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Real-time monitoring of total polyphenols content in tea using a developed optical sensors system

Shuai Qi, Qin Ouyang, Quansheng Chen*, Jiewen Zhao

School of Food and Biological Engineering, Jiangsu University, Xuefu Road 301, Zhenjiang 212013, Jiangsu, PR China

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ABSTRACT

A portable and low-cost optical sensors system consisting of hardware and software was developed and used for real-time monitoring total polyphenols content in tea in this work. This developed system was used for data acquisition. Partial least square (PLS) with several variable selection algorithms was used for modeling. Synergy interval partial least square (Si-PLS) was first used to select spectral subintervals of interest, and then competitive adaptive reweighted sampling (CARS) and genetic algorithm (GA) were comparatively employed to select the variables of interest from the subintervals of interest. The optimum model was achieved and stored in the developed software. Next, 20 independent samples were used to test the performance of this system. And the coefficient of variation (CV) of the final results was used to state the stability and reliability of this system. The results also showed that GA–Si-PLS performed better than CARS–Si-PLS model and the CVs for most of the samples were <5%. This study demonstrated this developed optical sensors system as a promising tool that could be used for real-time monitoring tea quality.

1. Introduction

Tea is one of the most widely consumed beverages in the world. It is reported that there exhibits a significant health protecting activity due to its polyphenols compounds in tea [1]. Tea polyphenols including flavonols, flavonoids and phenolic acids are the most significant group of tea components and have a wide range of pharmaceutical properties including anti-oxidative [2], anti-carcinogenic [3], antimicrobial activity [4], anti-arteriosclerotic [5] and anti-diabetic [6]. Besides, tea polyphenols are mainly responsible for the characteristic astringent and bitter taste of tea. In general, tea polyphenols content, as one of important indicator, is often used for tea quality assessment [7]. Currently, wet chemical analysis and human panel test are the most elementary and commonly used conventional methods for tea analysis. However, wet chemical analytical methods are expensive, laborious and invasive, and it is feasible only in laboratories; furthermore, all these methods would suffer lots of difficulties once face to real implementation in an industrial online configuration. Human panel test for assessing tea quality is carried out by some skillful ‘tea tasters’, and thus the practical evaluation of tea quality is entirely subjective, leading to inaccurate results owing to adaptation, fatigue and state of mind [8]. Therefore, demand for high quality of tea products obviously requires high standards for quality assurance and process control; satisfying this demand in turn requires an appropriate analytical tool for tea quality assessment.

Near infrared reflectance (NIR) spectroscopy is a fast, accurate and non-destructive technique that has been applied in multiple areas. It can be employed as a replacement of time-consuming chemical methods in food and agriculture product analysis. Researchers have also done a lot of work about applying this technology for qualitative and quantitative analysis of tea rapidly, including quality parameters prediction (like catechins, caffeine and polyphenols) [9–11] and varieties or grades identification [12–15]. Measurement of total polyphenols content in tea by NIR spectroscopy has also been studied in our previous reports [7,11] and good outcomes have been obtained. However, these studies mainly used commercial NIR instruments. These instruments are expensive, bulky and non-specific, therefore not suitable for tea quality monitoring in industrial processing line. It is increasingly demand for developing a portable, low-cost, and specific spectrometer instrument for on-site tea quality assessment. The current trend toward the use of NIR technology in situ has led to the miniaturization of optical components which has enabled the development of compact optical instruments [16,17]. Some advanced optical sensors systems with small size, low-cost and ease-of-use have appeared over the last few years [18,19], most

* Corresponding author. Tel.: +86 511 88790318/+86 511 8780201; fax: +86 511 88780201.
E-mail addresses: qschen@ujs.edu.cn, q.s.chen@hotmail.com (Q. Chen).

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of which are gradually becoming available in real-time and on-line monitoring [20–22].

Multivariate calibrations play an important role in spectral data analysis. Partial least squares (PLS) regression is one of the commonly used multivariate methods [23]. However, the classic PLS model based on full spectrum has some unrelated and collinear spectral variables that may influence the stability and prediction precision of the model. Variables selection can be highly beneficial for model performance improvement and structural simplification [24]. Synergy interval partial least squares (Si-PLS) can help in the search for some efficient spectral intervals to achieve a good model [25,26]. However, even in a small subinterval, there are still some collinear variables. Competitive adaptive reweighted sampling (CARS) and genetic algorithm (GA) were used to select the variables of interest from efficient intervals. Therefore, CARS–Si-PLS and GA–Si-PLS were comparatively used to calibrate models in this study.

The main objective of this study was to develop a portable and low-cost optical sensors system for real-time monitoring of tea quality. The specific procedures were outlined as follows: (1) a portable and low-cost optical sensors system consisting of hardware and software was developed; (2) Two algorithms of CARS–Si-PLS and GA–Si-PLS were comparatively used for modeling; (3) the independent samples were used for model test. This system will have a very promising application prospect in tea processing enterprises for tea quality assessment.

2. Optical sensors system

A portable and low-cost optical sensors system, as shown in Fig. 1, was developed by the Institution of Agro-Product Processing in Jiangsu University. The system mainly consists of a light source, a backscattering fiber-probe (QR400-7-VIS-BX, Ocean Optics Inc., USA), a grating system (SD1200, OTO Photonics Inc., Taiwan, China) equipped with a slit, a detector (ILX554B, Sony, Tokyo, Japan) and a computer supported with a data acquisition and control software (SSDAA V1.00, Jiangsu University, China). The light source consists of a 10-W halogen lamp and an air fan. A low-dropout voltage regulator provided the positive supply (+5 V) to the halogen lamp and air fan. Backscattering fiber probe was used to transfer photons from light source to tea sample and then to the grating system. The detector, with high quantum efficiency in region of 300–800 nm, is a charge coupled device (CCD) with 2048-elements high-sensitivity linear array (ILX554B, Sony, Tokyo, Japan), which was much cheaper than InGaAs detector. A fixed grating system, with a slit width of 25 μm, focuses the dispersed radiation onto the detectors. This system was low-cost, compact, portable, robust, and easy to connect with the computer via universal serial bus (USB).

Software of spectral data acquisition and analysis was compiled using Visual C++ 6.0 (Microsoft Co., Seattle, USA) under Windows XP. The graphical user interface (GUI) of the software in this system was shown in Fig. 2. The main user interface of the software included four sections: system menu bar, system operation panel, preview window, and the status panel. In the system menu bar, users can set spectrometer parameters, save spectral data and model, and test equipment. In the system operation panel, users can collect spectra and acquire model. The preview window was used to show the spectra of samples. The status panel consists of a read-only text box for displaying the hardware parameters, model messages and results.

3. Modeling and optimization

3.1. Samples

Two batches of green tea were provided by Damin Foodstuff Co., Ltd which is one of the largest tea comprehensive processing manufacturers around the world. One batch containing 30 samples called calibration set was used to establish models; and the other containing 20 samples called prediction set was used to test the performance of the final model. All samples were ground before the experiment. For each sample, about 30 ± 1 g of the whole tea leaves were put into a small electric coffee mill (HY-02, Huanya Tianyuan Machinery Technology Co., Ltd, Beijing, China) and ground for 10 s. After this procedure, the powder was sieved with a mesh width of 180 μm. The sieved powder was used for the subsequent analysis.

Table 1
Reference results of total polyphenols content of samples in the calibration set and prediction set.

Subsets	Unit (%)	S.N.[a]	Range	Mean	S.D.[b]
Calibration set	g/g	30	12.4533–26.4040	18.9197	3.1820
Prediction set	g/g	20	12.3400–25.1352	18.6756	3.0982

[a] S.N.: sample number.
[b] S.D.: standard deviation.

3.2. Data collection and preprocessing

Parameters setting, data collection and save were carried out by our developed software. The exposure integration time of the CCD was set as 600 ms. In order to get a stable database, each spectrum was the average of 16 scanning spectra pretreated with Savitzky–Golay smoothing (11 smoothing points) [27]. The range of spectra was from 300 nm to 1000 nm, resulting in 897 variables. All spectra data were saved as light intensity value in *.txt file format. The temperature was kept around 25 °C and the humidity was kept at a steady level in the laboratory. The average from three times data collection of one sample was used as the spectrum of the sample. Standard normal variate (SNV) is a mathematical transformation method of the spectral data used to remove slope variation and to correct for scatter effects due to differences in the particle sizes of materials.

3.3. Reference measurement

After the spectral data of all samples were acquired, total polyphenols content was measured by traditional chemical analysis, referred to the National Standard of China (GB/T 8313-2002). Absorbance at 540 nm of the reaction solution is determined in a 1 cm light-path cell by a UV-1601 spectrophotometer (Rayleigh Analytical Instrument, Beijing, China). Table 1 shows the reference results of total polyphenols content of samples in the calibration and prediction sets.

3.4. Multivariate analysis

NIR spectroscopy combined with variable selection method was used to develop PLS models for predicting total polyphenols content in tea. First, Si-PLS was used to select efficient spectral intervals; then, GA or CARS were used to select efficient variables from these efficient intervals. The performance of the final model was evaluated by correlation coefficient of calibration set (R_c) and root mean square error of cross validation (RMSECV) in the calibration set, and correlation coefficient of prediction (R_p) and root mean square error of prediction (RMSEP) in prediction set, the detail descriptions about which can be referred to Ref. [28].

Si-PLS algorithm used here was developed by Nørgaard et al. [29]. It is an all possible subinterval combination procedure tests based on all possible PLS of all subsets of subintervals. The basic principle of this algorithm is as follows: firstly, the full-spectrum region is split into a number of equidistant spectral subintervals (variable-wise); secondly, PLS regression models are constructed