

Performance of a near infrared spectrometer equipped with an autosampling accessory

Nathalie Szydlowski-Zanier,^a François Wahl^b and C. López García^b

^a*Institut Français du Pétrole, 1 et 4 avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex, France*

^b*Institut Français du Pétrole, BP 3, 69390 Vernaison France*

Introduction

Fourier transform near infrared spectroscopy (FT-NIR) spectrometers using multivariate calibration for modelling are currently used for accurate and repeatable analysis in numerous applications^{1–7}. Several sampling configurations are possible in order to acquire the NIR spectra. Some of these configurations include fixed-pathlength cells and disposable vials for with variable pathlength⁹. Calibrated pathlength cells have the inconvenience of requiring time and solvent consuming. On the other hand, non calibrated pathlength cells in automated mode have the advantage of saving operating costs since this system avoids cleaning and cells filling steps. To use disposable vials successfully, normalised spectra must be used in order to eliminate pathlength variation effect that affects the NIR model predictability. The aim of this work is to compare the performance of single fixed-pathlength cell sampling with multiple disposable vial sampling using identical FTNIR spectrometers via modelling of cetane number and hydrogen weight percent in gasoil. The disposable vial samples were analysed automatically thanks to a so-called AutoSamplIR accessory in an *ex-situ* configuration.

Experimental

Spectrometers

Two Bomem MB160 FT-NIR spectrometers with nitrogen purge were used for spectra acquisition. These instruments will be noted as “master” and “slave”. Each spectrometer was equipped with a DTGS (deuterated triglycide sulfide) detector, operating in transmission mode with a resolution of 4 cm⁻¹.

On both instruments, each spectrum presents three groups of bands: the first one with the higher intensity in the 5500–6000 cm⁻¹ region, and the two others with similar intensities but approximately ten times lower than the first one in the 8500–8000 cm⁻¹ and 7500–7000 cm⁻¹ regions.

The “Master” Instrument

The spectrometer referred as the master instrument is equipped with a manual vial sampling accessory in the Arid Zone sample compartment that uses a vial with calibrated pathlength. The sample temperature is stabilised by Peltier effect. The Peltier cell holder has a slot where a 2 mm cell fits exactly. One of the copper sheets contains an aperture of 2 × 5 mm to minimise the beam divergence and to characterise better the field of view of the NIR beam.¹⁰ This aperture decreases

the signal to noise ratio by 20% with respect to open beam. The temperature at which the calibration is developed is $27.1 \pm 0.5^\circ\text{C}$. The spectrometer is installed in a room where the ambient temperature can vary from 20 to 30°C . All spectra were obtained with the same calibrated 2 ± 0.02 mm cell (QX quality). Spectra were recorded using the Bomem GRAMS32 software after a delay time of 5 min while purging with a dry nitrogen flow of 3 l min^{-1} . The reference spectrum was recorded with the empty cell in the holder. Each sample was analysed twice with 100 scans per spectrum and the average spectrum was used when the difference between the two recordings of the sample was less than 0.002 absorbance units (AU) in the range $6400\text{--}4500 \text{ cm}^{-1}$. The maximum absorbance in the $4900\text{--}9000 \text{ cm}^{-1}$ region is around 0.8 absorbance units; the repeatability of the signal is about 0.0005 AU at this level.

The "Slave" Instrument

The slave instrument has an AutoSamplIR accessory which consists of a linear actuator with up to 20 cm travel with a stepper motor programmed to step from sample to sample. The accessory has 20 positions for respective 20 vials. The position of the vials was set as follows: position 0 for an empty vial for background recording, Positions 1 and 2 are for cyclohexane analysis for validation of the data set and Positions 3 to 19 for the vials filled with eight different samples (two vials per sample). The temperature of the device containing the vials is controlled to $27.5 \pm 0.5^\circ\text{C}$ via Peltier effect and spectrometer optics stabilised at 40°C . The spectrometer is installed in industrial environment. Disposable vials characteristics are: borosilicate glass NMR cylindrical vials (5 mm outer diameter) from Kimble with a $4.0 \text{ mm} \pm 0.15 \text{ mm}$ internal pathlength. The maximum absorbance in the $4900\text{--}9000 \text{ cm}^{-1}$ region is around 1.7 absorbance units for the studied gasoils. The absorbance repeatability at this level is around 0.01 AU.

The NIR beam is controlled via a stationary Jacquinot stop before entering the sample vial. The objective is to control the spectral response, minimise the distribution of pathlength due to the curving walls of the vials and restrict the light such that the signal-to-noise ratio (reduced by 60–70%). The maximum wavenumber deviation between different positions of the multi-vial clip is around 0.05 cm^{-1} . The 20 vials can be filled automatically with a Microlab SD Sampling system from Hamilton. In order to compensate for the lower signal-to-noise due to the Jacquinot stop each spectrum was determined by 200 scans per acquisition. The slave instrument with autosampler operates unattended during the analysis of samples using the Bomem CAAP software configured for the task. This software controls the FTNIR scanning, runs the chemometrics with GRAMS PLSplus and increments the autosampler.

Methods

Standardization algorithm

The spectra of the calibration data base samples were all recorded on the "master" instrument; a standardization function is calculated in order to take into account the differences between the master and the slave instrument (instrumental differences, temperature of the sample etc.). The standardization [Eqn (1)] is a linear correction of the absorbance A_i applied at each wavenumber i :

$$A_{i \text{ after standardisation}} = SLOPE_i * A_i + OFFSET_i \quad (1)$$

The coefficients $SLOPE_i$ and $OFFSET_i$ are calculated by comparing the values of the absorbance at wavenumber i of well-selected spectra measured on both the slave and the master instruments. The corrections are only significant in a few narrow areas, around 6500, 7500 and 8500 cm^{-1} .

Normalisation

Each sample is recorded twice and the average of these two recordings is the spectrum for calibration. The resulting spectrum, S , is then baseline corrected: a linear regression of the spectral intensities against the wavenumbers is calculated in the 4900–9000 cm^{-1} spectral range and subsequently subtracted from the spectrum S .

Modelling

PLS1 regressions were adopted for modeling. The accuracy of the models was evaluated by the root mean square error (*RMSE*) of cross-validation by leave one out and external validation.

Data sets

Two data sets were used for this work. The first one for the modeling cetane number (gasoil samples) referring to ASTM D613 method. The second one for the modeling of the weight percent of hydrogen (wt% H) referring to an IFP method¹¹ based on NMR measurements. The cetane number data set contains 72 samples including kerosene, atmospheric and heavy atmospheric gasoil samples from different origins and refining processes. The CN values are in the range 20 to 65. Figure 1 represents the projections of the samples on the two first components of the PLS model of the cetane number data set.

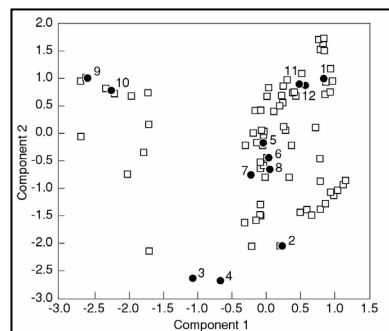


Figure 1. Projections of the 2 first components of the PCA in the CN model.

Results

The characteristics (clusters, *RMSE*, number of factors) of the NIR models of both slave and master instruments are listed in Table 1. The spectral range for calibration is between 4900 and 9000 cm^{-1} for both models. All the spectra of the calibration database were obtained with the master instrument only. The standardisation function was applied on the latter to evaluate the characteristics of the models on the slave instrument. The characteristics of the models are the same on the master and on the slave instruments. That means that the normalisation and the standardisation do not affect the performance of the models.

Table 1. Characteristics of NIR models for “master” and “slave” spectrometers.

| | Cluster | spectrometer | RMSE | # factors |
|-------|---------|--------------|-------|-----------|
| wt% H | 1 | master | 0.043 | 6 |
| | 2 | slave | 0.047 | |
| wt% H | 1 | master | 0.023 | 4 |
| | 2 | slave | 0.026 | |
| CN | — | master | 1.8 | 5 |
| | | slave | 1.8 | |

The agreement between reference values and the data derived from the master instrument was evaluated by external validation with 31 samples for the wt% H model and 140 samples for the CN model.

Figure 2 shows CN and wt% hydrogen prediction versus experimental values for calibration set and external validation. Two sets of lines appear on Figure 1(b) since the interval of confidence is

referred to the ASTM statistic values in the 42–57 CN range and also to an IFP Round Robin test evaluated in the 20–65 CN range. Both figures show that the NIR predicted values are within the 95% confidence interval ($CI = \pm 2\sigma_R$) of the reference method when the analysis is made once. Since the characteristics of the master and slave models are equivalent, confidence interval master results were assumed to be the same for the slave instrument.

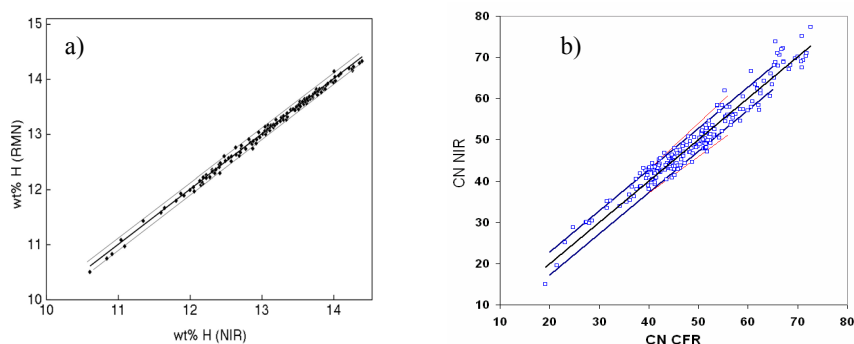


Figure 2. Parity plot of NIR predictions versus experimental values; a) wt% H, b) CN

Time dependent reproducibility of master model predictions has been determined analysing 5 years along a sample issued from hydrotreating of a Middle East feed. For the slave model, this parameter was obtained by analysis over a period of 1 month. Table 2 summarises the characteristics of reproducibility for both models compared to the reference methods. For both properties the standard errors of reproducibility of models are better than those of the reference methods.

Table 2. Standard errors of reproducibility of reference methods and NIR (“master” and “slave”) model predictions.

| Petrochemical analysis | σ_R | intra-lab reproducibility σ_R | |
|------------------------|------------------|--------------------------------------|-------------------------|
| | Reference method | Master model predictions | Slave model predictions |
| wt% H | 0.04 | 0.01 | 0.02 |
| CN | 1.4 | 0.04 | 0.16 |

Analysis of performance of the slave instrument models

A loss of performance was observed when analysing by duplicate the same sample with one-day interval on the slave instrument (without moving or refilling the vial). Analyses were carried out in order to understand these phenomena. Table 3 illustrates results of two examples.

Table 3. NIR predictions on the “slave” instrument of different samples in 2 consecutive days.

| Sample | Vial position | CN | | wt% H | |
|----------|---------------|-------|-------|-------|-------|
| | | day 1 | day 2 | day 1 | day 2 |
| Sample 1 | 3 | 61.17 | 61.42 | 14.38 | 14.38 |
| | 4 | 61.37 | 61.37 | 14.42 | 14.36 |
| Sample 2 | 13 | 40.97 | 41.43 | 12.80 | 12.77 |
| | 14 | 41.09 | 41.33 | 12.80 | 12.79 |

Comparing the same sample in the same vial analysed different days, several behaviours were identified. For Sample 1 in Position 3 only the wt% H predictions were in the $2\sigma_R$ range of the master model and CN prediction varied more than $2\sigma_R$ of the reference method. The opposite is observed for Sample 1 in Position 4 since CN predictions were stable but not the wt% H prediction.

For Sample 2 position 14, CN is not stable while wt% H is acceptable. In some other cases, like Sample 2 Position 13, both properties were not stable between the two days; the cetane number prediction was always greater for day2 than for day1. When not stable between the two days, the wt% H was either higher or lower.

The spectrum from day1 and day2 were subtracted for both samples as illustrated in Figure 2. It was observed that the temperature of the samples is stable since the shape of the difference spectra would look more similar to the spectrum of a sample. The difference spectra for Sample 1, Position 4 (a) shows mainly that there is a baseline instability (see the slope of the baseline) so a lack of repeatability in the region of high absorbance (i.e around $5700\text{--}5900\text{ cm}^{-1}$). For Sample 2, Position 14, it is observed that there is a reduced signal to noise ratio for the slave instrument and that there are variations in the quality of the purge (see the typical vibration–rotation bands of water in the regions $7000\text{--}7500\text{ cm}^{-1}$).

A difference spectrum of 0.007 absorbance unit in the $5700\text{--}5900\text{ cm}^{-1}$ region affects the wt% H by 0.03. It appears that there is a linear relation between the lack of repeatability and the shift of the prediction. NIR models were developed in the $6000\text{--}9000\text{ cm}^{-1}$ to avoid this problem but their performance was not improved. The stability of the purge affects mainly the prediction of the cetane number.

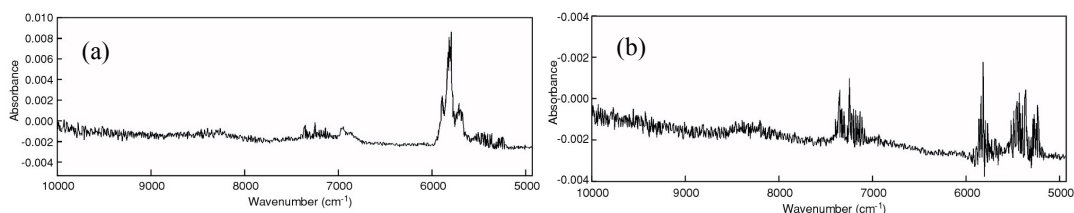


Figure 3. Difference of day1 and day 2 spectrum; (a) Sample 1, position 4 (b) Sample 2, Position 14.

Conclusions

The performance between two equivalent FT-NIR spectrometers with different sampling systems was evaluated referred as master and slave instrument. The master instrument had a single and defined pathlength while the slave is equipped with an auto SamplIR accessory and variable pathlength. NIR models for cetane number and hydrogen weight percent were developed in the master instrument and then transferred to the slave instrument. For both properties the confidence interval from models was always better than those from reference methods. However, a loss of the reproducibility of the predictions of the slave instrument was detected. These instabilities were due neither to temperature instability of the sample nor instrumental (shift of the NIR beam, lack of the positioning of the AutoSamplIR) nor to the transfer function.

Model for CN prediction was mainly affected by the purge instability which induces presence of water vapor bands. On the other hand a lack of repeatability at absorbance level of 1.7 affects the prediction of the wt% H.

The use of inexpensive and disposable vials represents a good compromise between *ex situ* and on-line FTNIR analysis. The amount of necessary samples is very small as the cleaning is no longer necessary and as the cell diameter is small. It allows a quick answer from the lab without requiring highly qualified technicians.

References

1. M.C. R. Symons, *Cell.Mol.Life Sci.*, **57(7)**, 999 (2000).
2. C. Solberg and G. Frediksen, *J. Near Infrared Spectrosc.*, **9(3)**, 221 (2001).
3. M.S. Sanchez, E. Bertran, L.A. Sarabia, M.C. Ortiz, M. Blanco and J. Coello, *Chemo. Intell. Lab. Syst.*, **53(1-2)**, 69 (2000).
4. L. Velasco and C. Molles, *Commun. Soil Sci. Plant Anal.*, **31(19 and 20)**, 2987 (2000).
5. M. Lanzendorfer, H. Schmalz, V. Abetz and A.H.E. Muller, *Polym. Prepr.*, **42(1)** 329 (2001)
6. J. Laska and J. Niziol, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A*, **353**, 561 (2000)
7. M. Blanco, S. MasPOCH, I. Villarroya, X. Peralta, J.M. Gonzalez and J. Torres, *Anal.Chim. Acta* **434(1)**, 133 (2001)
8. A. Espinosa, D. Lambert and M. Valleur, *Hydrocarbon Processing*, 86–92 (1995)
9. L.J. Burge, R.E. Cooley, D.L. Ellis and R.W. Roller, *At-Process.*, **5(1,2)** (2000)
10. U. Hoffmann, N. Zanier-Szydlowski, *Journal of Near Infrared Spectroscopy*, **7**, 33–45 (1999).
11. S. Gautier, A. Quignard, *Revue de l'Institut Français du Pétrole*, **50**, 2 (1995).
12. Statistical Methods, ISO Standards, Handbook 3, International Organisation for Standardisation, 3rd ed. (1989).
13. International Organisation for Standardisation, ISO/DIS 5725, 1 to 3, Drafts Versions (1994).