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# 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 (Mostafavi et al., 2010). Research during the last decades has confirmed 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 ± 1°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 $18.5 \times 10^{15}$ Bq. A potassium (sliver) 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 nonlinear 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 $\sigma^2$ (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:

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

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

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.