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"Strengthening Food and Feed Security and Energy Sustainability to Enhance Competitiveness"

DEPARTEMENT OF AGRICULTURAL ENGINEERING FACULTY OF AGRICULTURE UNIVERSITY OF LAMPUNG

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L-ASCORBIC ACID DETERMINATION USING FTIR-ATR TERAHERTZ SPECTROSCOPY COMBINED WITH PLS2 REGRESSION

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ABSTRACT

In this research, an explicit method of linear correction for temperature compensation was conducted for L-AA determination using Fourier transform infrared-attenuated total reflectance terahertz (FTIR-ATR THz) spectroscopy. The explicit method was done by direct inclusion of temperature as y-variable in the PLS2 regression. The result showed that using explicit method the quality of the developed calibration model for L-AA determination is a little bit superior with RMSECV=1.387% (w/w) and SDR_{cv}= 4.311. The performance of the PLS2 calibration model for L-AA determination with temperature compensation was quite good and able to predict the L-AA in three different temperatures with relatively high R^2_{pred} values. All prediction also resulted in low bias and SEP values.

Keywords : PLS2 regression, explicit method, global calibration model, FTIR-ATR terahertz spectroscopy, temperature compensation.

I. INTRODUCTION

In the previous reported study [1], it has been discussed the use of implicit method to compensate the influence of temperatures on L-AA determination by developing a global calibration model instead of using local calibration model. Global calibration models try to include implicitly the variation due to external effects such as temperature variations of the samples in the model, in much the same way as unknown chemical interferents can be included in an inverse calibration model. As long as the interfering variation is present in the calibration set, an inverse calibration model can, in the ideal case of additivity and linearity, easily correct for the variation due to the unknown interferents. It is assumed in global calibration models that the new sources of spectral variation can be modeled by including a limited number of additional PLS factors (resulted in more complex model) [2], [3].

In this present study, another way to compensate the influence of temperatures on L-AA determination will be presented. In this method, we add directly the temperatures as predicted variable results in an X block containing only the THz spectra and a Y block containing the temperature and L-AA. This method was called as an explicit method of temperature compensation [4], [5]. The explicit inclusion of the temperature into the calibration model is expected to improve the accuracy of L-AA determination. In this study explicit inclusion of the temperature is done by direct inclusion in the calibration models.

II. MATERIALS AND METHODS

A. Samples

55 samples of L-AA solutions at three different temperatures (22, 31 and 40°C) were used as samples. The samples were divided into two groups, calibration and validation as well as prediction sample set. The preparation of L-AA solution was as explained in previous study [1]. Table 1 shows the characteristic of the two sample sets in detail.

B. THz spectral acquisition

The THz spectral data of L-AA solution were acquired using an FTIR-ATR-THz based spectrometer equipped with a temperature controller (FARIS-1S, JASCO Co., Tokyo, Japan) (See reference [1] for detail).

Prediction items	Characteristics of samples	Calibration and Validation Set	Prediction Set
	Samples	105	51
T A A	Range	1.4414 ~ 21.3150	2.5586 ~ 21.2575
L-AA	Mean	11.53432	11.81985
	S.D	5.980041	5.855108
	Samples	105	51
Townshing	Range	22.1~ 41.9	22.1 ~ 41.9
Temperature	Mean	31.54858	31.61961
	S.D	7.522661	7.452087

Table 1. Characteristics of samples set used for developing calibration and validation model and for prediction of L-AA and temperature determination in 22, 31 and 40°C

L-AA is expressed as %(mass/mass). Temperature is expressed as degree Celsius (°C).

C. Temperature as Y variable in PLS2

Adding the temperature as predicted variable results in an X block containing only the spectra and a Y block containing the temperature and L-AA concentration (See Fig. 1). The simultaneous prediction of the y variable and the temperature is seen as a way to enable the model to identify the spectral regions which are temperature dependent. This is in line with inverse calibration, where the underlying variables causing the variation in the spectra are collected in the Y block. In this case the temperature is also causing variation in the spectra. Note that the temperature of the unknown sample does not have to be known; it will be predicted from the spectrum. The calibration method used is PLS2, where the suffix "2" indicates that there is more than one variable in the Y block. PLS2 uses the fact that there is correlation in the Y block or between the dependent variables (between L-AA and temperature). PLS2 might give poor results if this correlation is not present in the dataset [6].



Fig. 1. PLS2 on determination of L-AA and temperature.

The calibration model was evaluated based on the following parameter: number of PLS factors, coefficient of determination (R^2_{cal}), the RMSECV, and the standard deviation ratio (SDR) of calibration (SDR_{cv}). To evaluate the prediction performance of the developed calibration model, the following parameters were used: the coefficient of determination in prediction (R^2_{pred}), the root mean square error of prediction (RMSEP), bias between the actual and predicted value, the bias-corrected standard error of prediction (SEP) and the standard deviation ratio (SDR) of prediction (SDR_{pred}).

III. RESULTS AND DISCUSSION

A. Influence of temperature on the L-AA spectra

To show the influence of temperature on L-AA spectra data, a plot of PCA result was demonstrated. Fig. 2 shows the score of PC1 and PC2 of the result of PCA on spectra dataset. Here, PC1 and PC2 in total could be able to explain more than 95% of the variation on the L-AA spectral data. From Fig. 2, the temperature effect on the spectra can clearly be seen.





Using PLS2, a calibration model for L-AA determination and temperature were developed on Savitzky-Golay smoothing spectra (with 9 segments). It has to be noted that in block Y, there are two variables (L-AA and temperature) which has different scale. For this reason, before developing calibration model, the two variables were scaled by dividing the variables with its standard deviations (S.D).

To determine the optimal number of PLS factors, the values of RMSECV was used. The lowest RMSECV was corresponding with the optimal PLS factor. Fig. 3 shows the plot of RMSECV and PLS factor for L-AA and Fig. 4 shows the plot of RMSECV and PLS factor for temperature calibration model. It can be seen that for L-AA determination the optimal PLS factor was 5 while for temperature determination the optimal PLS factor was 4.



Fig. 3. Plot of PLS factors versus RMSECV for determination of L-AA.



Fig. 4. Plot of PLS factors versus RMSECV for determination of temperature.

Fig. 5 shows the scatter plot of actual and predicted L-AA using 5 PLS factor for calibration and validation, respectively. The calibration resulted in high coefficient of determination (R^2_{cal} =0.954). Low RMSECV could be obtained and it therefore resulted in high SDR_{cv} value. Using implicit method, the best calibration model for L-AA determination using combination of three different temperature (22, 31 and 40°C) resulted in RMSECV=1.3890 and SDR_{cv}= 4.305 (See reference [1]). Recent result using explicit method shows that the quality of the developed calibration model for L-AA determination is a little bit superior with RMSECV=1.387112 and SDR_{cv}= 4.311.



Fig. 5. Scatter plot between actual and predicted L-AA for calibration and validation using PLS2 regression method



Fig. 6. Scatter plot between actual and predicted temperature for calibration and validation using PLS2 regression method

C. Prediction of L-AA and temperature

Using the developed calibration model, a prediction for L-AA and temperature was done using combined prediction sample set (51 samples). Fig. 7 shows the scatter plot of actual and predicted L-AA in the prediction result. We can see here that both SEP and bias was low. It can be seen that using PLS2 we could succeeded to compensate the influence of temperature variations on L-AA determination.

In order to compare the prediction performance of temperature correction using PLS2 in this present study and that of using PLS1 in previous reported study [1], the prediction using PLS2 was also done independently for each sample temperature (22, 31 and 40°C). The results were shown in Table 2.



Fig. 7. Scatter plot between actual and predicted L-AA for prediction using PLS2 regression method.

The performance of the PLS2 calibration model for L-AA determination with temperature compensation was quite good and able to predict the L-AA in three different temperatures with relatively high R^{2}_{pred} values. All predictions also resulted in low bias and SEP values.

Table 3 shows the comparison between implicit (as explained in detail in reference [1]) and explicit method (in this present study) for linear correction of temperature influence on L-AA determination using FTIR-ATR THz spectroscopy. Here, we compared the prediction performance of implicit and explicit method for linear correction of temperatures in the term of RMSEP (%) and SDR_{pred} values.

Table 2. The performance of the PLS2 calibration model with temperature compensation for L-AA prediction using uncombined prediction sample set using the best calibration model of Savitzky-Golay smoothing spectra in

the range 20-450 cm ⁻¹ .							
Calibration model	Prediction Sample Set Temperature	R^{2}_{pred}	SEP	Bias	RMSEP	SDR _{pred}	
22,31 and 40°C	22°C	0.955	1.271	0.119	1.239	4.822	
Global calibration	31°C	0.906	1.861	0.709	1.940	3.081	
with inclusion temperature (PLS2)	40°C	0.957	1.244	- 0.051	1.208	4.945	

	Prediction results						
Temperature inclusion methods	RMSEP (%)			SDR _{pred}			
	22°C	31°C	40°C	22°C 31°C	40°C		
Global model using implicit methods (no temperature inclusion)							
Combined 2 temperature (22 and 31 °C)	1.310	1.858	1.408	4.562 3.216	4.244		
Combined 2 temperature (31 and 40°C)	1.216	1.908	1.262	4.914 3.132	4.735		
Combined 2 temperature (22 and 40°C)	1.234	2.011	1.152	4.843 2.972	5.187		
Combined 3 temperature (22, 31 and 40°C)	1.240	1.940	1.209	4.820 3.080	4.942		
Global model using explicit method							
Temperature as y-variable using PLS2	1.239	1.940	1.208	4.822 3.081	4.945		

Table 3. Effect of different temperature inclusion methods on the prediction of the L-AA determination using FTIR-ATR THz spectroscopy at temperature 22, 31 and 40°C.



Fig. 8. Scatter plot between actual and predicted temperature for prediction using PLS2 regression method.

For the explicit temperature inclusion techniques using PLS2 the prediction results were comparable to those for the global temperature calibration model (implicit method using PLS1) (in term of RMSEP and SDR_{pred}) (See Table 3). In the previous report, Peirs *et al.* [5] also showed the similar result.

The prediction result for temperature was also acceptable with high coefficient of determination (R^{2}_{pred} = 0.981) (See Fig. 8). The RMSEP = 1.053 was also quite low and hence resulted in high SDR_{pred} value (SDR_{pred}= 7.079).

IV. CONCLUSION

To summarize, it has been presented in this present study, a potential use of explicit method using PLS2 for L-AA determination with temperature compensation using FTIR-ATR THz spectroscopy. It was shown that using explicit method the quality of the developed calibration model for L-AA determination is a little bit superior with RMSECV=1.387112 and SDR_{cv}= 4.311. The performance of the PLS2 calibration model for L-AA determination with temperature compensation was quite good and able to predict the L-AA in three different temperatures with relatively high R^2_{pred} values. All prediction also resulted in low bias and SEP values. It can be concluded that linear correction of for fluctuation of temperature in L-AA determination using FTIR-ATR THz spectroscopy can be constructed using a direct inclusion techniques in which temperature was as y-variable in PLS2 regression method. The comparable result of PLS2 in which the two dependent variables of L-AA and temperature simultaneously predicted proved that there is a strong correlation between L-AA and temperature [7].

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REFERENCES

[1] M. Yulia, D. Suhandy, N. Kondo, and Y. Ogawa, "Investigation on the influence of temperature in l-ascorbic acid determination using FTIR-ATR terahertz spectroscopy: calibration model with temperature compensation," *Engineering in Agriculture Environment and Food*, vol. 7, pp. 148–154, 2014.

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- [2] F. Wülfert, W.T. Kok, and A.K. Smilde, "Influence of temperature on vibrational spectra and consequences for the predictive ability of multivariate models," Anal. Chem., vol. 70, pp. 1761-1767, 1998.
- H. Swierenga, F. Wülfert, O. E. de Nord, A. P. de Weijer, A.K. Smilde, and L. M. C. Buydens, "Development of robust calibration models in near infra-red spectrometric applications," *Anal. Chim. Acta*, vol. 411, pp.121–135, 2000. [3]
- F. Wülfert, W.T. Kok, O.E. de Nord, and A.K. Smilde, "Correction of temperature-induced spectral variation by continuous piecewise direct standardization," *Anal. Chem.*, vol. 72, pp. 1639–1644, 2000. [4]
- A. Peirs, N. Scheerlinck, and B. M. Nicolai, "Temperature compensation for near infrared reflectance measurement of apple [5] fruit soluble solids contents," Postharvest Biol. Technol., vol. 30, pp.233-248, 2003.
- [6]
- H. Martens, and T. Naes, "Multivariate Calibration," Wiley, Chichester, UK, 419 pp., 1998. A.M.K. Pedro, and M. M.C. Ferreira, "Simultaneously calibrating solids, sugars and acidity of tomato products using PLS2 [7] and NIR spectroscopy," Anal. Chim. Acta, vol. 595, pp. 221-227, 2007.