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Quantitative determination by temperature dependent near-infrared spectra: A further study

Jun Kang, Wensheng Cai, Xueguang Shao*

Research Center for Analytical Sciences, College of Chemistry, Nankai University, Tianjin, 300071, China

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ABSTRACT

Quantitative spectra-temperature relationship (QSTR) between near-infrared (NIR) spectra and temperature has been studied in our previous work (Talanta, 2010, 82, 1017-1021). In this study, applicability of the QSTR model for quantitative determination is further studied using the spectra of aqueous ethanol samples in the temperature range of 31–40 °C and the concentration range of 1–99%. The results show that QSTR model can be built by using the spectra in a small temperature range and the quantitative analysis can be achieved by only two spectra at different temperatures. Moreover, calibration curves for different concentration ranges (1–5%, 20–70%, 95–99%, v/v) are investigated by using linear and nonlinear curve fitting, respectively. Both of the linear and nonlinear curves are found to be applicable within these concentration ranges. Therefore, the temperature dependent NIR spectra may provide a new way for quantitative determination and may have high potential in bio-fluids analysis or industrial practices.

1. Introduction

Near infrared (NIR) spectroscopy has been extensively used in various fields, such as agriculture [1,2], food [3,4], petrochemical industry [5], soil sanitation [6], chemical industry [7,8], and pharmaceutical industry [9–11], etc. Due to its fastness, accuracy and non-destructive properties, it can be considered as a replacement of the conventional chemical analysis. However, as a kind of vibrational spectra, NIR spectra are sensitive to experimental conditions, such as temperature [12–16]. The variation of temperature will bring changes in NIR spectra, and the temperature induced spectral variation will affect the predictive ability of multivariate calibration models [17,18]. Temperature dependence is a major issue of in-line and on-line NIR measurements in industrial environments. Therefore, great efforts to correct the effect of temperature variation on NIR spectra have been made to improve the predictive ability of multivariate models [19–22]. From another point of view, rather than seeing spectroscopic temperature effects as the artefacts that have to be circumvented or eliminated, it seems to be more attractive to take the effects of temperature on NIR spectra as useful information and applied for quantitative determination [23,24].

The effect of temperature on NIR spectra has been studied, and both the peak positions and the absorption profile may change slightly with the temperature [12–16]. However, the difference between the spectra at different temperatures is not significant. It is difficult, therefore, to find a quantitative relationship directly from the spectra. In our previous work [24], the relationship of NIR spectra and temperature was quantitatively analyzed by using multivariate calibration method. The quantitative spectra-temperature relationship (QSTR) model between NIR spectra and temperature from 25 to 60 °C was established by using partial least squares (PLS) regression, which can be used for prediction of temperature of solution by NIR spectrum. Calibration curves for predicting the concentration of the components in mixtures were also established with the intercepts in the relationship of the measured and predicted temperatures for the mixtures of different concentration. Therefore, the potential for quantitative determination by using the temperature dependent NIR spectra was proven. However, further studies are still needed to make the method practical because more than 10 spectra at different temperatures were required and a large temperature range (25–60 °C) was used in the previous study. The high temperature may bring troubles for the measurements or even destroy the samples like bio-fluids.

In this study, efforts to make the method more practical were made. QSTR model in the temperature range 31–40 °C was established, and the required number of spectra was investigated for simplifying the measurements, and the samples of different concentration ranges (1–5%, 20–70%, 95–99%, v/v) were studied for extending the predictability of the calibration curves. Moreover, in order to improve the calibration curves, nonlinear curve fitting was also investigated besides linear regression.

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* Corresponding author. Tel.: +86 22 23503430; fax: +86 22 23502458.
E-mail address: xshao@nankai.edu.cn (X. Shao).

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2. Experimental

2.1. Reagents and sample preparation

Ethanol absolute (Concord Technology Co., Ltd. Tianjin, China) was of analytical grade. Purified water, provided by Wahaha Company (Hangzhou, China), was used throughout for preparation of the samples.

Aqueous solutions containing 1%, 2%, 3%, 4%, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 95%, 96%, 97%, 98% and 99% (v/v) ethanol were prepared for the investigation of the relationship between temperature and spectra and the establishment of the calibration curves. Four prepared ethanol solutions with water (3.5%, 35%, 45%, 96.5%, v/v), one prepared ethanol solution with carbonated drink (96.5%, v/v) and four Chinese alcohol liquors were used for validation of the calibration curves. The carbonated drink was pretreated by ultrasonic degassing before use, and the liquors were purchased from market and used directly without any pretreatment.

2.2. Temperature control and spectral measurement

A three-necked flask containing 100 mL samples was placed in an oil-bath system (Yuhua, Gongyi, China) consisted of a temperature control unit and a magnetic stirrer. The stability of the system for temperature control is ±1 °C, but the temperature was measured with a thermometer plugged into the flask. The temperature was controlled to change from 31 to 40 °C with a step of ca. 1 °C. The spectrum at each temperature was measured 10 min later when the temperature was changed.

All NIR spectra were measured from 5500 to 12,000 cm^{-1} by a Vertex 70 spectrometer (Bruker Optics Inc, Ettlingen, Germany) furnished with a transmittance optical fiber probe (Bruker Optics Inc, Ettlingen, Germany) of optical path 2 mm. A tungsten-halogen light source and InGaAs detector were used. The spectra are digitalized with ca. 4 cm^{-1} interval in the Fourier transform, each spectrum is, therefore, composed of 1686 data points. To increase signal to noise ratio, both air reference and sample spectra were measured with scan number 64.

2.3. Modeling and data processing

PLS regression was used for modeling the relationship of the temperature and spectra, and the performance of PLS regression models was evaluated in terms of the correlation coefficient (R) between the measured and predicted values and the root mean square error of cross validation (RMSECV), which was obtained by leave-one-out cross validation (LOO-CV). The number of latent variables for PLS model was determined by using the LOO-CV with F-test [25]. Furthermore, due to the drifting baseline or background in the spectra, continuous wavelet transform for approximate derivative (CWTAD) technique was used for spectral pre-processing. Haar wavelet was used with the scale parameter 20. All the calculations were carried out in Matlab (Math Works, Inc., Natick, MA).

3. Results and discussion

3.1. Quantitative spectra-temperature relationship

The quantitative relationship between NIR spectra and temperature has been studied in our previous work [24] and the QSTR model was proven to be reliable in the temperature range from 25 to 60 °C. In practical uses, however, the measurements were found time-consuming and the high temperature may make the method unusable. Thus, the QSTR model in the temperature range of 31–40 °C was investigated.

Table 1
Relationship between the measured and predicted temperatures by cross validation.

Sample	R	RMSECV	Regression equation[a]
Water	0.9996	0.0795	$y = 1.01x - 0.238$
Water–ethanol (1%, v/v)	0.9998	0.0519	$y = 1.00x - 0.0386$
Water–ethanol (2%, v/v)	0.9991	0.1258	$y = 1.01x - 0.295$
Water–ethanol (3%, v/v)	1.0000	0.0253	$y = 0.999x + 0.0236$
Water–ethanol (3.5%, v/v)	0.9998	0.0535	$y = 1.00x + 0.0009$
Water–ethanol (4%, v/v)	0.9998	0.0504	$y = 1.00x - 0.0673$
Water–ethanol (5%, v/v)	0.9995	0.0929	$y = 1.00x - 0.0945$
Water–ethanol (10%, v/v)	0.9999	0.0286	$y = 1.00x - 0.0297$
Water–ethanol (20%, v/v)	0.9998	0.0306	$y = 1.00x - 0.139$
Water–ethanol (30%, v/v)	0.9993	0.1077	$y = 1.00x - 0.128$
Water–ethanol (35%, v/v)	0.9995	0.0895	$y = 0.999x + 0.0559$
Water–ethanol (40%, v/v)	0.9995	0.0929	$y = 1.00x - 0.0584$
Water–ethanol (45%, v/v)	0.9997	0.0678	$y = 1.00x - 0.0069$
Water–ethanol (50%, v/v)	0.9998	0.0637	$y = 1.01x - 0.301$
Water–ethanol (60%, v/v)	0.9995	0.0955	$y = 1.00x - 0.156$
Water–ethanol (70%, v/v)	0.9997	0.0736	$y = 1.00x - 0.0221$
Water–ethanol (80%, v/v)	0.9996	0.0766	$y = 1.00x - 0.0012$
Water–ethanol (90%, v/v)	0.9995	0.0867	$y = 0.996x + 0.124$
Water–ethanol (95%, v/v)	0.9990	0.1277	$y = 1.00x - 0.129$
Water–ethanol (96%, v/v)	0.9996	0.0824	$y = 1.00x - 0.0842$
Water–ethanol (96.5%, v/v)	0.9979	0.1865	$y = 1.00x - 0.149$
Water–ethanol (97%, v/v)	0.9989	0.1395	$y = 1.01x - 0.289$
Water–ethanol (98%, v/v)	0.9992	0.1200	$y = 1.01x - 0.326$
Water–ethanol (99%, v/v)	0.9992	0.1147	$y = 1.01x - 0.185$
Ethanol–carbonated drink (96.5%, v/v)	0.9992	0.1179	$y = 1.01x - 0.253$
Alcohol liquor (1)	0.9995	0.0894	$y = 1.00x - 0.0731$
Alcohol liquor (2)	0.9995	0.0953	$y = 1.00x - 0.143$
Alcohol liquor (3)	0.9998	0.0506	$y = 1.00x - 0.0126$
Alcohol liquor (4)	0.9995	0.0965	$y = 0.995x + 0.186$

[a] y is the predicted temperature and x is the measured temperature.

At first, the relationship between the predicted and measured temperature of pure water was studied by using 10 spectra measured at different temperatures in the range of 31–40 °C. The results are listed in the first line of Table 1. In the calculation, the wavenumber region 6136–5500 cm^{-1} was selected according to the model of ethanol aqueous solutions in our previous work [24], and three latent variables were used for the PLS model. A very good linearity was found between the predicted and measured temperature. The correlation coefficient (R) is as high as 0.9996, and the root mean square error of the cross validation (RMSECV) is only 0.0795. This result indicates that the quantitative relationship between temperature and NIR spectra still exists in the temperature range 31–40 °C, and can be modeled by PLS regression.

The same experiments and calculations were performed for the twenty-three aqueous ethanol solutions (1%, 2%, 3%, 3.5%, 4%, 5%, 10%, 20%, 30%, 35%, 40%, 45%, 50%, 60%, 70%, 80%, 90%, 95%, 96%, 96.5%, 97%, 98% and 99%, v/v), the prepared ethanol-carbonated drink mixture (96.5%, v/v) and the four Chinese alcohol liquor samples, respectively. The results of cross validation are summarized in Table 1 from line 2 to 29. It is clear that the quality of the QSTR models is almost the same as that of the pure water. All the correlation coefficients (R) are above 0.99. It can be, therefore, concluded that QSTR model can be achieved for multicomponent mixture samples. The method provides a new and convenient way to predict temperature of mixture solutions by NIR spectroscopy.

3.2. Linear calibration curves

For quantitative determination of the compositions in a mixture, a calibration curve was achieved in our previous study, which was established by a linear fitting of the bias in the relationship between the measured and predicted temperatures of a mixture with different concentration [24]. The calibration curve has been

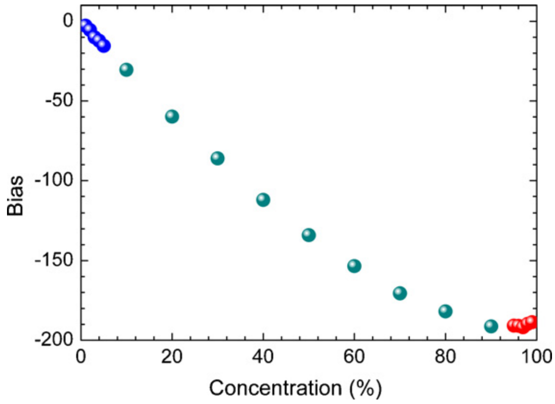

Fig. 1. Relationship of ethanol concentration from 1% to 99% (v/v) and the bias in the relationship of the measured and predicted temperature.

proven workable in the temperature range 25–60 °C and the concentration range 5–80% (v/v) for aqueous ethanol solutions. In order to investigate the applicability of the method, calibration curves in temperature range 31–40 °C and concentration range 1–99% was investigated.

Fig. 1 shows the relationship of ethanol concentration and the bias in the relationship between the measured temperatures and the predicted ones by the QSTR model of pure water. In the calculations, 10 spectra measured at different temperatures from 31 to 40 °C was used, and the wavenumber region 6136-5500 cm^{-1} was used as in our previous work [24]. Each point in the figure corresponds to an aqueous ethanol solution of 1%, 2%, 3%, 4%, 5%, 10%, 20%, 30%, 40%, 50%, 60%, 70%, 80%, 90%, 95%, 96%, 97%, 98% and 99% (v/v), respectively. From Fig. 1 it can be seen that it is difficult to obtain a calibration curve for the concentration from 1% to 99% (v/v) by linear regression because the linearity in the range of 1–5% is not so good and an obvious curvature can be found in the high concentration range.

In order to analyze the origin of the curvature, Fig. 2 was plotted displaying the measured spectra of some samples with different ethanol contents and their derivatives. The latter was calculated by CWTAD and used in the modeling. There are clearly two spectra bands relating the O–H and C–H groups. The former one is a broad peak locating in the regions below 7800 cm^{-1}, and the latter one is located in the region of 6050–5500 cm^{-1}, respectively. With the increase of the concentration, the O–H band drops clearly and the C–H band vice versa. Therefore, the curvature in Fig. 1 may be explained by two variation factors that govern the calibration curve. One is the effect of ethanol on the spectral information of water at low concentration, and the other is the effect of water on that of ethanol at high concentration.

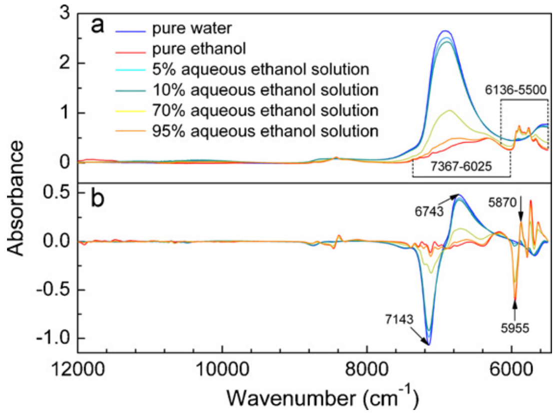

Fig. 2. NIR spectra (a) and derivatives (b) of water, ethanol and aqueous ethanol solutions (5%, 10%, 70% and 95%, v/v) at 36 °C.

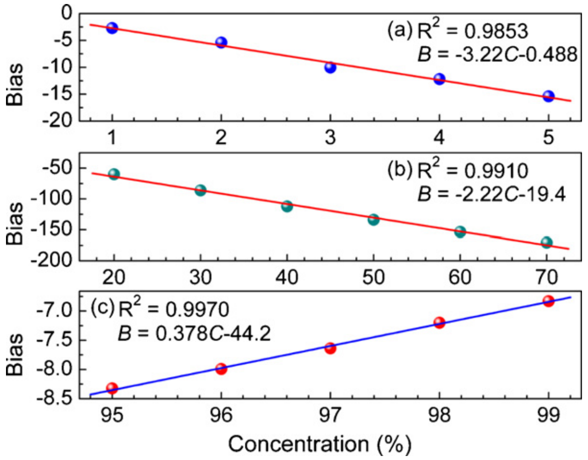

Fig. 3. Linear calibration curves in the concentration range of 1–5% (a), 20–70% (b) and 95–99% (c).

According to the assumption, it should be better to establish calibration curves in different concentration ranges by using the spectral information of different spectral bands. Considering the concentrations of the real samples studied in this work, calibration curves for three concentration ranges (1–5%, 20–70% and 95–99%, v/v) were established, respectively. The variation of the bias with concentration in the three ranges was plotted in Fig. 3(a), (b) and (c), respectively. The optimized spectral bands used for the three models are 6136–5500 cm^{-1} for 1–5% and 20–70% (v/v), and 7367–6025 cm^{-1} for 95–99% (v/v). Clearly, very good linearities were obtained. The coefficients of determination (R^2) of linear regression are as high as 0.9853, 0.9910 and 0.9970, respectively.

3.3. Nonlinear calibration curves

Using nonlinear calibration curve may be a better way to model the relationship between the bias and concentration. Therefore, nonlinear curve fitting was performed and calibration curves for ethanol in aqueous solution of the three concentration ranges (1–5%, 20–70% and 95–99%, v/v) were shown in Fig. 4 (a), (b) and (c), respectively. It is can be seen that the curves in Fig. 4(a) and (c) are approximately straight lines. The coefficients of determination R^2 are 0.9801 and 0.9955, which are also very near to that by linear fit-

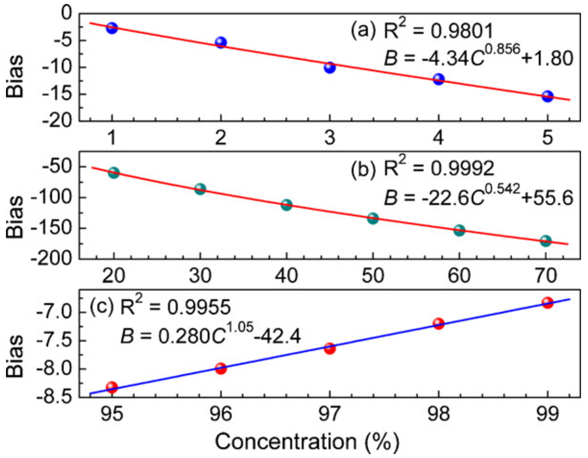

Fig. 4. Nonlinear calibration curves in the concentration range of 1–5% (a), 20–70% (b) and 95–99% (c).

Table 2
Quantitative results obtained with 10 spectra at different temperatures from 31 to 40 °C.

No.	Sample	Reference value (%)	Linear calibration curve		Nonlinear calibration curve	
			Predicted value (%)	Recovery (%)	Predicted value (%)	Recovery (%)
1	Water–ethanol mixture	3.50	3.54	101.1	3.51	100.3
2	Water–ethanol mixture	35.00	36.13	103.2	34.98	99.9
3	Water–ethanol mixture	45.00	46.57	103.5	45.23	100.5
4	Water–ethanol mixture	96.50	96.02	99.5	97.97	101.5
5	Ethanol–carbonated drink mixture	96.50	96.59	100.1	98.54	102.1
6	Alcohol liquor (1)	35.43	36.40	102.7	35.23	99.4
7	Alcohol liquor (2)	45.50	45.84	100.7	44.47	97.7
8	Alcohol liquor (3)	56.17	55.79	99.3	55.27	98.4
9	Alcohol liquor (4)	62.31	60.39	96.9	60.62	97.3

Table 3
Quantitative results obtained with the two spectra measured at 35 and 37 °C.

No.	Sample	Reference value (%)	Linear calibration curve		Nonlinear calibration curve	
			Predicted value (%)	Recovery (%)	Predicted value (%)	Recovery (%)
1	Water–ethanol mixture	3.50	3.37	96.3	3.34	95.4
2	Water–ethanol mixture	35.00	35.49	101.4	34.40	98.3
3	Water–ethanol mixture	45.00	46.72	103.8	45.38	100.8
4	Water–ethanol mixture	96.50	98.34	101.9	100.33	104.0
5	Ethanol–carbonated drink mixture	96.50	97.24	100.8	99.21	102.8
6	Alcohol liquor (1)	35.43	35.73	100.8	34.62	97.7
7	Alcohol liquor (2)	45.50	45.00	98.9	43.62	95.9
8	Alcohol liquor (3)	56.17	55.89	99.5	55.38	98.6
9	Alcohol liquor (4)	62.31	59.58	95.6	59.67	95.8

ting. However, the coefficient of determination R^2 for the nonlinear curve in Fig. 4 (b) is found to be 0.9992, which is better than that by linear fitting. The results indicate that non-linear calibration curves may be necessary when concentration range is large, but there is no obvious difference between the linear and non-linear curves in Figs. 3 and 4.

3.4. Validation of the calibration curves

To validate the calibration curves for the quantitative determination of the ethanol concentration, four prepared ethanol solutions with water (3.5%, 35%, 45%, 96.5%, v/v), one prepared ethanol solution with carbonated drink (96.5%, v/v) and four Chinese alcohol liquors were used. At first, NIR spectra of the samples were measured at 10 different temperatures in the range 31–40 °C. Then the predicted temperatures were calculated by the QSTR model of the pure water, and the bias can be obtained by linear regression of the measured and predicted temperatures. Taking the value of the bias as the input of the calibration curves, concentrations of ethanol in the samples can be predicted. The predicted results by the linear and nonlinear calibration curves are listed in Table 2. The reference value in the table was measured by gas chromatography, and the values are the average of three measurements. It can be seen that the recoveries are between 96.9% and 103.5% with the linear calibration curve, and between 97.3% and 102.1% with the nonlinear calibration curve. Therefore, both the calibration curves can produce reliable predictions. Although the results obtained by the nonlinear calibration curve are slightly better than that by the linear calibration curve, it is hard to show which curve is better because errors also exist in the reference values.

To simplify the method for quantitative determination, further investigation of the calibration curves using less number of spectra was performed. In the calculation, the bias was calculated by using only two spectra measured at 35 and 37 °C. The results are displayed in Table 3. It can be seen that the recoveries are between 95.6% and 103.8% with the linear calibration curve and between 95.4% and 104.0% with the nonlinear calibration curve. Obviously the results are comparable with that listed in Table 2. Therefore, once a calibration curve is established, two spectra at different temperatures are enough to obtain a reliable prediction. This may make the method more promising for the practical uses.

4. Conclusion

Quantitative determination by temperature dependent NIR spectra was investigated taking of the ethanol solutions and alcohol liquor samples as examples. The validity of QSTR model was proven for water, aqueous ethanol solutions and alcohol liquors in the temperature range from 31 to 40 °C. For quantitative determination, calibration curves of different concentration ranges built by using different spectral regions were found to be more effective. With the segmented calibration curves, all the samples of the synthetic and real alcoholic liquor samples were satisfactorily quantified. Furthermore, calibration curves obtained by both linear regression and nonlinear curve fitting were proven to be workable for quantitative determination, the former is simple and the latter is reliable when concentration range is large. The practicability of the method was also proven by quantitative prediction using only two spectra measured at 35 and 37 °C. Therefore, the temperature dependent NIR spectra may be a new alternative for temperature measurements and quantitative determination, although further validation on the universality and practicability of the method for various complex samples is still needed.

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