Tolerance of near infrared calibrations to temperature variations; a practical evaluation

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Introduction

In many industrial near infrared (NIR) applications, sample temperature can not be controlled precisely. In the case of in-line measurements, the sample temperature changes continuously with the process.[1] When at-line NIR is employed, measurements often rely solely on chemometric capabilities to overcome all sorts of perturbations. Among other things, the NIR procedures often neglect control of the sample temperature before scanning.

The effect of sample temperature on an NIR spectrum of pure compounds has been well described in the literature. Physical and chemical phenomena[2] have been proposed to explain the observed changes of overtone and combination bands. While absorptions characterising CH vibrations are mainly affected by density variations, absorptions characterising OH and NH groups also depend on both intra- and inter-molecular[3,4] associations. Spectral changes of a water spectrum related to hydrogen bonds have been studied in detail.[5,6] Absorption coefficients of OH overtones, characterising pure acids and alcohols, have been calculated as a function of temperature.[7–9]

Few papers, however, have investigated temperature effects on complex matrices: Calibration strategies to handle differences of 10°C have been tested for ternary mixtures of alcohols in water.[10] Works on aqueous samples have shown that variations smaller than 5°C lead to spectral modifications in the OH first overtone region[11,12] and hence lack of robustness of NIR models.[13]

The present paper aims to investigate the effect of small temperature variations (up to 5ºC) on NIR spectra, in order to optimise NIR modelling for temperature-sensitive applications. It addresses the complex matrices of process ester samples with only a residual level of water (below 1%). Transmittance NIR spectra have been recorded for the calibration and validation sets at different temperatures between 60 and 70ºC. After investigation of the observed spectral changes, partial least square (PLS1) models,[14] implicitly including temperature variance, have been made for hydroxyl (OH) number determination. Finally, the sensitivity of these NIR calibrations to temperature has been evaluated by the "Taguchi principle".[15]

Material and methods

The calibration set includes 12 process ester samples, collected from seven batches, over a period of six months. The six validation samples all originate from five recent batches. Their OH values have been determined using A.O.C.S. method Cd 13–60: 1993 in parallel with NIR scanning. Reference data obtained for the validation samples only span the lower side of the calibration set. In fact, since NIR is used to monitor advancement of the esterification, validity of NIR predictions is of special interest close to the end of the reaction. The matrix then consists mainly of the ester, with a small quantity of unreacted acid and alcohol and a residual level of water (lower than 1%).

The sampling accessory ("OHval", Bomem) allows the analysis of samples in disposable glass vials (8 mm external diameter, Phase Separations). Complete equilibration of the sample temperature is obtained after 10 min in a heated sample holder (controlled by a thermocouple at +/− 0.1°C). The sample temperature has been calibrated at each selected level (60–70°C), using an external temperature Pt-100 sensor. Filling each vial with 0.6 g (+/− 0.02 g) of the ester product ensures a precision for the sample temperature of +/− 0.2°C. In order to avoid any change of the sample mixture during the experiment, the vials have been closed by a crimped cap.

NIR spectra have been recorded using an FT-NIR (MB 160, Bomem) equipped with an InAs detector. Scanning (128 scans) covers the region from 10,000 to 4000 cm^{-1} (resolution of 16 cm^{-1}). A reference has been taken at each temperature.

Spectra have been exported to Unscrambler software (6.11b, Camo AS) and corrected for baseline drift (one point correction at 9119 cm^{-1}) before investigation.

Results and discussion

Influence of temperature changes on spectral data

OH analysis by NIR is based on the correlation between absorption intensities of OH-related bands and concentration of unreacted alcohol molecules. The regions of interest (OH first overtone, OH combinations) may, however, be affected by some uncontrolled factors. Since the influence on NIR spectra of small temperature variations is the object of this paper, changes in the temperature variable have been carefully designed. On the other hand, the measuring bloc used for this study also implies uncontrolled pathlength differences (between and/or within vials), which could result in significant spectral changes. To minimise this unwanted effect, three vials have been scanned for each sample.

The spectra recorded at five temperatures (60.2, 64.1 65.0, 65.7 and 70.1°C, +/− 2°C) have been overlaid in the range 1100 to 1660 nm (9119–6033 cm^{-1}). Figure 1 shows the spectral changes observed for a given vial ("Vial 10") filled with sample "Cal 4". The absorption intensity of the OH first overtone (maximum at ~ 1410 nm) clearly increases as the temperature increases. This observation holds for all samples characterised by a hydroxyl value higher than 15 mg KOH g^{-1}, but the relation between maximum intensity of the OH band and temperature is not immediately clear for the samples with a low hydroxyl value (for example, sample "Val 1").

Conversely, the CH second overtone range (maximum at ~ 1210 nm) shows an opposite trend. For all samples, the absorption intensity of the CH band decreases as the temperature increases. Figure 2
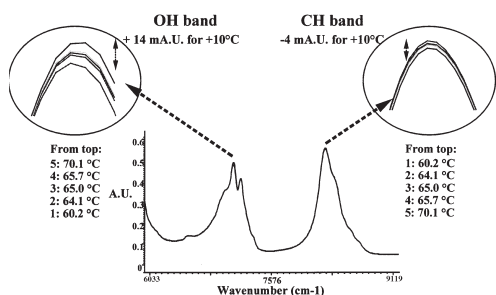

Figure 1. Spectral changes recorded for the "Vial 10" (sample "Cal 4"), when increasing the temperatures from 60 to 70°C.
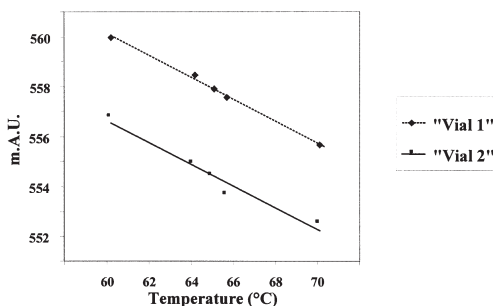
Figure 2. Relation between absorption intensity of the CH band at 8262 cm^{-1} and temperature for two vials filled with the same sample ("Val 1").

shows the correlation observed for two vials ("Vial 39" and "Vial 40") filled with the same sample "Val 1". This decrease in the absorption intensity observed for the CH band results, probably, from the density changes. Note that the computed gradient (around -0.5 mA U $(°C)^{-1}$ for the two vials, Figure 2) is of the same order as the offset between the slopes characterising the two selected vials, thus the spectral variations observed between vials.

The OH absorption intensity at 1410 nm has then simply been corrected for this density effect, dividing by the absorption intensity of the CH band at 1210 nm. It then shows a positive correlation with the temperature for all samples (including those with low hydroxyl values), indicating an increase in "H-bonding" free molecules (Figure 3). The gradient increases with both hydroxyl value and water content (from 0.5 to 3.5 mA U $(°C)^{-1}$), since the temperature effect is probably more pronounced as the concentration in alcohol and water increases. Evidence of other chemical changes (for example, hydrolysis) could not be found in the observed spectral changes.
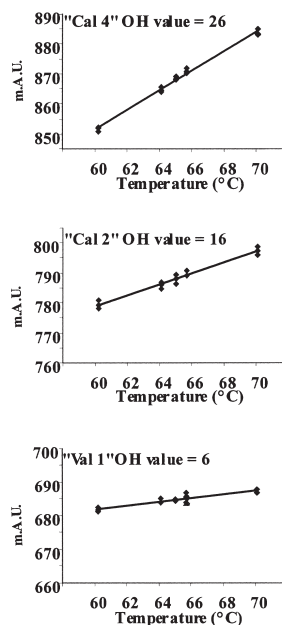

Figure 3. Relation between absorption intensity of the OH band at 7098 cm^{-1} (corrected for density changes) and temperature for three samples ("Cal 4", "Cal 2" and "Val 1").

Models including temperature variance

NIR models for OH predictions have been built on the OH first overtone range (1350–1505 nm), using the calibration set. The PLS1 approach[14] has been selected to ensure all relevant structure of the data matrix to be used, despite the systematic variations of the sample temperature introduced. All calibrations are based on 12 samples, each measured three times: in the first model M_1, three vials have been filled from each sample and all measurements have been carried out at 65.0°C (+/– 0.2°C). The next two models M_2 and M_3 include the temperature variation implicitly (respectively 65°C, +/– 1°C and +/– 10°C). A single vial has been used per sample and scanned once at three different temperatures. In the text below "PC" is used for "PLS factor".

These three models have at first been evaluated by cross-validation; each segment includes the three spectra recorded for one of the 12 samples. The correlation between spectral data and OH values is straightforward for all calibrations and the first PC describes most of the variations in the wet chemistry data. As expected, model M_1, made from spectra at 65.0°C (+/– 0.2°C), gives the lowest prediction error (*RMSEP* [CV, 1PC] = 1.19). Including some temperature variation reduces the predictive ability of the models. Nevertheless, the cross-validation did not reveal any real differences in the *RMSEP* of the two models M_2 and M_3 (1.53 and 1.58, respectively).

Evaluation of the model robustness to temperature

In order to further evaluate the sensitivity of these three models to temperature changes, validation samples have been scanned at seven different temperatures (60.2, 63.0, 64.1 65.0, 65.7, 66.8 and 70.1°C, +/– 0.2°C). Again, the effect of pathlength variations has been reduced by measuring each vial

Table 1. Evaluation of the PLS models.

Model name	Number of PLS factor (PCs)	Robustness calculation	
		Avg. *RMSEP*	S/N (*RMSEP*)
M_1	PC1	129	21
	PC2	135	25
M_2	PC2	1.44	33
	PC1	1.33	22
M_3	PC1	1.37	21
	PC2	1.41	30

at all temperatures. The OH values given by the three models have been computed for the six validation samples.

The prediction errors given by the three models for each temperature have been recorded. Figure 4 shows the *RMSEP* obtained when using two PCs. Based on these data, both average *RMSEP* and signal-to-noise ratio (S/N) can be calculated[15] and are summarised in Table 1. Robustness to the temperature variations can then be evaluated by the S/N. The values calculated for M_2 and M_3 with two PCs are higher than the one characterising the reference model M_1, based on spectra at 65ºC and one PC. Therefore, sensitivity to temperature clearly decreases when including implicitly some temperature variations in the calibration set.
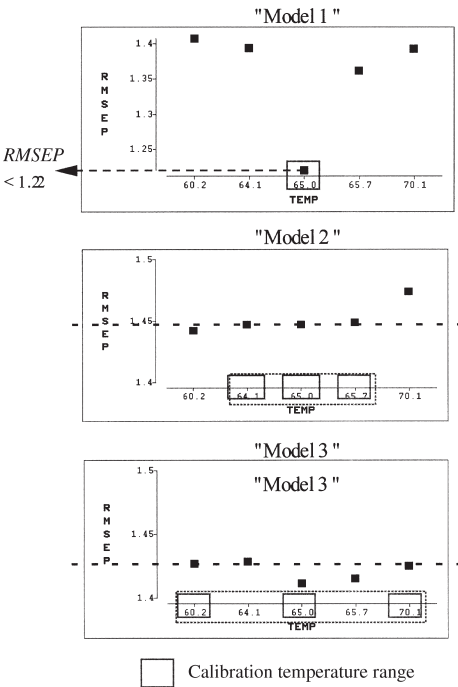
As expected, the lowest *RMSEP* is computed when using the model M_1 (made from spectra at 65ºC to predict OH values of the validation set at 65ºC, Figure 4). Note that this calibration also gives the lowest average *RMSEP* (Table 1). Therefore, a precise control of the temperature during both calibration and validation leads to the model with the best predictive ability. The gain in robustness to small temperature changes is achieved by a loss in precision in the predictions and the calibration strategy should be carefully adapted to the needs of each application. Finally, the comparison of the *RMSEP* values obtained for M_2 and M_3 at different temperatures (Figure 4) shows that the PLS algorithm can overcome the temperature variations, when these have been included in the model. Thus, the distribution of the sample temperature in the calibration set should to be optimised together with the temperature variance.

Figure 4: Effect of the sample temperature on the prediction error of the three test models (two PCs).

Conclusion

Process samples of esters containing a residual level of water have been submitted to small temperature variations around 65ºC (up to + 13ºC). The effects on NIR transmittance spectra and resulting hydroxyl predictions have been investigated. The following conclusions can be drawn:

1. small temperature variations around 65ºC mainly cause changes in H-bonding. For the samples collected at the end of the reaction, the resulting spectral variations in the NIR range remain in the same order as the density effect. However, they become significant with the complex matrices characterising the earlier samples. Since these spectral variations are not overcome by the common methods developed for correction of density changes, this may lead to higher prediction errors.

2. an accurate and precise control of the sample temperature prior to scanning leads to the lowest prediction error. Therefore, for temperature sensitive products, the validity of NIR analyses relies strongly on the temperature stabilisation procedure[16]

3. in the case of in-line measurements, the calibration strategy should be determined according to the variations in sample temperature expected in the future. The PLS algorithm can overcome the temperature variations, which have been included in the calibration set. However, a number of PLS factor and both temperature range and distribution have to be carefully optimised.

Acknowledgements:

References

1.   B.D. Mindel, *La rivista dei Combutibili* **49,** 467 (1995).
2.   J. Lin, C.W. Brown, W.C. McCabe, S. Subramanian and H.F. Fisher, *J. Phys. Chem.* **74,** 4360 (1970).
3.   F.O. Libnau, O.M. Kvallieim, A.A. Christy and J. Toft, *Vib. Spectrosc.* **7,** 243(1994).
4.   I. Noda, Y. Liu and Y. Ozaki, *Appl. Spectrosc.* **48,** 1095 (1994).
5.   H. Maeda; K. Buijs and G.R. Choppin, *J. Chem. Phys.* **39,** 2035.
6.   Y. Ozaki and Y. Wang *J. Near Infrared Spectrosc.* **6,** 19 (1998).
7.   M. Iwahashi, M. Suzuki, N. Hachiya, Y. Hayashi, K. Matsuzawa, Y Fujimoto and Y. Ozaki, *J. Phys. Chem.* **97,** 3129 (1993).
8.   M.A. Czarnecki, M. Czarnecka, Y. Ozaki and M. lwahashi, *Spectrochim. Acta* **5OA,** 1521 (1994).
9.   H. Maeda, Y. Wang, Y. Ozaki, M. Suzuki, M.A. Czarnecki and M. Iwahashi, *Chemometrics and Intelligent Laboratory Systems* **45,** 121 (1999).
10. F. Wulfert, W.T. Kok and A.K. Smilde, *Anal. Chem.* **70,** 1761 (1998).
11. J. Lin, *Appl, Spectrosc.* **52,** 1591 (1998).
12. R. Cinier and J. Guilment *J. Near Infrared Spectrosc.* **6,** 291 (1998).
13. K. Sumio, A. Hideyuki and M. Iwamoto *J. Near Infrared Spectrosc.* **3,** 211 (1995).
14. H. Martens and T. Næs, *Multivariate Calibrations.* John Wiley & Sons, Chichester, UK (1989).
15. V.A.L. Wortel and W.G. Hansen, in *Near Infrared Spectroscopy: The Future Waves,* Ed by A.M.C. Davies and P. Williams. NIR Publications, Chichester, UK, p. 306 (1996).
16. S.C.C. Wiedemann, W.G. Hansen, V.A.L. Wortel and L.W.J. Gielen *J. Near Infrared Spectrosc.* **5,** 149 (1997).