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Quantitative determination based on the differences between spectra-temperature relationships

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ABSTRACT

In the Near-infrared (NIR) spectral measurement it is not always possible to keep the experimental conditions constant. The fluctuations in external variables, such as temperature, will result in a nonlinear shift and a broadening of the spectral bands. In this study, the temperature-induced spectral variation coefficient (TSVC) was obtained by using loading space standardization (LSS). The relationship between TSVC and normalized squared temperature was quantitatively analyzed and applied to the quantitative determination of the compositions in mixtures. NIR spectra of peanut-soy-corn oil mixtures measured at seven temperatures were analyzed. It was found that, the relationship between TSVC and normalized squared temperature can be established by using LSS. Furthermore, the quantitative determination of the compositions in a mixture can be achieved by using the difference between the relationships, i.e., the slope of the relationship. The calibration curves between slope and composition volume are found to be reliable with the correlation coefficients (R^2) as high as 0.9992. Quantitative determination by the calibration curves were also validated. Therefore, the method can be an effective tool for investigating the effect of temperature and quantitatively analysis.

1. Introduction

Among the characteristics of near-infrared (NIR) spectra [1–5], one of the most remarkable is its high sensitivity to temperature changes [6–9]. The temperature changes have a particular marked effect on the absorption bands for functional groups forming inter- or intra-molecular hydrogen bonds, nonlinear shifts and a narrowing of the spectral bands [10–12]. Chemometric methods were extensively studied to correct the effect of temperature variation on NIR spectra because it was known as a perturbation that affects NIR spectra and the predictive ability of multivariate models [13–21].

The NIR spectra measured under different temperatures, however, can reflect the nonlinear shift changes and broadening of the spectral bands. In other words, temperature can be considered as a constructive parameter that provides detailed chemical information when systematically changed during a measurement. The number of publications about this strategy is much smaller than that of papers focused on the elimination of spectroscopic temperature effects. A three-way tensor model, which was generated by temperature dependent NIR spectra, was proposed for the application of quantitative analysis [22]. A quantitative spectra-temperature relationship (QSTR) model between NIR spectra and temperature was established using partial least squares (PLS) regression [23–25] and applied to the quantitative determination of the compositions in mixtures [26,27]. A QSTR model was also established by the temperature coefficients of multilevel simultaneous composition analysis (MSCA) in the between-temperature model, and quantitative analysis was achieved by the concentration coefficients of MSCA in the within-temperature model [28].

The main reason why PLS or MSCA were used to establish QSTR model is it is hard to explain the details directly from the inspection of the spectral variations by temperature changes [26–28]. The temperature-induced spectral variations, however, can be obtained by loading space standardization (LSS) [15,29]. LSS was proposed by Chen to maintain the validity of multivariate calibration models for chemical processes affected by temperature fluctuations [15,29]. The main idea behind the LSS approach is to perform standardization on the loading space, as opposed to the original data space, so that the spectra measured at test

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temperature can be transformed to the spectra which appears to have been measured under the reference temperature. On the other hand, LSS gives the difference between spectra measured at test temperature and spectra measured at reference temperature. Previous results showed that the influence of temperature variations on the spectra can be effectively removed by using LSS [15,29]. These applications proved that the spectral difference obtained by using LSS can give a view on the temperature-induced variation in the NIR data.

In this study, we considered temperature not as a nuisance factor but as a constructive parameter and investigated the spectral variations in NIR spectra caused by temperature changes. More specifically, the temperature-induced spectral variations were obtained by using LSS [15,29] and temperature-induced spectral variation coefficient (TSVC) was defined. According to previous research [13,30–33], second-order polynomials can be used to account for the temperature effects on NIR spectra. In order to extract the useful information from the effects of temperature on NIR spectra, the relationship between TSVC and normalized squared temperature was established and quantitatively analyzed. Furthermore, the difference between the relationships, i.e., the slope of the relationship, was found to be a quantitative reflection of concentration. Compared with the quantitative determination by using QSTR model built with PLS and MSCA in previous works [26–28], we obtained the spectral variations induced by temperature changes from the measured spectra. Thus, the spectra-temperature relationships were established directly by using TSVC and normalized squared temperature. The mixture of peanut oil, soy oil and corn oil was used in this paper because edible oils are sensitive to temperature changes.

2. Experimental

2.1. Materials and sample preparation

In this experiment, the samples were mixtures of peanut oil (Luhua Co., Ltd. Laiyang, China), soy oil (Wilmar International, Singapore) and corn oil (Wilmar International, Singapore). The mixture design is shown in Fig. 1 [13], and volume fraction levels that obey this design were mixed and are given in Table 1. It can be seen from Fig. 1 that 19 samples were divided into five groups based on the volume of soy oil (V_{soy}). The volume of soy oil was 0, 1, 2, 3 and 4 in Group 0, 1, 2, 3 and 4, respectively. In each group, the volume proportion for soy oil was the same between samples while the volume proportion increased for the corn oil, but decreased for the peanut oil. For specific volume fraction of each sample, please refer to Table 1.

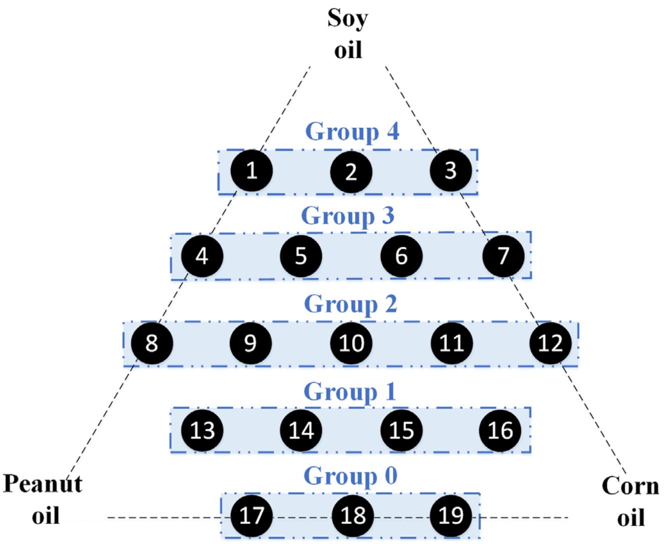

Fig. 1. Mixture design and group design. All the 19 samples were divided into five groups based on the volume of soy oil (V_{soy}). The volumes of soy oil were 0, 1, 2, 3 and 4 in Group 0, 1, 2, 3 and 4, respectively. In each group, the volume proportion for soy oil was the same between samples while the volume proportion increased for the corn oil, but decreased for the peanut oil.

Table 1
Volume fractions of the samples*.

Group	Sample	V_{soy}	V_{peanut}	V_{corn}
4	1	4	2	0
	2	4	1	1
	3	4	0	2
3	4	3	3	0
	5	3	2	1
	6	3	1	2
	7	3	0	3
2	8	2	4	0
	9	2	3	1
	10	2	2	2
	11	2	1	3
	12	2	0	4
1	13	1	4	1
	14	1	3	2
	15	1	2	3
	16	1	1	4
0	17	0	4	2
	18	0	3	3
	19	0	2	4

[*] V_{soy} is the volume of soy oil. V_{peanut} is the volume of peanut oil. V_{corn} is the volume of corn oil.

2.2. Temperature control and spectral measurement

The spectra collecting system consisted of five parts: a light source, a spectrometer, fiber optics, a temperature-controlling sample holder and a computer. An AvaLight-HAL-S tungsten-halogen lamp (Avantes, Apeldoorn, The Netherlands) was employed as the light source. The temperature in the experiment was controlled by a QNW qpod 2e sample holder of optical path 10 mm (Quantum Northwest, Inc., Liberty Lake, USA). The precision of the sample holder for temperature control is ±0.01°C. The program "Q-Blue-Wireless Temperature Control program" was used to control the temperature of oil samples at a selected temperature rapidly and precisely. Edible oils, such as peanut oil, soy oil and corn oil, are sensitive to the lower temperature ranges. In this study, the temperature changed from −2 °C to 10 °C, at intervals of 2 °C. The spectrum at each temperature was measured when the temperature does not change for 45 min.

All transmittance spectra were measured from 1041 nm to 1772 nm by AvaSpec-NIR256–1.7(TEC) Near-Infrared Spectrometer (Avantes, Apeldoorn, The Netherlands). The spectra are digitalized with ca. 3 nm interval resulting in 256 data points. Each sample was scanned in ten times and the mean spectrum from the ten measurements was used for analysis. As examples, Fig. 2 shows the spectra of five samples in Group 2 with different volume ratios of peanut oil and corn oil (V_{peanut}:V_{corn}=4:0, 3:1, 2:2, 1:3, 0:4) and the same volume of soy oil (V_{soy}=2) under seven temperatures. The difference between the spectra measured at different temperatures can be carefully seen from Fig. 2. It can be also seen that the effects of temperature in NIR spectra tend to become more