Irradiation dose detection of irradiated milk powder using visible and near-infrared spectroscopy and chemometrics

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ABSTRACT

The objective of this study was to examine the possibility of applying visible and near-infrared spectroscopy to the quantitative detection of irradiation dose of irradiated milk powder. A total of 150 samples were used: 100 for the calibration set and 50 for the validation set. The samples were irradiated at 5 different dose levels in the dose range 0 to 6.0 kGy. Six different pretreatment methods were compared. The prediction results of full spectra given by linear and nonlinear calibration methods suggested that Savitzky-Golay smoothing and first derivative were suitable pretreatment methods in this study. Regression coefficient analysis was applied to select effective wavelengths (EW). Less than 10 EW were selected and they were useful for portable detection instrument or sensor development. Partial least squares, extreme learning machine, and least squares support vector machine were used. The best prediction performance was achieved by the EW-extreme learning machine model with first-derivative spectra, and correlation coefficients = 0.97 and root mean square error of prediction = 0.844. This study provided a new approach for the fast detection of irradiation dose of milk powder. The results could be helpful for quality detection and safety monitoring of milk powder.

Key words: visible and near infrared spectroscopy, milk powder, irradiation dose, extreme learning machine

INTRODUCTION

Food irradiation has about 100 yr of history and it was developed as a scientifically established technology and a safe food process (Farkas and Mohácsi-Farkas, 2011). It is a process of exposing food to a carefully controlled amount of energy in the form of high-energy photons or charged particles to destroy microorganisms or parasites that might be present in foods (Mostafaei et al., 2010). Research during the last decades has con-

firmed that irradiation effectively improves the microbiological quality of dried products (Yusof et al., 2007). In many countries, irradiated food must be labeled to safeguard the consumer's right of choice. On the other hand, high-dose irradiation can lead to physicochemical changes and significantly deteriorate sensory properties of food (Kim et al., 2006). As reported, γ -irradiation can also affect proteins by causing conformational changes, oxidation of amino acids, formation of protein free radicals, and recombination and polymerization reactions (Urbain, 1986).

Currently, food irradiation is approved by national legislations in over 55 countries and the volume of irradiated food is estimated to exceed 500,000 t annually worldwide (Chen et al., 2012). With extensive use of irradiation technology in the food industry, a need exists to develop an effective and reliable method to determine food irradiation doses. Many methods exist to detect irradiated food, such as thermoluminescence analysis, GC, electron spin resonance analysis, HPLC, and so on. But these methods depend on expensive test equipment and professional knowledge. The samples require complicated preprocessing.

Near-infrared (NIR) spectroscopy is a rapid and noninvasive spectroscopic method that has been successfully used in the study of many food products (Cruz Ortiz et al., 2006; Liu et al., 2009b). In the current study, the possibility of applying NIR spectroscopy to the quantitation of irradiation dose of irradiated milk powder was examined. Six different pretreatment methods and 5 different prediction models were compared. Regression coefficients analysis was applied to select effective wavelengths (EW) for future commercial application.

MATERIALS AND METHODS

Sample Processing

The research milk powder was purchased from a local market. All of the milk powders were from the same manufacturer (Yahua Dairy Co., Hunan Province, Changsha, China). A total of 150 samples were used; these samples were separated into 5 groups and each

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group included 30 samples. Samples were irradiated with ^{60}Co γ -rays, with a dose rate of 2 kGy/h, resulting in doses of 0, 1.5, 3.0, 4.5, and 6.0 kGy. Irradiated and nonirradiated control samples were stored for 7 d at a constant temperature of $25 \pm 1^\circ\text{C}$ and relative humidity of 70%. Sample processing was finished in the irradiation center of the Institute of Nuclear Agricultural Sciences of Zhejiang University (Zhejiang, China). The irradiation equipment designed source capacity of ^{60}Co γ was 18.5×10^{15} Bq. A potassium (silver) dichromate dosimeter was used to measure γ -ray absorbed doses.

Reflectance Measurement

Reflectance measurement was carried out using an ASD HandHeld FieldSpec spectrometer (Analytical Spectral Devices, Boulder, CO); the wavelength region was in the visible/NIR region (325 to 1,075 nm) and the resolution of the instrument was 1.5 nm. Each spectrum was scanned 30 times and sample spectra acquired by averaging 3 spectra. The ASD View Spec Pro software (Analytical Spectral Devices) was used in spectral data acquisition.

Data Pretreatment

In this work, we investigated and compared 6 pretreatment methods, including Savitzky-Golay smoothing (**SG**), standard normal variate (**SNV**), multiplicative scatter correction (**MSC**), first derivative (**1-Der**), second derivative (**2-Der**), and detrending. These pretreatment methods can remove the spectral baseline shift, noise, and light scatter influence (Chu et al., 2004). The performance of these pretreatments was determined by the prediction results of full-spectrum partial least squares (**PLS**) and extreme learning machine (**ELM**) models. The pretreatment process and PLS model were implemented by Unscrambler v9.8 prediction engine software (CAMO AS, Oslo, Norway).

Effective Wavelength Selection

It is time consuming to use full spectra for computation. Extracting the useful information from the spectra can reduce the computation time and produce better prediction and simpler models. Regression coefficient (**RC**) analysis was used to select EW in this study. The size of coefficients indicated the importance of variables for predicting target attributes in the PLS analysis, so the variables that had large absolute values were selected as EW for further studies (Liu et al., 2009a).

Chemometric Models

Partial least squares is the most important linear calibration method in the analysis of NIR spectra (Geladi

and Kowalski, 1986; Balabin, 2010). The purpose of PLS is to establish a linear model to predict irradiation dose of irradiated milk powder from the spectral data. Latent variables were used as the direct inputs of PLS models and the number of latent variables was obtained by cross-validation of the calibration set.

Extreme learning machine is a new fast-learning neural algorithm that has been successfully applied in solutions to classification and regression problems (Wang et al., 2008; Mohammed et al., 2011). It is an algorithm for single-hidden layer feed-forward networks. Compared with the traditional learning algorithms for neural networks, ELM not only tends to reach the smallest training error but also the smallest norm of output (Huang et al., 2006).

Least squares-support vector machine (**LS-SVM**) is a powerful calibration method to handle linear and non-linear problems with a good statistical basis (Suykens and Vandewalle, 1999). The radial basis function can model nonlinear relationships between spectra and target attributes, reduce the computational complexity of the training procedure, and give good performance. Thus, in the current study, the radial basis function kernel was chosen; the other 2 crucial elements for LS-SVM models were input variables and model parameters. In this study, the selected EW by regression coefficient analysis were used as the input variables and the model parameters γ [model regularization parameter of the radial basis function (RBF), the kernel function of the LS-SVM model] and σ^2 (kernel width of RBF) were determined by a 2-step grid search technique.

In this paper, we considered correlation coefficients (r) and root mean square error of prediction (**RMSEP**) as the main evaluation standards. The RMSEP can be interpreted as the average prediction error. A good model should have low RMSEP and high correlation coefficient between predicted and reference values. The calibration models of ELM and LS-SVM were performed using Matlab v7.0 software (The MathWorks Inc., Natick, MA). The correlation coefficient and RMSEP are given as follows:

$$r = \sqrt{1 - (SS_R/SS_T)};$$

$$\text{RMSEP} = \sqrt{\sum_{i=1}^n (y_i - y_i^*)^2 / n},$$

where SS_R and SS_T are the residual and total sum of squares, respectively; y and y^* represent the measured and predicted values, respectively; and n is the number of samples.

RESULTS AND DISCUSSION

Reflectance Spectra Features

Measured visible/NIR reflectance spectra in the range of 400 to 1,000 nm are shown in Figure 1. As can be seen, the trends of all samples were quite similar. Minor reflectance peaks can be observed around 968 nm, which is associated with the O-H stretch second overtone of water and alcohol (ROH; Osborne et al., 1993).

Results of Full-Spectrum Models

The processed spectral data was first applied in the PLS model; the models were evaluated using correlation coefficients and RMSEP. As mentioned above, there were 5 different groups with 5 different irradiation doses; 10 validation set samples were randomly extracted from every group. Therefore, in this study, 50 samples were selected as validation sets and the remaining 100 samples were used as calibration sets.

Figure 2 represents the prediction results of full-spectrum PLS models with 6 pretreatment methods. The average correlation coefficient of PLS models was

over 0.9 and the linear calibration method showed good performance in this study. The highest correlation coefficient was attained by SNV and MSC spectra ($r = 0.96$) and the lowest RMSEP was obtained by raw spectra, with RMSEP = 0.900. Savitzky-Golay smoothing, SNV, MSC, and 1-Der were selected as the optimal pretreatment methods in this step.

The prediction results of ELM models with 4 selected pretreatment methods can be seen in Table 1. Through comparison, RMSEP of all ELM models increased. The average RMSEP of PLS models was 0.910 and for ELM models it increased to 0.958; thus, PLS models showed more reliability.

Checking the prediction capacity of ELM models with 4 pretreatment methods from Table 1, SG and 1-Der spectra gave better performance and these 2 kinds of processed spectral data resulted in higher correlation coefficients in the ELM model than when applied to the PLS model. The best result was a correlation coefficient of 0.97 and RMSEP of 0.907, which was achieved by SG spectra combined with the ELM model. The prediction results given by linear and nonlinear calibration methods suggested that SG and 1-Der were suitable pretreatment methods.

Figure 1. Original visible near-infrared (NIR) reflectance spectra of milk powder.

Table 1. The prediction results of irradiation dose of irradiated milk powder by extreme learning machine (ELM) models with full spectra

Pretreatment ¹	Nodes (no.)	r	RMSEP ²	Bias
Raw	17	0.96	0.918	0.641
SG	18	0.97	0.907	0.693
SNV	19	0.96	1.042	0.788
MSC	9	0.96	0.966	0.647
1-Der	7	0.96	0.957	0.739

¹SG = Savitzky-Golay smoothing; SNV = standard normal variate; MSC = multiplicative scatter correction; 1-Der = first derivative.

²Root mean square error of prediction.

Selected EW

Taking the optimal pretreatment methods into consideration, the EW selected by RC are shown in Table 2. The average number of selected EW was 7, which means that the input variables reduced by 98.8%.

The values of the RC, which indicated the contribution of spectra (raw spectra) to the calibration model, are shown in Figure 3. From Figure 3, some obvious peaks and valleys were easy to observe. According to the preliminary studies, the threshold value was de-

Table 2. Selected effective wavelengths (EW) by regression coefficient (RC)

Pretreatment ¹	n	Selected EW (nm)
Raw	6	403, 409, 420, 428, 989, 1,000
SG	8	406, 420, 519, 599, 642, 832, 987, 1,000
1-Der	7	407, 418, 422, 429, 979, 983, 993

¹SG = Savitzky-Golay smoothing; 1-Der = first derivative.

terminated as ± 6 and certain peaks and valleys with absolute values over 6 were selected.

The wavelength range from 973 to 1,020 nm was considered as one of the characteristic bands of protein; the selected EW (989 and 1,000 nm) in this region could be attributed to the second overtone of N-H stretching vibrations (Workman and Weyer, 2007). The selected wavelengths (403, 409, 420, and 428 nm) in the visible range might be related to fats, because the fats contain double conjugate bonds that absorb in the visible range of the spectrum.

Performance of EW-Based Models

Three kinds of EW-based models were developed, including EW-PLS, EW-ELM, and EW-LS-SVM. In

Figure 2. Prediction results of full-spectrum partial least squares (PLS) models. RMSEP = root mean square error of prediction. SG = Savitzky-Golay smoothing; SNV = standard normal value; MSC = multiplicative scatter correction; 1-Der = first derivative; 2-Der = second derivative.

Figure 3. Selected effective wavelengths by regression coefficients (raw spectra). The dashed horizontal lines show the upper and lower cutoff threshold values.

LS-SVM models, the optimal combination of (γ and σ^2) within the region of 10^{-3} to 10^3 was selected based on several attempts. The results (1-Der spectra) of the 2-step grid search are shown in Figure 4.

The prediction results of EW-based models are shown in Table 3. As shown in Table 3, the prediction results of the EW-ELM model outperformed the EW-PLS and

EW-LS-SVM models. The best result was a correlation coefficient of 0.97 and RMSEP of 0.844 by the EW-ELM model with 1-Der spectra. The sample plots in the prediction set can be seen in Figure 5. Through further comparison, for 3 calibration methods, the pretreated spectra had better prediction results than the raw spectra, which indicates that the pretreatment

Table 3. The prediction results of irradiation dose of irradiated milk powder by different models

Model ¹	Pretreatment ²	LV (no.)/Nodes (no.)/(γ , σ^2) ³	Validation	
			r	RMSEP ⁴
EW-PLS	Raw	3/-/-	0.85	1.143
	SG	5/-/-	0.96	0.909
	1-Der	2/-/-	0.95	0.839
EW-ELM	Raw	-/42/-	0.93	1.047
	SG	-/9/-	0.96	0.926
	1-Der	-/14/-	0.97	0.845
EW-LS-SVM	Raw	-/-/(1.0647 $\times$ 103, 114.8837)	0.90	1.064
	SG	-/-/(7.6724 $\times$ 103, 76.1098)	0.92	1.486
	1-Der	-/-/(12.9362, 23.2813)	0.96	0.811

¹EW-PLS = effective wavelength-partial least squares; EW-ELM = effective wavelength-extreme learning machine; EW-LS-SVM = effective wavelength-least squares-support vector machine.

²SG = Savitzky-Golay smoothing; 1-Der = first derivative.

³LV = latent variables; γ = model regularization parameter; σ^2 = kernel width; - = none.

⁴Root mean square error of prediction.

Figure 4. Two-step grid search for the optimal γ (model regularization parameter) and σ^2 (kernel width) for the prediction [first-derivative (1-Der) spectra].

Figure 5. Predicted versus reference values of irradiation dose of milk powder by effective wavelength-extreme learning machine (EW-ELM) models.

method was an important strategy to improve prediction performance.

Comparing full-spectrum models and variable compression models, the EW-PLS models gave better performance than full-spectrum PLS models, except for raw spectra. The reason might be that the selected wavelengths represented the most useful information of full-spectra and variables that contained little information for model calibration were removed. For 1-Der spectra, the selected wavelengths outperformed the full spectra in PLS and ELM models, not just with improved correlation coefficients but also with reduced RMSEP. This indicates that 1-Der was the optimal pretreatment method in our study and the EW selected by RC analysis was reliable.

Taking optimal pretreatment into consideration, for 1-Der spectra, the optimal full-spectrum model was ELM with correlation coefficient of 0.96, and the optimal EW-based model was EW-ELM with correlation coefficient of 0.97. The prediction accuracy of nonlinear ELM method was better than that of the linear PLS method. It indicated that nonlinear information could improve prediction accuracy. Focusing on the 2 nonlinear calibration methods, EW-ELM model slightly outperformed the EW-LS-SVM model. The main reason might be that ELM with higher generalization ability avoids many difficulties faced by gradient-based learning methods (Zhu et al., 2005). Extreme learning machine was a successful regression tool in spectroscopy analysis.

CONCLUSIONS

Near-infrared spectroscopy shows the feasibility for rapid and noninvasive quantitation of irradiation dose in irradiated milk powder. The 1-Der method was selected as the optimal pretreatment method in this study. Regression coefficient analysis was successfully applied to select the most relevant EW. The ELM provided a more accurate and robust model in this study, which indicates that it was a useful calibration method in the NIR spectroscopic techniques. The best prediction performance was achieved by the EW-ELM model with 1-Der spectra; the correlation coefficients and RMSEP were 0.97 and 0.844, respectively. This study has significance for the fast and online detection of irradiation doses of milk powder, which could be helpful for food quality detection and food safety monitoring.

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