



Time-resolved spectral-image laser-induced breakdown spectroscopy for precise qualitative and quantitative analysis of milk powder quality by fully excavating the matrix information

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ARTICLE INFO

Keywords:

Laser-induced breakdown spectroscopy
Quality of milk powder
Adulteration
Calcium
Qualitative and quantitative analysis

ABSTRACT

A novel and effective method named time-resolved spectral-image laser-induced breakdown spectroscopy (TRSI-LIBS) was proposed to achieve precise qualitative and quantitative analysis of milk powder quality. To verify the feasibility of TRSI-LIBS, qualitative and quantitative analysis of milk powder quality was carried out. For qualitative analysis of foreign protein adulteration, the accuracy of models based on TRSI-LIBS was higher than those based on LIBS, with an accuracy improvement of about 5% to 10%. For the quantitative analysis of foreign protein adulteration and element content, the quantitative analysis models based on TRSI-LIBS also had better effect. For instance, limit of detection (LOD), determination coefficient of prediction (R^2_p), root-mean-square error of prediction (RMSEP) and average relative error of prediction (AREP) of quantitative model of calcium (Ca) content based on TRSI-LIBS improved from 1.47 mg/g, 0.95, 0.35 mg/g and 23.29% to 0.81 mg/g, 0.98, 0.20 mg/g and 12.60%.

1. Introduction

Milk powder is a kind of nutritious food made from fresh milk through filtration, degreasing, heating, concentration and drying. Milk powder is rich in vitamins, minerals, protein and other essential nutrients for the human body, so it is not only the sole suitable substitute for breast milk, but also suitable for all consumers (Jiang, Hua, Zhang, Lou, Wen, & Chu, 2018; P. F. Scholl, Farris, & Mossoba, 2014). Therefore, the global demand for milk powder is enormous. According to relevant reports, the global production of milk was 816 million tons in 2016, showing rapid growth (Moncayo, Manzoor, Rosales, Anzano, & Caceres, 2017).

With the increasing demand for milk powder, the quality of milk powder has become one of the main concerns. To ensure the quality of milk powder, the Codex Alimentarius Commission of the Food and Agriculture Organization of the United Nations and the World Health Organization have determined the standards of milk powders (Jablonski, Moore, & Harnly, 2014). However, to obtain greater economic benefits, a large number of milk powder still have quality problems. The

common quality problems of milk powder include the mixing of different animal milk powder (Brandao, Neto, de Carvalho dos Anjos, & Bell, 2017), the adulteration of foreign protein (Scholl, PF, Farris, SM, Mossoba, & MM, 2014), the substandard content of elements (Ahmed, Mohammed, Amin, & Abdelraheem, 2016) and so on, which will not only reduce the nutritional value of milk powder, but also affect human health and even cause death (Brandao et al., 2017). The melamine scandal in 2008, which led to a large number of babies being hospitalized with kidney stones, was a harrowing example. Therefore, the quality inspection of milk powder is very important.

In the past decades, varieties of analytical techniques have been used to evaluate the quality of milk powder, including high-performance liquid chromatography (HPLC) (Jablonski, Moore, & Harnly, 2014), near-infrared spectrometry (NIRS) (Inácio, Moura, & Lima, 2011), inductively coupled plasma mass spectrometry (ICP-MS) (Sager, McCulloch, & Schoder, 2018) and nuclear magnetic resonance (NMR) (Sandie, Mller, Andrew, Whittaker, et al., 2011). However, those methods have disadvantages, such as tedious sample preparation, complex operation, high price, and can not meet the current needs of

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<https://doi.org/10.1016/j.foodchem.2022.132763>

Received 1 June 2021; Received in revised form 17 February 2022; Accepted 19 March 2022

Available online 21 March 2022

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milk powder detection. Therefore, a simple, rapid and in-situ method for quality detection of milk powder is urgently needed.

Laser-induced breakdown spectroscopy (LIBS) is an emerging spectroscopic analytical technology based on the interaction mechanism between laser and matter. The principle of LIBS is to generate plasma by instantaneous ablation of the material with high-energy pulsed laser, and then analyze the elemental composition of the samples according to the plasma emission spectra (Y. Chu, Zhang, He, Chen, Sheng, Zhang, et al., 2020; Zhang, Chu, Ma, Zhang, Cui, Hu, et al., 2020). LIBS is known as the “future super star” (Winefordner, Gornushkin, Correll, Gibb, Smith, & Omenetto, 2004) in analytical chemistry with its advantages of simple sample preparation, easy operation, micro-damage, fast and in-situ. It has been widely used in various fields, such as metallurgical process monitoring (Sturm, Meinhardt, Fleige, Fricke-Begemann, & Eisbach, 2017), coal quality detection (Sheta, Afgan, Hou, Yao, Zhang, Li, et al., 2019), atmospheric environmental quality monitoring (Butler, Cairns, Cook, & Davidson, 2017), tumor identification (Liu & Zhang, 2008) and so on (Knight, Scherbarth, Cremers, & Ferris, 2000; Peng, Liu, Zhou, Song, Zhang, Ye, et al., 2016). In recent years, LIBS has proved to be an effective analytical tool in the field of food detection (Y. He, Zhao, Zhang, Li, Bao, & Liu, 2020; Mbesse Kongbonga, Ghalila, Onana, & Ben Lakhdar, 2014), but few LIBS works were reported on the quality detection of milk powder. In 2016, I. H. Boyaci et al. (Bilge, Sezer, Eseller, Berberoglu, Topcu, & Boyaci, 2016) used LIBS to conduct qualitative and quantitative analysis of whey adulteration in milk powder. Principal component analysis (PCA) was used for qualitative analysis, and the accuracy rate was 80.5%. Partial least squares regression (PLSR) was used to quantitatively analyze the adulteration of whey. Determination coefficient (R^2) and limit of detection (LOD) values were 0.981 and 1.55% for adulteration with sweet whey powder, and 0.985 and 0.55% for adulteration with acid whey powder, respectively. In 2020, M. Zhao et al. (Zhao, Markiewicz-Keszycka, Beattie, Casado-Gavalda, Cama-Moncunill, O'Donnell, et al., 2020) combined LIBS, fourier transform mid-infrared (FT-IR) and Raman spectroscopy for quantitative analysis of calcium (Ca) in milk powder, and the results showed that LIBS had the best quantitative effect, followed by the combination of FT-IR and Raman spectroscopy. Those studies verified the feasibility of LIBS in the quality analysis of milk powder. However, due to the sample morphology, laser energy and other factors, LIBS spectra are unstable (Hou, Wang, Lui, Yuan, Li, Li, et al., 2013). The fluctuation will not only lead to the decrease of the accuracy of qualitative analysis, but also affect the performance of quantitative analysis (Feng, Wang, Li, & Ni, 2010), which seriously limits the further promotion of LIBS in quality analysis of milk powder. Therefore, more research should be conducted to improve the performance of LIBS.

In this work, a new method of time-resolved spectral-image laser-induced breakdown spectroscopy (TRSI-LIBS) was proposed for high precision qualitative and quantitative analysis of milk powder quality. TRSI-LIBS performed feature selection after obtaining the LIBS time-resolved spectra of the samples, and formed the spectral images according to spectral dimension and delay time dimension. In this method, the qualitative and quantitative analysis of the milk powder quality were realized by fusion of the histogram of oriented gradient (HOG) features of the spectral images and spectral intensities. TRSI-LIBS not only uses the spectral information, but also can effectively obtain the matrix information of the samples through the time-resolved spectral images. To verify the effectiveness of this method, we compared the qualitative and quantitative analysis of foreign protein adulteration and the quantitative analysis of Ca content in milk powder with the traditional LIBS. The results proved that TRSI-LIBS can effectively extract matrix information from samples and improve the performance of qualitative and quantitative analysis.

2. Materials and method

2.1. Samples and sample preparation

This work systematically studied the quality of milk powder from qualitative and quantitative aspects. Samples used in this work include milk powder (MP), five kinds of foreign proteins (rice hydrolyzed protein (RHP), soybean protein isolate (SPI), wheat hydrolyzed protein (WHP), peanut protein (PP), egg white (EW)), and whey, all of which were brought from the local market in China.

For the qualitative and quantitative analysis of foreign protein adulteration, milk powder and five kinds of foreign protein were used. As shown in Fig. 1S, ICP-MS was used as a reference method to determine the elemental composition of milk powder and five kinds of foreign protein, and the results showed that their element content was significantly different. For each foreign protein, eight different mixtures of 1, 3, 5, 8, 10, 15, 20 and 25% (w/w) concentrations were prepared, and 2 repeated samples were made for each concentration gradient to provide statistic and improve the reproducibility and accuracy of the measurement. A total of 86 samples were used for qualitative and quantitative analysis of foreign protein adulteration, including 6 pure milk powder samples. For the quantitative analysis of Ca, Ca in milk powder was diluted by whey, and finally obtained a total of 18 samples (2 repeated samples) with Ca content ranging from 0.29 to 6.12 mg/g (0.29, 0.41, 0.87, 1.02, 1.22, 1.53, 2.04, 3.06 and 6.12 mg/g).

All experimental samples were pressed by electric tablet press. To ensure homogeneity of the mixed powder, the mixed powder was transferred to an oscillator and vibrated for about 20 min. After that, five grams of mixed powder was then pelleted by applying a pressure of 30 tons for 1 min. The thickness and diameter of the pellets were about 3 mm and 40 mm, respectively. The pressed pellets were directly used for LIBS analysis without further treatment.

2.2. Experimental setup

The schematic diagram of LIBS system used in this work is shown in Fig. 2S. The laser beam was generated by a Q-switched Nd: YAG laser (Beamtech Optronics Co., Ltd., Nimma-400, wavelength: 532 nm; pulse duration: 8 ns). After beam splitting by a plate beamsplitter (350–1000 nm R:T = 50:50), the laser beam was focused on the sample surface through a quartz lens ($f = 150$ mm) to produce plasmas. The sample was placed on a three-dimensional electric displacement platform (Beijing Jiangyun Juli Technology, DZY110TA-3Z) so that the laser pulse would impinge on a fresh location on the sample each time. The plasma emission was gathered with an optical collector and then guided by an optical fiber to an echelle spectrometer (resolution: $\lambda/\Delta\lambda = 5000$; spectral range: 200–950 nm; United Kingdom, Andor Tech., Mechelle 5000) coupled with an intensified charge-coupled device (ICCD) (United Kingdom, Andor Tech., iStar DH-334 T). The laser and spectrometer were simultaneously controlled by a digital delay generator (Stanford Research Systems, DG645). A complementary metal-oxidesemiconductor (CMOS) (Thorlabs, DCC1545M, resolution: 1280×1024 pixels) was used to monitor sample surfaces. The LIBS system used in our experiment realized the autofocus function based on the cooperation between the electric displacement platform and CMOS.

2.3. LIBS measurements

Before the experiment, optimization was performed to determine the optimal parameters. The optimal experimental parameters of this study are as follows, the laser energy was set as 80 mJ and repetition frequency was 1 Hz. The gate delay of the spectrometer was set from 1 μ s to 4.8 μ s, with 0.2 μ s as a step to obtain the time-resolved spectra of the samples. The gate width and exposure time were fixed to 1 μ s and 0.5 s, respectively.

All samples were measured in the atmosphere. To expose a new

position of the sample surface each time, the samples moved with 500 μm step distance along with the electric displacement platform. Each spectrum was accumulated twice to improve its signal-to-noise ratio (SNR). In the qualitative analysis of foreign protein adulteration, 10 groups of time-resolved LIBS spectra (a total of 200 LIBS spectra) were obtained for each sample. Each foreign protein with different adulterations (1, 3, 5, 8, 10, 15 and 25%) was regarded as the same class, and a total of 920 groups of time-resolved spectra of 6 kinds of samples were used for the qualitative analysis of foreign protein adulteration. In the quantitative analysis of foreign protein adulteration, the spectral data were the same as in the qualitative analysis, but each type of foreign protein was quantitatively analyzed separately for different adulteration degrees (1, 3, 5, 8, 10, 15 and 25%). Finally, quantitative analysis models of the adulteration degrees of 5 kinds foreign proteins were established. In the quantitative analysis of Ca content, the spectra acquisition method was the same as above, and 180 groups of time-resolved spectra of 18 samples were obtained.

2.4. Data analysis

In this work, a new method, time-resolved spectral-image laser-induced breakdown spectroscopy, was proposed for qualitative and quantitative analysis of milk powder quality. Compared with traditional LIBS, TRSI-LIBS needs to acquire the time-resolved spectra of the samples, and the spectral processing methods are different. As shown in Fig. 1, the process of TRSI-LIBS is described in detail. Time-resolved spectra of the samples need to be obtained first. Due to the redundancy of LIBS spectra, feature selection of spectra is necessary before subsequent processing. The traditional feature selection methods in LIBS, such as genetic algorithm (GA) (J. He, Pan, Liu, & Du, 2019), random forest (RF) (Sheng, Zhang, Niu, Wang, Tang, Duan, et al., 2015) and atomic spectral database line selection, can be used. In this study, 33 lines were selected from the whole spectrum, including lines of carbon (C), nitrogen (N), oxygen (O), hydrogen (H), potassium (K), Ca, sodium (Na), magnesium (Mg) and molecular bands CN according to ICP-MS results and National Institute of Standards and Technology (NIST) atomic spectral database (Colao, Fantoni, Lazic, Paolini, Fabbri, Ori, et al., 2004). The details of the selected lines are listed in Table S1. After

feature selection, the obtained data are constructed into spectral images according to the spectral dimension and the delay time dimension. To obtain matrix information such as the variation trend of spectral intensity of elements with delay time from spectral images, the image features need to be extracted. In this work, the histogram of oriented gradient (HOG) was used to describe the features of the spectral images. The features are constructed by calculating and counting oriented gradient of local area in the images, so it has powerful edge detection ability and photometric invariance ability (P.-Y. Chen, Huang, Lien, & Tsai, 2013; Mizuno, Terachi, Takagi, Izumi, Kawaguchi, & Yoshimoto, 2012). Finally, the HOG features extracted from the spectral images are fused with the spectral intensities and used as the input data of the qualitative and quantitative analysis models for the quality analysis of milk powder.

2.5. Evaluation indexes

To verify the effectiveness of TRSI-LIBS, the accuracy in qualitative analysis and the determination coefficient (R^2), the root-mean-square error (RMSE), the average relative error (ARE) and the limit of detection (LOD) in quantitative analysis were applied as evaluation indexes. Their expressions are as follows (Allegrini & Olivieri, 2014; Moncayo, Manzoor, Rosales, Anzano, & Caceres, 2017; Rui, Yuan, Yun, Tang, Zhihao, Zhu, et al., 2019):

$$\text{Accuracy} = \frac{100}{n} \sum_{i=1}^n \delta_i \quad (1)$$

$$R^2 = 1 - \frac{\sum_{i=1}^n (\hat{y}_i - y_i)^2}{\sum_{i=1}^n (y_i - \bar{y})^2} \quad (2)$$

$$\text{RMSE} = \sqrt{\frac{\sum_{i=1}^n (\hat{y}_i - y_i)^2}{n}} \quad (3)$$

$$\text{ARE} = \frac{100}{n} \sum_{i=1}^n \frac{|\hat{y}_i - y_i|}{y_i} \quad (4)$$

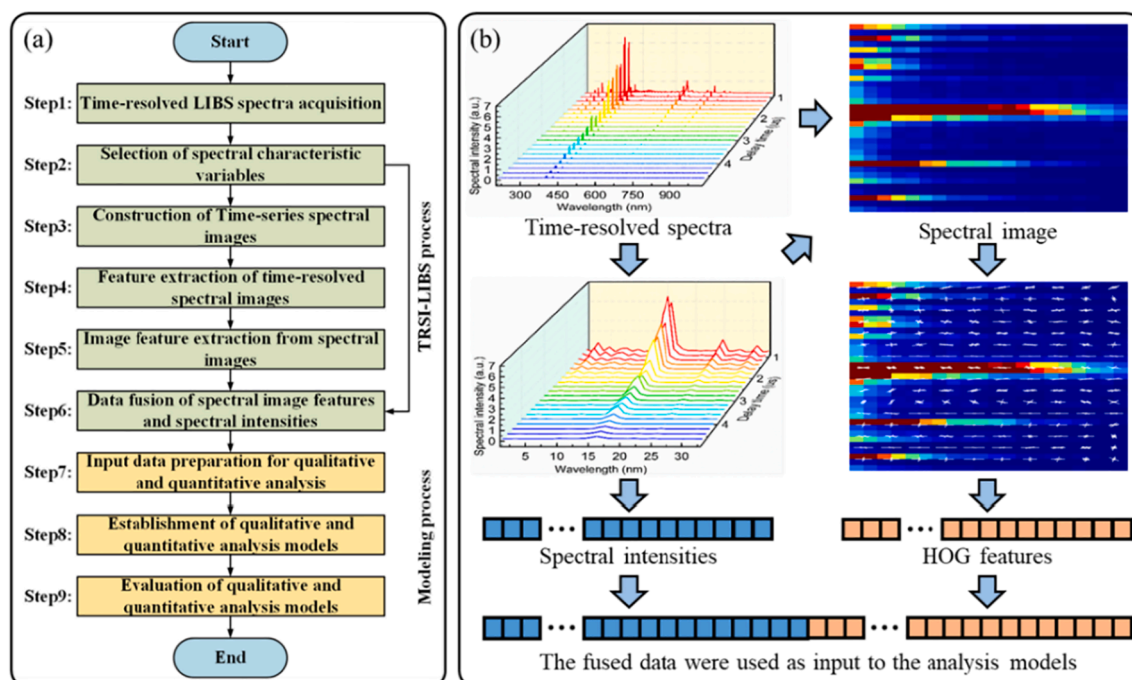


Fig. 1. (a) The flow chart of TRSI-LIBS modeling method, and (b) the schematic diagram of TRSI-LIBS data processing.

$$LOD = 3.3s_{pu}^{-1} [(1 + h_{0min} + 1/n)var_{pu}]^{1/2} \quad (5)$$

where n is the number of samples, δ_i is either 1 when a spectrum is classified correctly or 0 otherwise, y_i is the certified concentration of the sample i , \bar{y} is the average value of y_i over n sample, \hat{y}_i is the predicted concentration of sample i , s_{pu} is the slope of the pseudo-univariate line, h_{0min} is the minimum leverage when the concentration of analyte is 0, var_{pu} is the variance of the regression residuals.

3. Results and discussion

Previously, we have introduced TRSI-LIBS in detail. To verify the effectiveness of this method from the experiment, we compared the analytical performance differences between traditional LIBS and TRSI-LIBS from the qualitative and quantitative aspects of milk powder quality, including qualitative and quantitative analysis of foreign protein adulteration and quantitative analysis of element content in milk powder.

3.1. Qualitative analysis of foreign protein adulteration

In the qualitative analysis of foreign protein adulteration, pure milk powder and adulteration samples of 5 foreign proteins (rice hydrolyzed protein, soybean protein isolate, wheat hydrolyzed protein, peanut protein and egg white) with different adulteration degrees (1, 3, 5, 8, 10, 15, 20 and 25%) were analyzed. LIBS spectra (gate delay: 1 us; gate width: 1 us) of pure milk powder and adulteration samples of 5 foreign proteins are shown in Fig. 3S, and their time-resolved spectra are shown in Fig. 4S. As we can see, the elemental composition of milk powder and its foreign protein adulteration samples was very similar (C, N, O, H, K, Ca, Na and Mg), with only differences in spectral intensity. Therefore, it was very difficult to carry out qualitative and quantitative analysis only by a single spectrum. However, their time-resolved spectra had great differences, which would play a great role in qualitative and quantitative analysis. Then, we compared the performance of traditional LIBS and TRSI-LIBS in the classification of foreign protein adulteration in milk powder.

Traditional LIBS only uses a single spectrum of each sample for analysis. After optimization, we used a single spectrum (gate delay: 1 us; gate width: 1 us) of the milk powder and its foreign protein adulteration samples to conduct classification research. It is necessary to select the features of the spectra before analysis due to the redundancy of LIBS spectra. As shown in Table S1, 33 spectral lines were selected as the input data of the classification model. To make the analysis results universal, three classification models were selected for analysis, namely support vector machine (SVM) (Yang, Qiao, Chen, Ding, & Tian, 2015),

k-nearest neighbor (KNN) (J. Chen, Pisonero, Chen, Wang, & Duan, 2020) and random subspace method-linear discriminant analysis (RSM-LDA) (Y. W. Chu, Chen, Sheng, Zhang, & Guo, 2020). Fig. 2 shows the results of three classification models based on traditional LIBS. The accuracies of the cross-validation set of SVM, KNN and RSM-LDA models reached 80.98, 75.61 and 79.25%, respectively, while the accuracies of the prediction set were 81.50, 76.03 and 79.07%, respectively. The results showed that the accuracies of these classification models were not very ideal. The reason is that, according to the results of ICP-MS, milk powder and its foreign protein blends have almost the same element composition. In particular, the element content of milk powder and its mixture of WHP and RHP is almost the same.

The process of TRSI-LIBS has been explained in Section 2.4. Fig. 3 shows the spectral images of milk powder and its foreign protein adulteration samples. After feature selection and other steps, TRSI-LIBS obtained fusion data by fusing spectral intensities with HOG features of spectral images, and took them as input data of qualitative analysis model. Based on TRSI-LIBS, three classification models of foreign protein adulteration in milk powder, SVM, KNN and RSM-LDA, were established, and the results are also shown in Fig. 2. The accuracies of the cross-validation set of SVM, KNN and RSM-LDA classification models based on TRSI-LIBS reached 89.03, 82.32 and 83.23%, respectively, and the accuracies of the prediction set were 90.40, 83.47 and 84.90%, respectively.

It can be seen that the accuracies of different qualitative models based on TRSI-LIBS were significantly higher than those of models based on traditional LIBS. The accuracies of both the cross-validation set and the prediction set improved by about 5 to 10%, which proved the effectiveness of TRSI-LIBS in qualitative analysis.

3.2. Quantitative analysis of foreign protein adulteration

In the above qualitative analysis, different adulteration degrees (1, 3, 5, 8, 10, 15, 20 and 25%) of the same foreign protein in milk powder were regarded as the one class. In this section, we would carry out quantitative analysis on the adulteration degrees of foreign protein in milk powder. The quantitative models of adulteration degrees of five foreign proteins were established. To facilitate the subsequent analysis, we only analyzed the results of the quantitative model of RHP adulteration in milk powder based on LIBS and TRSI-LIBS in detail.

A statistical method, partial least squares regression (PLSR), was used to quantitatively analyze the quality of milk powder. PLSR looks for a linear regression model by projecting the predicted variable and the observed variable into a new space, so it can establish the relationship between predicted variable and observed variable more effectively (Singh & Sarkar, 2018). The PLSR quantitative models of RHP

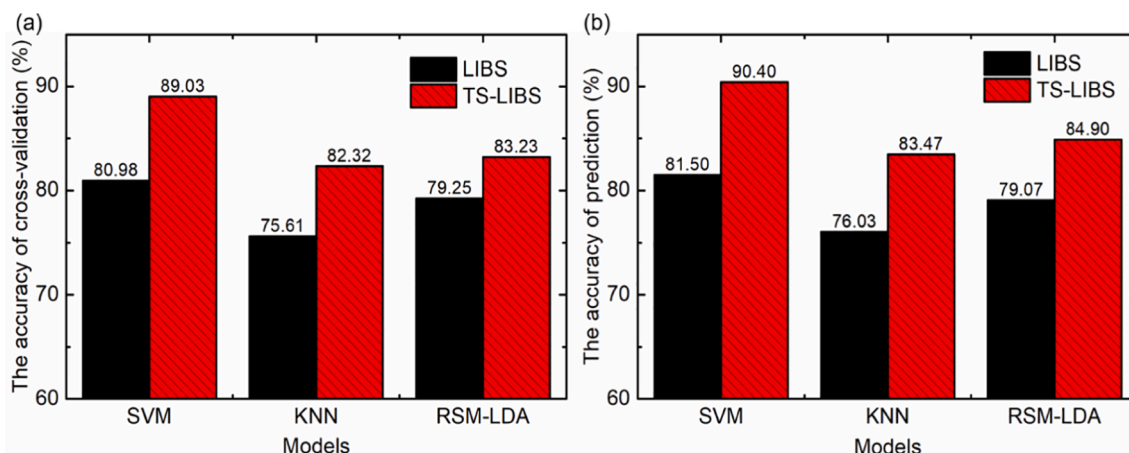


Fig. 2. Qualitative analysis results of (a) cross-validation set and (b) prediction set of foreign protein adulteration in milk powder based on LIBS and TRSI-LIBS.

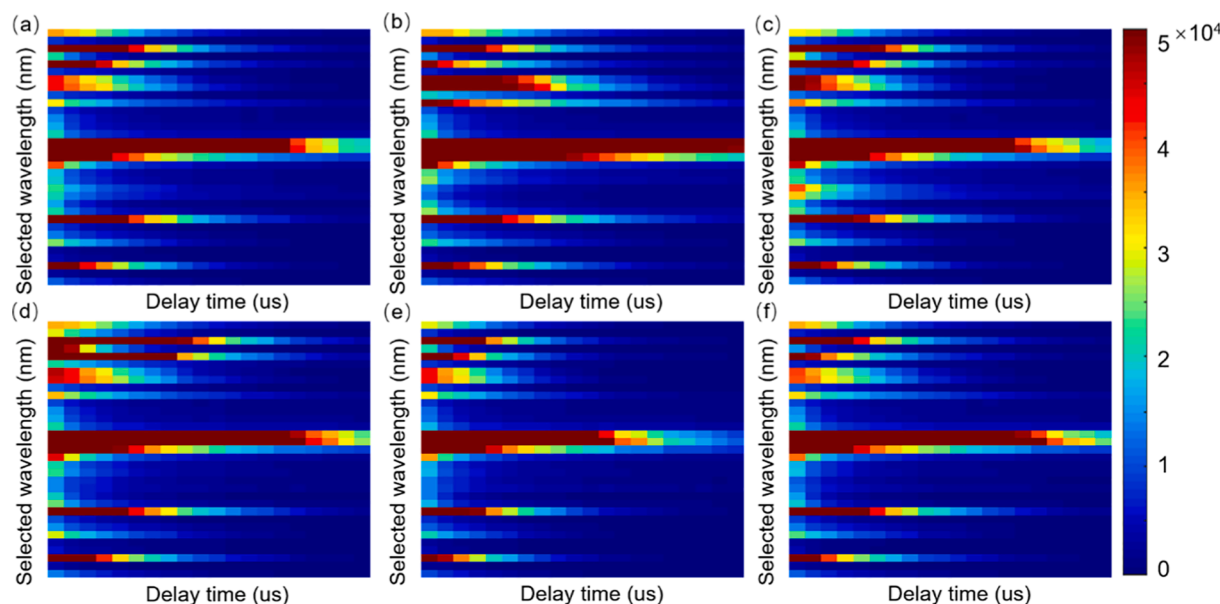


Fig. 3. Time-resolved spectral images of (a) soybean protein isolate, (b) rice hydrolyzed protein, (c) egg white, (d) peanut protein, (e)wheat hydrolyzed protein adulteration samples and (f) milk powder.

adulteration degrees in milk powder were also established based on traditional LIBS and TRSI-LIBS. The data preprocessing of traditional LIBS and TRSI-LIBS in quantitative analysis was the same as the method used in above qualitative analysis. As shown in Table 1, for the RHP adulteration, LOD, determination coefficient of cross-validation (R^2_{cv}), root-mean-square error of cross-validation (RMSECV) and average relative error of cross-validation (ARECV) of PLSR prediction model established based on LIBS were 9.45%, 0.90, 2.68% and 50.11% respectively, and determination coefficient of prediction (R^2_p), root-mean-square error of prediction (RMSEP) and average relative error of prediction (AREP) were 0.84, 2.65% and 26.62%, respectively. The evaluation indexes of the PLSR quantitative model based on TRSI-LIBS were significantly improved. LOD, R^2_{cv} , RMSECV and ARECV increased to 6.86%, 0.95, 1.87% and 35.96%, respectively, and R^2_p , RMSEP and AREP increased to 0.93, 1.78%, and 23.15%, respectively. The experimental results of RHP adulteration degrees quantitative model preliminarily verified the effectiveness of TRSI-LIBS in quantitative analysis.

Four other foreign proteins were used to further verify the applicability of TRSI-LIBS in quantitative analysis. Table 1 shows the evaluation indexes of the PLSR quantitative models for foreign protein adulteration degrees. It can be seen that no matter what kind of foreign protein, the evaluation indexes of the quantitative model based on TRSI-LIBS were superior to that based on LIBS. The above experimental results further proved the effectiveness of TRSI-LIBS in quantitative analysis.

Table 1

Comparison of quantitative analysis results of 5 foreign protein adulteration in milk powder by LIBS and TRSI-LIBS.

Adulteration samples	Method	LOD%	Cross-validation set			Prediction set		
			R^2_{cv}	RMSECV%	ARECV%	R^2_p	RMSEP%	AREP%
Wheat hydrolyzed protein	LIBS	23.19	0.62	5.28	93.40	0.45	5.29	94.01
	TRSI-LIBS	20.63	0.68	4.87	95.34	0.57	4.70	66.73
Soy protein isolate	LIBS	16.98	0.75	4.23	73.49	0.50	4.98	75.82
	TRSI-LIBS	9.49	0.91	2.56	52.04	0.78	3.83	50.37
Rice hydrolyzed protein	LIBS	9.45	0.90	2.68	50.11	0.84	2.65	26.62
	TRSI-LIBS	6.86	0.95	1.87	35.96	0.93	1.78	23.15
Peanut protein	LIBS	7.32	0.94	1.93	35.98	0.92	1.94	23.83
	TRSI-LIBS	5.94	0.95	1.81	40.68	0.97	1.29	18.92
Egg white	LIBS	8.78	0.92	2.40	44.51	0.84	2.56	41.37
	TRSI-LIBS	7.43	0.94	2.03	42.41	0.91	2.16	29.62

3.3. Quantitative analysis of Ca content

In this study, by adding whey to milk powder, samples with 9 gradients of Ca content, ranging from 0.29 to 6.12 mg/g, were prepared for quantitative analysis. The performance of PLSR quantitative models of Ca content based on LIBS and TRSI-LIBS were also compared. As shown in Fig. 4, for the PLSR quantitative model based on traditional LIBS, LOD, R^2_{cv} , RMSECV and ARECV were 1.47 mg/g, 0.95, 0.42 mg/g and 24.58% respectively, and R^2_p , RMSEP and AREP were 0.95, 0.35 mg/g and 23.29%, respectively. The experimental results showed that the performance of the quantitative analysis model based on TRSI-LIBS was better than that based on traditional LIBS. LOD, R^2_{cv} , RMSECV and ARECV were improved to 0.81 mg/g, 0.98, 0.26 mg/g and 16.75%, respectively, and R^2_p , RMSEP and AREP were improved to 0.98, 0.20 mg/g, and 12.60%, respectively.

Based on the above-mentioned quantitative analysis results of foreign protein adulteration and Ca content in milk powder, the effectiveness and wide applicability of TRSI-LIBS in quantitative analysis were comprehensively verified.

3.4. Discussion

According to the experimental results in this study, it can be seen that TRSI-LIBS is superior to traditional LIBS in qualitative and quantitative analysis performance. The following is a detailed analysis of the main reasons why TRSI-LIBS is better than traditional LIBS. First, TRSI-LIBS

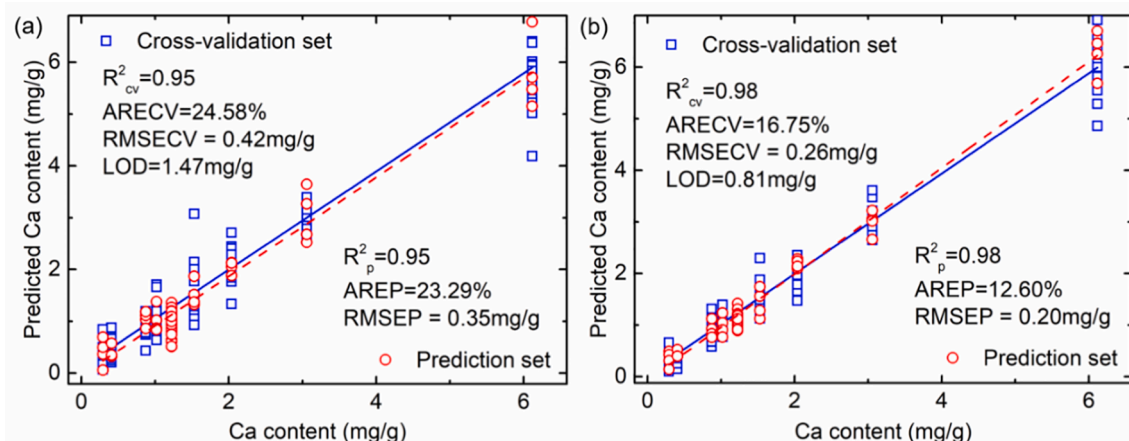


Fig. 4. Quantitative analysis results of Ca content in milk powder based on (a) LIBS and (b) TRSI-LIBS.

not only uses the intensity information of LIBS spectra, but also can effectively mine the information brought by the matrix. Matrix effect has always been regarded as one of the difficult problems affecting qualitative and quantitative analysis of LIBS, but matrix effect can also bring useful information for qualitative and quantitative analysis. The variation trend of spectral intensity of elements in different matrixes with delay time is also important analysis information. Fig. 5 shows the variation trend of spectral intensity of Mg, Ca, Na and K in milk powder and its foreign protein adulteration samples with delay time. The

variation trend of elements in samples of different substrates with delay time is disparate, which is very important for qualitative and quantitative analysis. TRSI-LIBS can fully excavate this information by extracting HOG features from spectral images. Second, the time-resolved spectra of the samples obtained by TRSI-LIBS are less affected by fluctuations and have strong robustness. On the one hand, traditional LIBS only obtains a single spectrum of the sample, which is greatly affected by fluctuations, resulting in poor performance of qualitative and quantitative analysis. However, TRSI-LIBS obtains multiple spectra under different delay time,

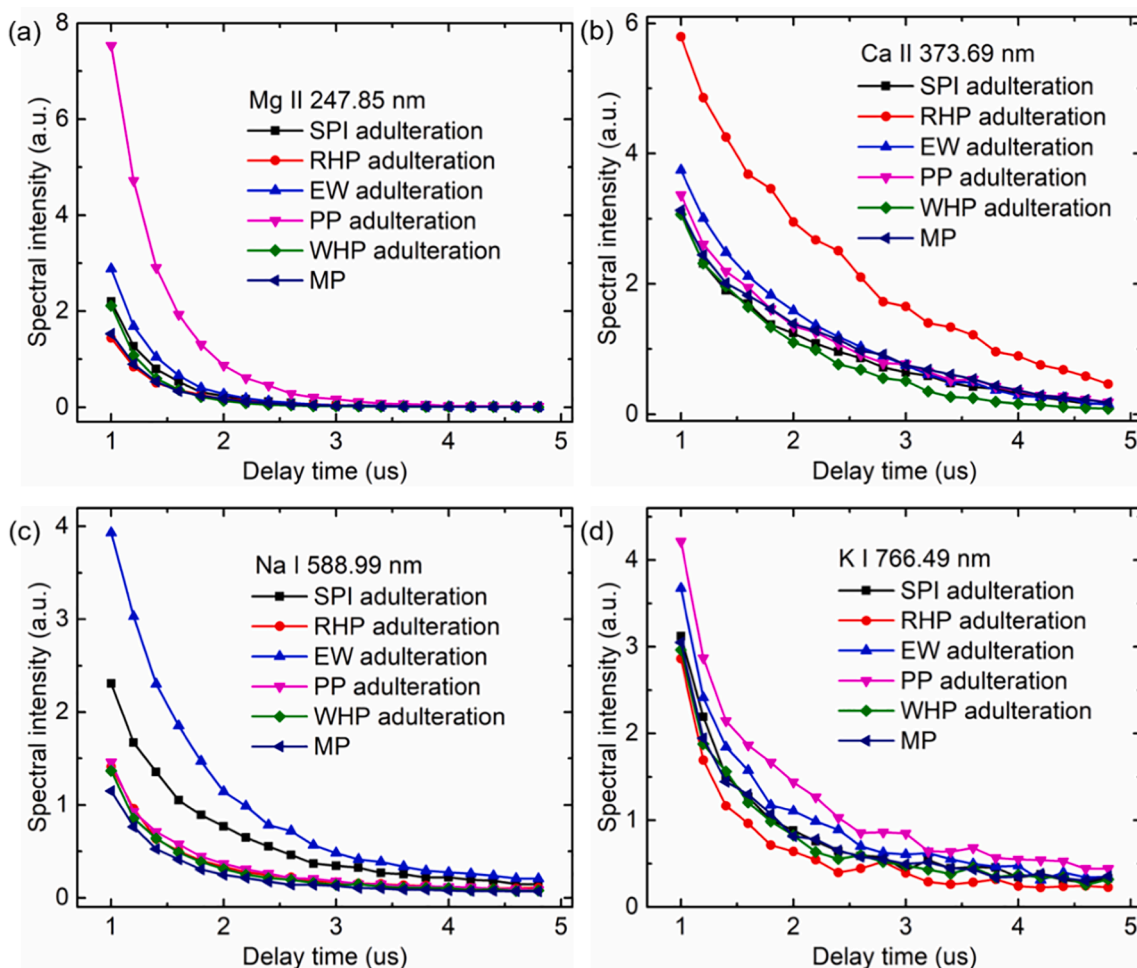


Fig. 5. The variation trend of spectral intensity of (a) Mg, (b) Ca, (c) Na and (d) K in milk powder and its foreign protein adulteration samples with delay time.

and the spectral information is more abundant. When one or several spectra of multiple spectra fluctuate, it has less impact on the results of qualitative and quantitative analysis than traditional LIBS. On the other hand, if the spectra fluctuate due to the changes of the external environment, the spectral variation trend obtained through the HOG features of the spectral images can also correct the spectral fluctuation and improve the robustness of the spectra.

It has been verified by experimental results and principle analysis that TRSI-LIBS is effective and widely applicable not only in qualitative analysis, but also in quantitative analysis.

4. Conclusion

In summary, TRSI-LIBS was demonstrated to have high precision in analyzing the quality of milk powder qualitatively and quantitatively. Compared with traditional LIBS, TRSI-LIBS can not only effectively excavate the matrix information, but also enhance the robustness of spectral information, so it can effectively improve the performance of qualitative and quantitative analysis. To verify the effectiveness of TRSI-LIBS experimentally, qualitative and quantitative analysis of milk powder quality was carried out. For the qualitative analysis of foreign protein adulteration in milk powder, we compared the qualitative analysis results of three models based on traditional LIBS and TRSI-LIBS. The prediction accuracies of the three qualitative models based on TRSI-LIBS increased from 81.50, 76.03 and 79.07% to 90.40, 83.47 and 84.90%, compared with that based on LIBS. For the quantitative analysis of foreign protein adulteration and Ca content, the same results were got. For example, LOD, R^2_p , RMSEP and AREP of Ca content quantitative model based on TRSI-LIBS were improved from 1.47 mg/g, 0.95, 0.35 mg/g and 23.29% to 0.81 mg/g, 0.98, 0.20 mg/g and 12.60%, compared with the traditional LIBS. These results demonstrate that TRSI-LIBS is a reliable and stable high-precision qualitative and quantitative analysis method, which is not only applicable to the quality analysis of milk powder, but also suitable for other fields. All in all, the integration of TRSI-LIBS in the analysis system can effectively improve the qualitative and quantitative analysis performance of the system, and further promote the application of LIBS in various fields.

CRedit authorship contribution statement

Deng Zhang: Conceptualization, Methodology, Formal analysis. **Junfei Nie:** Data curation. **Xuechen Niu:** Visualization, Investigation. **Feng Chen:** Investigation. **Zhenlin Hu:** Software. **Xuelin Wen:** Validation. **Yuqiong Li:** Funding acquisition, Writing – review & editing. **Lianbo Guo:** Funding acquisition, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was financially supported by the Fundamental Research Funds for the Central Universities [grant number 2021yjsCXCY073]; the National Natural Science Foundation of China [grant numbers 62075069, 61575209]; the Youth Innovation Promotion Association, Chinese Academy of Sciences [grant number 2018024].

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.foodchem.2022.132763>.

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