.56 nm and 255.33 nm; **(c)** the characteristic peak of Cl element at 837.59 nm.

Differences of LIBS Spectra among Different Matrixes and Pesticides

In order to study the method to differentiate the pesticides by LIBS, we analyzed the difference of LIBS spectra among different pesticides and matrixes.

Different matrixes. Fig. 5 shows the LIBS spectra of apple sample contaminated with the chloripyrifos solution (1:100) on the surfaces of apple and pear.

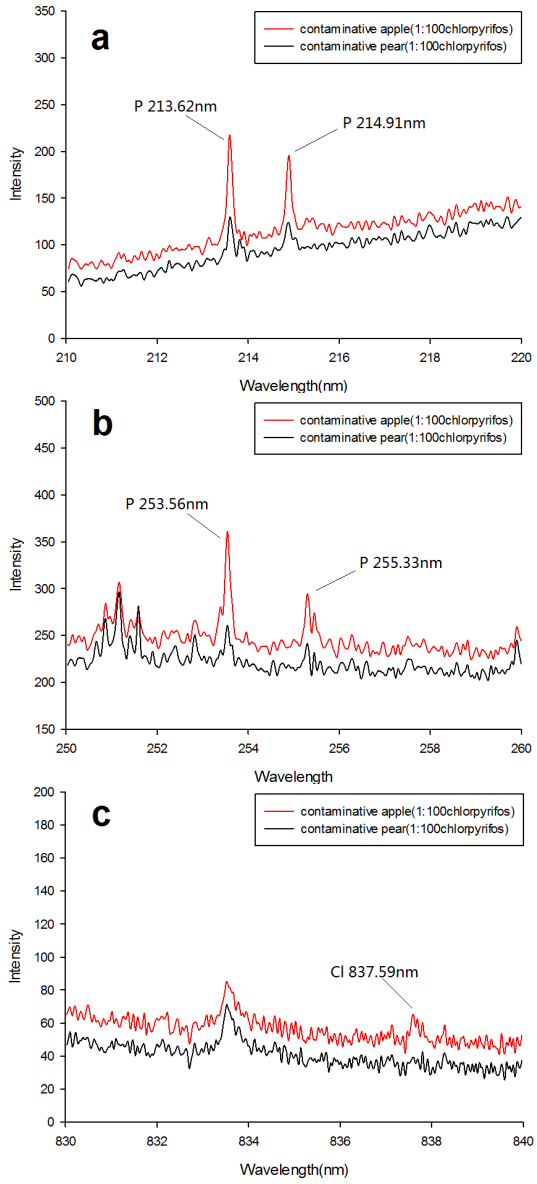
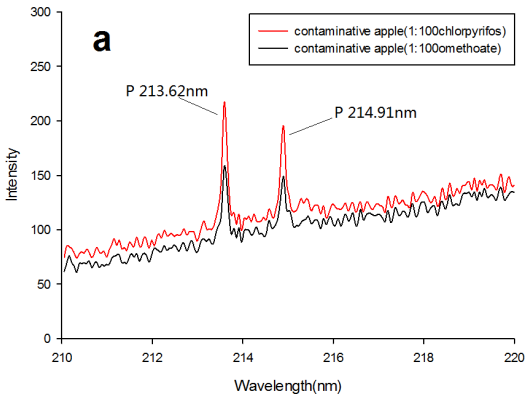


Fig.5 The LIBS spectra of apple sample contaminated with the chlorpyrifos solution in different matrixes(apple and pear): **(a)** the characteristic peaks of P element at 213.62 nm and 214.91 nm; **(b)** the characteristic peaks of P element at 253.56 nm and 255.33 nm; **(c)** the characteristic peak of Cl element at 837.59 nm.

The characteristic peaks of P in the apple matrix contaminated with the chlorpyrifos solution are stronger than those in the pear matrix contaminated with the chlorpyrifos solution. We attributed the difference to the physical property between apple and pear. The peel of Red Fuji apple was very smooth and the flesh was firm. Therefore, the chlorpyrifos solution smeared on the surface of apple was difficult to be absorbed. On the contrary, the peel of Housui pear was coarse and the flesh was sparse. Therefore, the chlorpyrifos solution smeared on the surface of pear was easy to be absorbed. The difference of the physical properties led to the intensity of the LIBS signal of the pesticide residues was different on the surfaces of different fruits. From the analysis, we concluded that the intensity of the pesticide LIBS signal varied with the matrix.

Different pesticides. Fig. 6 shows the LIBS spectra of apple sample contaminated with the solution of chlorpyrifos and omethoate in the dilution ratio of 1:100. Both chlorpyrifos and omethoate contain the elements of P and S, but the chlorpyrifos also contains Cl. As shown in Figs. 6a and 6b, the characteristic peaks of P element of chlorpyrifos are obviously higher than that of omethoate. We attributed the distinction to the physical properties of the pesticides, such as viscosity and volatility. The viscosity and volatility of different pesticides made the residual quantity was different. So the LIBS spectrum presented distinction in intensity. As shown in Fig. 6c, the characteristic peak of Cl at 837.59 nm is observed in chlorpyrifos, whereas it cannot be observed in the omethoate because omethoate does not contain Cl. The characteristic peaks of LIBS spectra show significant differences among different pesticides, as well as the intensities of the characteristic peaks.

According to the above analysis, we can conclude that the LIBS signal is closely related to matrixes and pesticides.



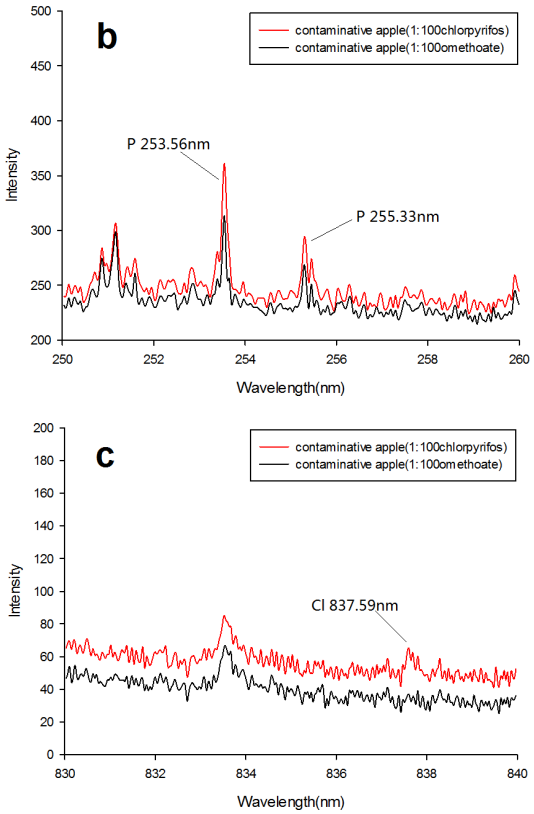
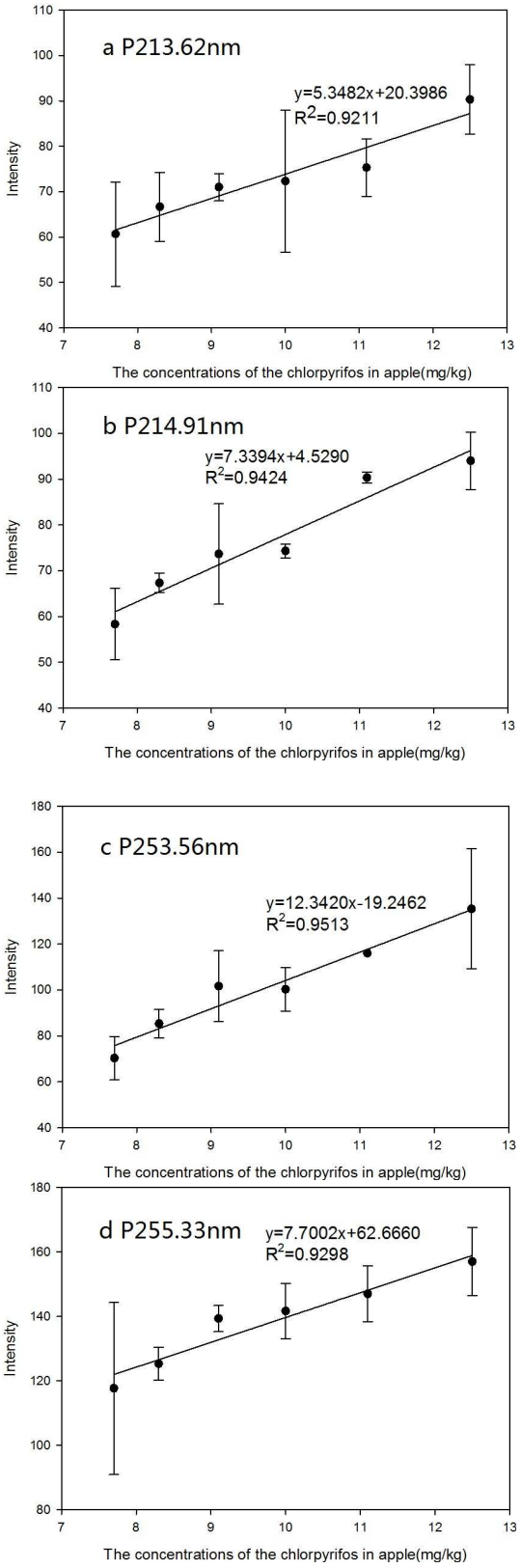


Fig. 6 The LIBS spectra of different pesticides(chlorpyrifos and omethoate): **(a)** the characteristic peaks of P element at 213.62 nm and 214.91 nm; **(b)** the characteristic peaks of P element at 253.56 nm and 255.33 nm; **(c)** the characteristic peak of Cl element at 837.59 nm.

Quantitative analysis of pesticide residues

We quantitatively analyzed the relationship between the pesticide concentration and the intensity of characteristic peaks (213.62 nm, 214.91 nm, 253.56 nm, 255.33 nm, and 837.59 nm). And we fitted the calibration curve by the apple samples contaminated by the chlorpyrifos solution that the concentration we used were 1:80, 1:90, 1:100, 1:110, 1:120 and 1:130. Fig. 7 shows the calibration curves of the LIBS characteristic peaks of chlorpyrifos in apple fitted by the method of single variable linear regression.



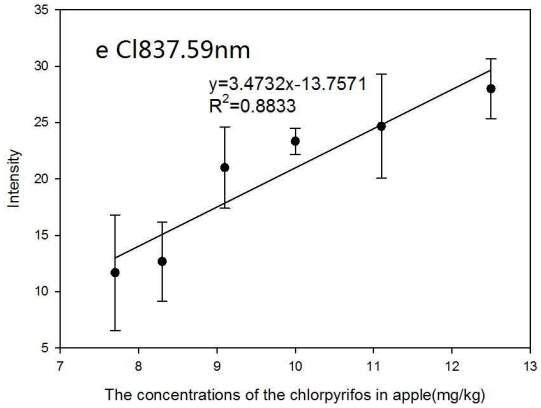


Fig. 7 The quantitative analysis of LIBS characteristic signal of chlorpyrifos in apple sample: **(a)** the calibration curve of the P element at 213.62 nm; **(b)** the calibration curve of the P element at 214.91 nm; **(c)** the calibration curve of the P element at 253.56 nm; **(d)**the calibration curve of the P element at 255.33 nm;**(e)** the calibration curve of the Cl element at 837.59 nm.

All the correlation coefficients (R^2) are larger than 0.88, which indicating that the fitting curves are reliable. From the curves we know that the intensity of the LIBS spectra has a linear relationship with the solution concentration. Therefore, we can use the calibration curve to detect the chlorpyrifos quantitatively. It should be noted that slopes of the calibration curves at different wavelength are different. We think this may be caused by the following reasons: 1) Each wavelength of spectral characteristics has different detection limit and signal-noise ratio, and the concentrations in calibration curve is near the detection limit, then may lead to a different slopes in calibration curves. 2) The pre-processing method (e.g. background subtraction etc.) may caused the slopes of calibration curves in different wavelength varied.

In order to explore the detection ability of the LIBS for pesticide residues, we calculated the LODs of the characteristic peaks. At first, we subtracted the intensity of background from the original LIBS signal to acquire the actual intensity of characteristic peak. Then we calculated the LODs by the equation which defined as 2 σ /k, where σ is the standard deviation of background and k is the slope of calibration curve[12,20-22]. Table 2 shows the LODs of the characteristic peaks. We can see the LODs of P element at 213.62nm, 214.91nm, 253.56nm and 255.33nm are 4.3mg/kg, 2.1mg/kg, 1.5mg/kg, and 6.9mg/kg,, respectively. And the LOD of the Cl element at 837.59nm is 3.0mg/kg. The Chinese standard of the chloripyrifos residue of apple is 1mg/kg[23]. Although the LODs we calculated are a little bigger than the Chinese standard, we can observed the characteristics of P element in the apple sample contaminated with the chlorpyrifos of 1:1000 purged with argon, which is equivalent with 1mg/kg. So the method of LIBS is reliable for the detection of pesticide residues.

If a wide range of the concentration of pesticides solution are used, the calibration curve and the LOD will be more accurately. This section is only a exploration for the quantitatively detection using LIBS.

Table 2 The LODs of P and Cl of chlorpyrifos

Elements	Wavelength(nm)	LOD
P I	213.62 nm	4.3mg/kg
P I	214.91 nm	2.1mg/kg
P I	253.56 nm	1.5mg/kg
P I	255.33 nm	6.9mg/kg
Cl I	837.59 nm	3.0mg/kg

The quantification analysis of pesticide residues and the calculation of the LOD provide the reference for the quantitative LIBS detection of the pesticide residues on the surfaces of agricultural products.

Conclusions

Based on our previous study, we analyzed the characteristics of the chlorpyrifos LIBS signal in the paper. We observed the characteristic peaks of P at 253.56 nm and 255.33 nm, which were not observed in our previous study. We also discussed the influences of the pesticide concentration and argon on the LIBS spectra. The intensity of LIBS signal had a linear relationship with the concentrations of pesticides. Argon could enhance the intensity of LIBS signal of pesticides. We also analyzed the distinction in the intensity of LIBS signal among different matrixes and pesticides. At last, we discussed the quantitative detection of pesticide residues. However, the detection limits of the method is higher than Chinese standard if no argon were used, we believe some methods could lower the LOD: 1) a more sensitive calibration model may be established using some chemometrics methods; 2) the LIBS spectral characteristics in ultraviolet region of P and S is much obvious than the viable band and thus can achieve much lower LOD. We will further study the above methods and present in our future publications.

Overall, the paper provided a reference for the detection of pesticide residues on the surfaces of agricultural products as well as a reference for the application of the LIBS.

Acknowledgements

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