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## ARTICLE

## The Application of Laser-Induced Breakdown Spectroscopy in Domestic Detergent Residues Detection

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With the increasingly wide application of detergents, the hazards of detergent residues have gained extensive attention. The paper aims to explore the application of LIBS (Laser-Induced Breakdown Spectroscopy) in the detection of detergents. In the study, three materials (porcelain, stainless steel, and bamboo) were used as the carrier of detergents and their LIBS spectra were acquired and analyzed. Four brands of detergents that are commonly used in Chinese family were used in the experiment. In the analysis of detergent spectra, the compositions were identified according to emission lines and the elements of Ca, Na, C, H and N were found in detergents. The emission lines of CN and Na were significant and representative and could be utilized to develop rapid detecting system. After detergents were diluted by 2000 times, the characteristic spectral lines of Na at 568.82 nm and 616.22 nm were still measured, which indicates that the method could detect the detergent residues as low as 35.4  $\mu\text{g}/\text{cm}^2$ . The spectral characteristics were further studied using chemometrics method and it is demonstrated that there are obvious differences among the samples with different concentrations of detergent. Furthermore, we studied the matrix effects and found the spectral features were not influenced by the carrier materials. It is demonstrated that LIBS is an effective method to detect detergent residues on dishware and its detection limit meets FDA (U.S. Food and Drug Administration) requirements.

### 1. Introduction

Domestic detergents as cleaning products are widely used to clean clothes, tableware, fruits and vegetables. The excessive use of detergents caused a lot of detergent residues in domestic sewage. Domestic sewage directly discharged into natural waters without treatment will poison aquatic plants and animals. Detergents can decrease the activity of plant enzymes or even destroy the structures of enzymes<sup>1</sup>. Detergents in waters will severely poison aquatic organisms and lead to cell death and serious reproductive dysfunction<sup>2</sup>. Long-term exposure of human body to residual detergents also leads to serious consequences. Detergent poisoning can seriously damage the central nervous system and respiratory system<sup>3</sup>. Eye surgery instruments cleaned with detergents caused severe toxic anterior segment syndrome<sup>4</sup>. The wide application of automatic dishwashers also increases the risk of the detergent poisoning in children<sup>5</sup>. There are more than 20 kinds of ingredients in domestic detergents, and one of the main ingredients is surfactant<sup>6</sup>, which account for about 5%~30% of domestic detergents. Surfactants are generally divided into three kinds: anionic surfactants, cationic surfactants, and nonionic surfactants<sup>7</sup>. Nonionic surfactants are mainly composed of alkylphenols (APS), such as nonylphenol (NP) and octylphenol (OP). With the similar function to hormones, APS can interact with estrogen receptor

proteins and cause the endocrine disorder<sup>8,9</sup>. As an antimicrobial or antibacterial agent, Triclosan is also used in domestic detergents, but it can increase the bacterial drug resistance<sup>10</sup>. Moreover, triclosan can react with chlorine in tap water to generate some harmful ingredients including chloroform<sup>11</sup>, chlorinated phenoxyphenols, chlorinated phenols, and trihalomethanes<sup>12,13</sup>. In addition, partial detergents even contain dioxins which are cancer-causing ingredients<sup>14</sup>. Because of the presence of these harmful substances, the long-term use of tableware or food packaging materials with residual detergents will poison human body. The food and beverage industry is a great detergent consumer<sup>15</sup>. Therefore, it is necessary to develop an online or in-situ detecting technique of residual detergents.

Detergent composition is complex and the detergent detection can be realized through detecting the composition. Various detergent detection methods are available<sup>16</sup>, such as Fourier transform infrared spectroscopy (FTIR)<sup>17</sup>, nuclear magnetic resonance spectroscopy (NMR)<sup>18</sup>, spectrophotometry<sup>19</sup>, high performance liquid chromatography (HPLC)<sup>20</sup>, potentiometric sensors or biosensors<sup>21-23</sup>. Each method has its own applicable scope. FTIR generally requires the sample pre-processing step and cannot realize the direct measurement. NMR, spectrophotometry, and HPLC have complex operation processes. The sensor methods require the probes to detect analytes as well as a lot of liquid samples. However, the quantity of residual detergent on tableware is so less that it is not convenient for sampling. However, the above methods are not applicable for the direct online measurement of detergent residues on tableware.

As a promising technology, laser induced breakdown

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spectroscopy (LIBS) is considered to be the only technique for direct online element analysis. The principle of LIBS is described as follows. Firstly, pulsed laser is used to irradiate samples. Secondly, the materials of samples are ablated to form plasma. Thirdly, the atomic emission spectra excited from the plasma are obtained by a spectrometer and analyzed in order to identify the element compositions in the samples. The technology can be used in material identification, classification, and qualitative and quantitative analysis. Because LIBS can detect almost all elements and does not require the sampling step, it has great advantages and potential in small-scale on-line detection. LIBS has been widely applied in the analysis of solid samples<sup>24</sup>, liquid samples<sup>25</sup>, and gas samples<sup>26</sup>. Ma successfully detected residual chlorpyrifos on the surface of apples<sup>27</sup> with LIBS. However, the application of LIBS in the measurements in residual detergents was seldom reported.

In this work, we studied the LIBS spectral features of detergent and attempted to explore the feasibility of applying LIBS technology in the detection of residual detergents in tableware. The paper aims to explore the LIBS spectral features of detergents and study the detergent detection capability of LIBS. Moreover, the influences of different substrates on detergent detection capability of LIBS were studied. We attempted to detect different brands of detergents with the LIBS technology.

## 2. Materials and Methods

### 2.1 Samples

The samples are household detergents, especially the commercial products used in kitchen utensils cleaning. Four detergent brands were selected: Diaopai (Nice Group Co., Ltd., Lishui, Zhejiang, China), Goldenfish (Yiqing Daily Chemical Co., Ltd., Tongzhou, Beijing, China), Libai (Liby Enterprise Group Co., Ltd., Guangzhou, Guangdong, China) and Qiaoshou (Reckitt Benckiser Group plc, Slough, Berkshire, England & Wales), which are commonly used in the kitchen of Chinese. The detergents used in this study were purchased in Wal-Mart supermarket located in Banjing Road of Beijing. Their packaging specification was 500 g/bottle and 10 mL of each type of detergent was used as the study sample.

Three kinds of commonly used Chinese tablewares were chosen as the substrate materials for detergents: porcelain dishes (Eurohome Porcelain Technology Co., Ltd., Guangzhou, Guangdong, China), bamboo chopsticks (Hongshun Bamboo & Wood Products Co., Ltd., Yiyang, Hunan, China), and stainless steel spoons (Qianxin Stainless Steel Product Co., Ltd., Jieyang, Guangdong, China). The porcelain dishes with ivory color and glaze surface were made of china clay and their middle parts were decorated with blue paint. The chopsticks were made from natural bamboo and the polished surfaces were not painted with any color or wax. They were cut into short sticks (about 5 cm). The stainless steel spoons used in this study were small flat-bottomed spoons, and the surfaces were polished. All these dinning tools were washed with deionized water and dried in the fume hood.

The sample processing is the dilution procedure with deionized water. The dilution factors were respectively 100, 500, 1000, and 2000. A drop of detergent was respectively transferred onto the surfaces of dishes, bamboo sticks and spoons with a clean glass rod. According to the features of different materials, detergents were

dropped on different clean and smooth locations of dishes, bamboo sticks, and spoons. Detergent samples were dropped on the area of the dishes without paintings and the middle part of bamboo sticks. Detergent samples were dropped on the relatively flat position on the back of the stainless steel spoons. After dropping detergent samples on the surface of 3 tablewares, porcelain dishes, bamboo chopsticks, and stainless steel spoons were dried naturally in a clean environment.

In the experiment, the detergent was diluted 100, 500, 1000, and 2000 times and the concentrations were 10 mg/mL, 2 mg/mL, 1 mg/mL and 0.5 mg/mL, respectively. Each time 20  $\mu$ L diluent was took and dropped on the surface of the dishes. The drops formed a spot with diameter of about 0.6 cm. So the residues on the dishes were about 0.707 mg/cm<sup>2</sup>, 0.141 mg/cm<sup>2</sup>, 70.8  $\mu$ g/cm<sup>2</sup> and 35.4  $\mu$ g/cm<sup>2</sup>, respectively.

### 2.2 Experimental setup

The experimental system was composed of laser, delay generator, spectrometer, and 3D precise motion platform (Fig. 1). The laser was driven by the digital delay generator Dawa-200. It was a Q-Switched Nd: YAG Laser produced by Beamtech Optronics Ltd. (Beijing, China). The wavelength of the laser beam was 1064 nm and the pulse width was less than 7 ns with the repetition frequency of 10 Hz. The beam divergence angle was less than 1 mrad and the maximum output energy was 200 mJ. The spectrometer was HR2000+ produced by Ocean Optics Company. Its spectral range was from 200 to 1100 nm with the spectral resolution of 0.2 nm and the signal-to-noise ratio of 250:1. The 3D axial movement of the platform was driven by stepper motors to adjust the position of the samples on the platform.

### 2.3 Spectra measurement and data analysis

In the experiment, the direction of the laser emitted from the Nd: YAG laser source was changed by mirrors and then focused on the sample surface by the focusing lens. The laser pulse energy was optimized and set to be 120 mJ and the laser spot size on sample surface was set to be 100  $\mu$ m. The samples to be measured were broken up by laser to form plasma. The atomic emission spectra excited from the plasma were collected into the fiber and guided to the spectrometer. In order to eliminate the plasma continuum effects, the spectra were collected after the 1- $\mu$ s delay. The acquisition spectral range of the spectrometer was set to be 200-900 nm and the integration time of sampling was set to 2 ms. After sampling, the spectra collected by spectrometer were transmitted to computer through data transmission line.

The spectral data were analyzed by the Unscrambler 9.7 (CAMO Software, AS., Oslo, Norway). The figures in this paper were drawn with SigmaPlot V12.5 (Systat Software, Inc., San Jose, USA).

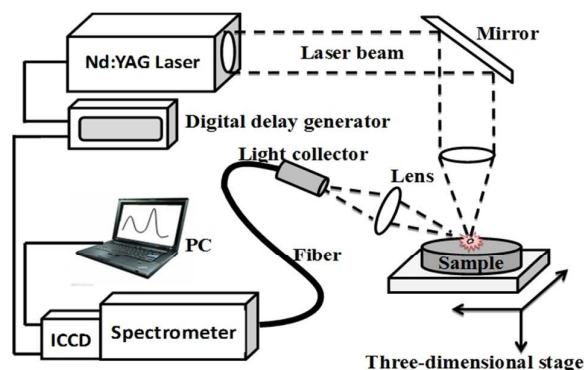


Fig. 1. Experimental setup used for detergent detecting. It mainly includes a sample stage, a laser, a delay generator, a spectrometer and the beam path structure.

### 3. Results and Discussion

#### 3.1 Selection and characterization of spectral features

The typical LIBS spectrum was shown in Fig. 2. The spectrum was collected from Diaopai detergent on a porcelain dish. The concentration of the detergent was diluted by 100 times and dishes were dried in the fuming cupboard after dropping detergent on the dish. The laser excitation energy was 120 mJ and the delay time was 1  $\mu$ s. The element identification of the spectral lines was carried out based on NIST Atomic Spectra Database and the SpecLine software. As shown in Fig. 2, the spectral lines of some atoms and molecules such as Si, Ca, Na, C, H<sub>2</sub>, and N were found. In these elements, Si may come from the material of porcelain dish. Ca is a kind of common element and may come from the substrate or the detergent sample. C, H<sub>2</sub>, and N are from the detergent or the surrounding air. It is identified that Na is from the detergent sample. Sodium Alcohol Ether Sulphate (RO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>-SO<sub>3</sub>Na (n=2 or 3, R is 12-15 alkyl) as a kind of alkaline anion surfactant is often added in detergents. Tetrasodium ethylenediaminetetraacetate (Na<sub>4</sub>EDTA) as a stable chelate can prevent the deposition in the container or on pipe surface and usually accounts for a large proportion in the detergent (even reach 40%)<sup>28</sup>. In addition, a certain proportion of sulfonic acid sodium salt is usually added into detergents because sulfonic acid (R-SO<sub>3</sub>H, R is hydrocarbyl) has a good solubility in water. Its sodium salt can decrease the water hardness effectively. Due to the presence of these compounds in detergents, the spectral lines of Na element in detergents are obvious.

Then the spectrum of Diaopai detergent on the dishes was compared with that collected from the same dishes without detergents. Three characteristic wavebands were found: 382-390 nm, 568-570 nm, and 615-617 nm. The three wavebands showed the significant differences between the sample and the blank matrix material.

The LIBS spectral signatures at the band of 382-390 nm were shown in Fig. 3. The spectral lines of CN were observed at 385.09, 385.47, 386.19, 387.14, and 388.34 nm. Similar to the spectral line of H<sub>2</sub> motioned above, these lines of CN were also molecular spectral lines. They were maybe from the ablation of the native CN

molecular bonds in detergents irradiated by laser<sup>29</sup>. The CN molecular bands was discovered can also be formed through the interaction of C<sub>2</sub> in sample materials with atmospheric nitrogen (N<sub>2</sub>) i.e. C<sub>2</sub> + N<sub>2</sub> → 2CN<sup>30</sup>. In the band of 384-389 nm it was the CN violet bands corresponding to B<sup>3</sup>Σ<sup>+</sup> → X<sup>2</sup>Σ<sup>+</sup> transitions<sup>31</sup>. Besides the CN lines, several weak peaks at 383.33, 383.93, 385.58 and 386.37 nm were found in this waveband. Because these spectral lines were found in the spectra of both detergent and blank substrate dishes, we deduced that they were the spectral lines of Fe contained in dishes. When the laser was irradiated on the detergent, Fe in dishes was excited to emit the atomic spectrum. However, in the detergent's spectral bands at 385.58 and 386.37 nm, the peaks of Fe were not clear. The results may be interpreted as follows. The laser energy was not high enough to excite the deeper materials and only the detergent on the surface of the substrate was excited. Therefore, the spectral lines at these two bands were covered by the signal of detergent.

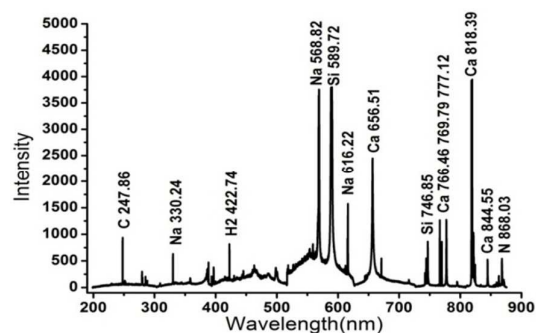


Fig. 2. LIBS spectrum of domestic detergent in the spectral range of 200-900 nm

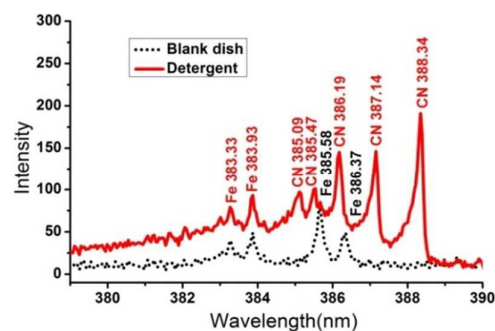


Fig.3. Spectral comparison at the waveband of 382-390 nm. CN bands can be observed in the spectrum of detergent but was absent in that of blank dish

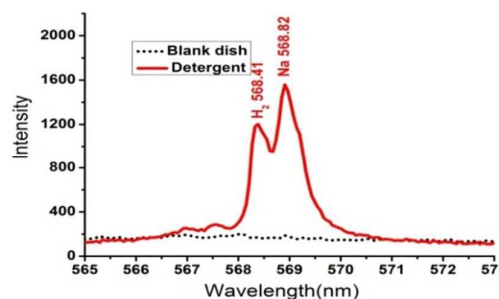




Fig. 4. Spectral comparison at 568-570 nm, molecular spectral line of H<sub>2</sub> and atomic spectral line of Na were shown in the detergent spectrum while there was no signal at this band of the blank dish.

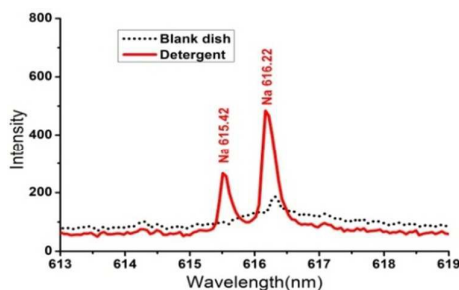


Fig. 5. Spectral comparison at 615-617 nm, two spectral lines of Na at 615.42 nm and 616.22 nm were obviously in the spectrum of detergent.

The second spectral waveband of detergent and blank dish at 568-570 nm was shown in Fig. 4. There were two adjacent strong peaks at 568.41 and 568.82 nm in the spectrum of detergent, while the two peaks were not found in the spectrum of blank dishes. The two peaks were strong because they were caused by the component with a relative high concentration in the detergent. The two peaks were the emission lines of Na (568.82 nm) and H<sub>2</sub> (568.41 nm). The Na element was from the sodium salt and H<sub>2</sub> may come from the surfactant or other organic macromolecular in detergent, such as the dodecyl acid diethanol amide (DADA)<sup>32</sup>. The molecular bonds were broken up by laser and the H element was excited. In the energy dissipation process, H atoms are combined into hydrogen molecules to emit the molecular spectra.

The content of sodium salt in detergent was so high that the spectral lines of Na were obvious. Characteristic lines of Na were found at 568-570 nm and 615-617 nm. The two peaks at 615.42 and 616.22 nm were both emitted from Na, as shown in Fig. 5.

In the LIBS spectra of detergent and substrate dish (Fig. 3, Fig. 4, and Fig. 5), at the bands of 382-390 nm, 568-570 nm and 615-617 nm, the obvious characteristic spectral lines of detergent were observed and could be easily distinguished from the spectra of porcelain dishes. According to the above characteristic peaks, we can realize the detection of detergent and even develop quick detection devices.

### 3.2 Spectral performance of different concentrations of the detergent

Detergents are usually dissolved and diluted in water before usage. Here, we studied the spectra of different concentrations of detergents.

The Diaopai detergent was selected as the representative detergent. In the pretreatment process, the samples were diluted by 100 times, 500 times, 1000 times and 2000 times. Then these diluted samples were dropped on different clean porcelain dishes, respectively. The LIBS spectra of the residual detergents on the dishes were collected after the liquid drops were dried. Fig. 6 shows the spectra of different concentrations of the detergent at the three wavebands of 382-390 nm, 568-570 nm, and 615-617 nm.

After the detergent was diluted, the characteristic peak of CN became weak and the emission spectra of Fe element in matrix

became relatively strong (Fig. 6(a)) because the dried film on the dish surface formed with the diluted detergent was thin and easily to be broke though by laser, and the spectra of the elements in dishes were excited. As shown in Fig. 6(a), only the weak CN peaks at the bands of 387.14 and nm 388.34 nm were observed. When the detergent was diluted by 2000 times, the characteristic peaks disappeared, indicating that LIBS technology was unable to detect the residual Diaopai detergent diluted by 2000 times according to these peaks. Unlike the original detergent spectral line, the emitted spectral peaks of H<sub>2</sub> at about 568.41 nm in the spectrum of the diluted detergent were wide and obscure (Fig. 6(b)) because the concentration of H element in diluted detergent was so low that it could not easily form H<sub>2</sub> after being excited by laser. The spectral line (568.82 nm) of Na element was still observed, but the peak of Na became very weak after the detergent was diluted by 2000 times. Therefore, it was difficult to determine the residual detergent according to this characteristic peaks. At the band of 615-617 nm,

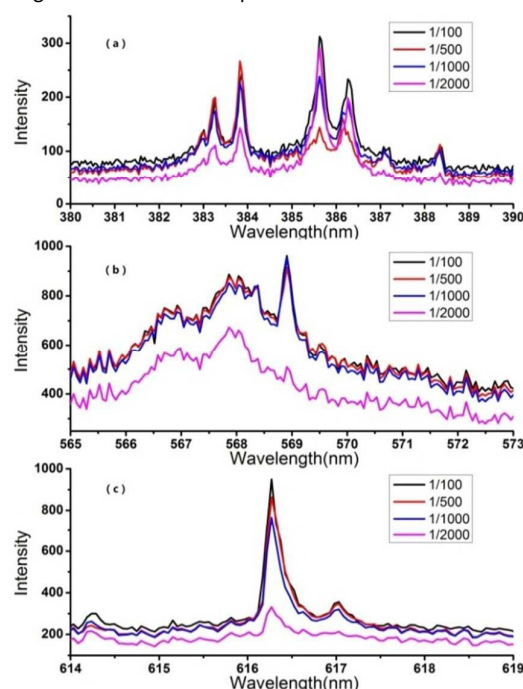


Fig. 6 LIBS spectra of detergent with four concentrations at three wavebands

the emission peaks were mainly from Na element. As shown in Fig. 6 (c), the peak intensities at 616.22 nm were gradually decreased with the increase in the dilution factor of the detergent. Even after the detergent was diluted by 2000 times, the spectral line at this band was still observed, demonstrating that the interference of detergent spectra was small at this position in the measurement process and that the LIBS technique had the potential to realize the quantitative measurement on the basis of this peak.

According to the spectral line intensity of Na element, in order to achieve quantitative measurement, it is necessary to strictly limit the sources of Na elements. Na is the element in widely used food processing agent, NaCl and easily remains on the tableware.

Therefore, it is difficult to determine the residual detergent on tableware according to the Na element. In other applications of detergents, such as medical equipment cleaning, packaging materials cleaning in beverage production line, washing fruits or vegetables, furniture cleaning, and edible oil removal, the emission lines of the Na element in the LIBS spectra are still the good basis to realize quantitative measurement of detergent residues because there is no other Na source in these applications.

In order to further explore the feasibility of LIBS spectra application in the quantitative measurement of detergents, we carried out the principal components analysis (PCA) with the data of LIBS spectra of different concentrations of detergents at the three bands (382-390 nm, 568-570 nm, and 615-617 nm). Eleven spectral data for each concentration were used for the PCA calculation (Fig. 7). Three main components were chosen in the calculation and their total contribution rate was as high as 92% (PC1 was 79%, PC2 was 11% and PC3 was 2%), which demonstrated that three components

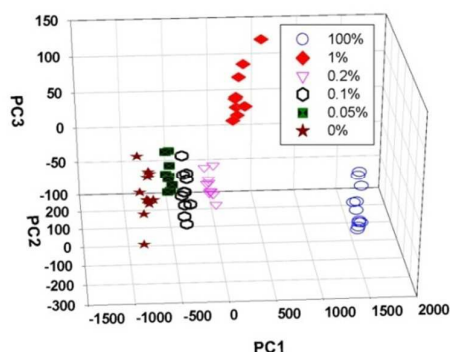


Fig. 7. PCA result of detergent with different concentrations. The original detergent (100%), the samples diluted 100 times (1%), 500 times (0.2%), 1000 times (0.1%), 2000 times (0.05%) and the samples without any detergent (0%) were separated obviously.

were enough to represent the characteristics of the spectral data. In the PCA results shown in Fig. 7, all the samples of different concentrations especially the samples with original concentration and the blank dishes could be differentiated from each other and the same concentration of samples showed the obvious clustering trend.

### 3.3 Influences of different substrates and different brands

In addition to porcelain, there are a large number of stainless steel and wooden tablewares. The problem on the detergent residues on these tablewares is an important topic. We collected the LIBS spectra of detergents on porcelain dishes, stainless steel spoons, and bamboo chopsticks. The settings of laser energy and delay time were the same when collecting the spectra of detergents with different substrates. The LIBS spectra of detergents were compared and analyzed. The spectral analysis was still focused on the three wavebands at 382-390 nm, 568-570 nm and 615-617 nm (Fig. 8).

The main characteristics of LIBS spectra excited from Diaopai detergent with different materials as substrate were basically the same in the three bands and no interferential spectral line was observed. It was demonstrated that in the three bands, as long as the laser energy was appropriate, there were no significant ionization excited from the substrates and the detergent LIBS spectra were not affected by the substrate materials. Therefore, the LIBS technique could be used to detect detergents according to the spectra at these three wavebands in many different fields.

Lots of detergent brands are available in the market and each brand has different compositions. We bought four brands of detergents (Diaopai, Libai, Qiaoshou, and Goldenfish) from the supermarket to study the adaptability of LIBS to detect different brands of detergents. After collecting the spectra of different detergents, we still analyzed the spectra at the three bands of 382-390 nm, 568-570 nm, and 615-617 nm (Figs. 8d, 8e, and 8f). In these three wavebands, the spectral characteristics of the four brands of detergents were similar, indicating that the main compositions of the four brands of detergents were the same or similar. However, the relative intensity of these spectral lines was slightly different, indicating that there were some differences among the main compositions of these detergents. The result showed that the LIBS technique was competent for detecting different brands of detergents. Especially when the type of the used detergent was known, more accurate measurement results can be obtained.

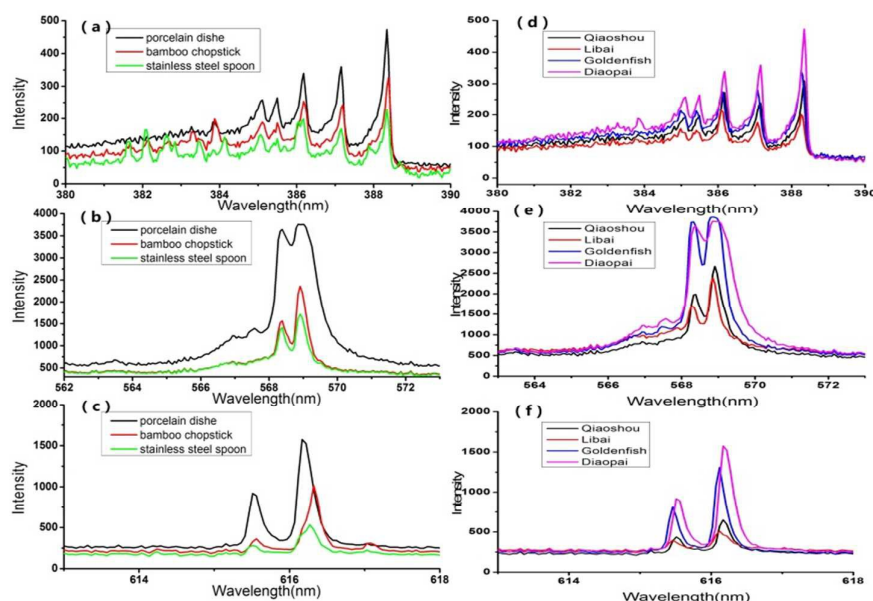


Fig.8. Detergent spectra at the three wavebands (382-390 nm, 568-570 nm and 615-617 nm) with different substrates (a,b,c) and different brands (d,e,f)

## Conclusions

In this work, we studied the application of LIBS in detecting the detergents on porcelain dishes, stainless steel spoons, and bamboo chopsticks. Three characteristic bands of the LIBS spectra were found. At the band of 382-390 nm, CN emission lines were observed. The molecular emission line of  $H_2$  was observed at the band of 568-570 nm and the Na emission lines were found at the band of 615-617 nm. With these emission lines, especially the Na spectral line at 616.22 nm, it was possible to develop the quick quantitative measurement equipment of detergents in the field without Na element.

In the analysis of PCA, the detergent samples of different concentrations were separated obviously from each other, demonstrating that the LIBS technology could be used in qualitative measurement and quasi-quantitative measurement. The LIBS technology even successfully identified the detergent samples diluted by 2000 times. In this experiment, the PCA scores of the detergent samples respectively diluted by 100 times, 500 times and 1000 times showed little differences. It might be caused by the non-uniform detergent residues on tablewares. After the detergent samples dropped on the tableware, they flowed on the glazed surface for a short distance and led to a little difference in the detergent concentration on different positions of the tableware. When the LIBS spectra were collected, because of the position of the little laser spot (just 100  $\mu\text{m}$ ) was small, the concentrations of the chosen position had some differences. Therefore, there were some deviations in the results of the samples. This kind of problem can be solved by calculating the average of the spectral data collected from different positions for many times. The LIBS technology can achieve the qualitative detection of detergent and has the potential of quantitative measurement. This technique does not require sampling and can detect almost all elements. It is especially suitable for online measurements. It is convenient, fast, and easy to

miniaturization. It is creative and practical using this technique to develop small detergent online analytical instruments that can be installed in the food industry production line or household dishwashers and realizing the roboticized measurement of detergent.

It should be noticed that the detergent diluted 2000 times can be successfully detected. It illustrated that the LIBS method can detect the residual detergent with a concentration lower than  $35.4 \mu\text{g}/\text{cm}^2$ . If the dishes with detergent that used in the experiment filed with water, a concentration of  $13 \mu\text{g}/\text{mL}$  should be considered that may be absorbed by human being according to a residue of  $35.4 \mu\text{g}/\text{cm}^2$ . This result can be compared with that from other methods. The Total Organic Carbon (TOC) method can detect the concentration of detergent residue of  $2.489 \mu\text{g}/\text{mL}$ <sup>33</sup>. The detection limit of Capillary Electrophoresis (CE) is about  $0.6 \mu\text{g}/\text{mL}$ <sup>34</sup>. Impedimetric chemical sensors can detect detergent residue as low as  $5 \text{ ppm}$ <sup>23</sup>. And by high-performance liquid chromatography, the nonylphenol polyethoxylates in household detergents can be detected at concentration of 0.2%. The majority aim of this study was to show the ability of LIBS for the detection of detergent and its spectral characteristics, so we had not validated the exactly LOD. Maybe some of the above methods has better LOD than LIBS, but LIBS has the advantages of one-line, fast and no samples preparation which are unable to be offered by the previous methods. U.S. Food and Drug Administration (FDA) have made relevant provision that the concentration of detergent residues generally should not exceed  $100 \mu\text{g}/\text{mL}$ <sup>35</sup>. So, the LOD of LIBS method meets the FDA requirement.

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