Assessing the ability of a FT-NIR pre-calibrated instrument for prediction of chemical composition in Iberian pig meat

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Introduction

The use of Fourier transform (FT) in the analysis of near infrared (NIR) spectra had not been tried until 1981. Since the last decade, FT-NIR spectrometers are being used in pharmaceutical, petrochemical and chemical areas[1] and more recently are being also used for agro-food applications.[2–4]

FT-NIR spectrometers have been reported to have several advantages over dispersive spectrometers.[1] These include higher scanning speed, higher optical resolution without reduce signal-to-noise ratio and better wavelength accuracy and precision facilitating calibration transfer from one instrument to another.[1,5,6]

Some FT-NIR instruments are on the market pre-calibrated for different applications, which allows to get results from the first day avoiding the need to spend time to develop calibrations. Büchi Labortechnik AG has launched the NIRLab N-200 FT-NIR spectrometer which is pre-calibrated for the analysis of different food products such as meats from different types (pork, beef and veal).[7] A robust calibration for meat compositional analysis could be very useful for the meat industry. However, to develop a global calibration which can be of use for all types of meats and meat cuts is far from being an easy task.

The aim of this study is to evaluate fresh meat calibrations developed by Büchi Labortechnik AG for using with the NIRLab N-200 FT-NIR spectrometer for its ability to analyse fresh Iberian pig meat.

Material and methods

Experimental samples

Homogenised samples of Iberian pig meat were used in this study. These samples were being kept frozen and vacuum-packed in plastic bags. Previously to the NIR analysis samples were defrosted by placing them in individual plastic containers exposed to the room temperature.

The number of samples used for the evaluation of the precalibrated meat application and for the development of specific calibrations was 15 and 79, respectively.

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FT-NIR analysis and reference data

FT-NIR diffuse reflectance spectra of the samples were collected with a Büchi NIRLab N-200 FT-NIR spectrometer. Spectra were acquired working with the NIRLabWare programme, in the spectral range of 10000–4000 cm^{-1} (1000–2500 nm) and at 3.85696 cm^{-1} of resolution.

Two spectra were measured per sample and the mean spectrum was used for the development of the calibration equations.

Moisture, fat and protein contents of each sample were determined by AOAC International methods.[8]

Chemometric methods

NIR spectral and chemical data were managed by using the NIRCal Software, version 4.21.[9] Calibration equations were calculated automatically working with the Calibration Wizard option which allows to develop the calibrations on the basis of only a few specifications about the samples (substance type as liquid, paste…), analysis mode (reflectance probe, transflectance probe…), calibration type (quantitative or qualitative) and calibration behaviour (robust or as precise as possible). The software selects automatically the different combinations of data pretreatments, calibrations wavelengths and calibrations algorithms according to the information given above and calculates the possible calibrations[9]. The five best calibrations are kept in the project. The following statistical parameters were used to select the best calibration: Q-value, which is a measure of the quality of the calibration (Q = 0 useless calibration; Q = 1 ideal calibration), standard error of estimation (*SEE*), standard error of prediction (*SEP*), regression coefficient of the calibration set (C-Set *R*) and regression coefficient of the validation set (V-Set *R*).

Results and discussion

Evaluation of the meat application

The meat application developed by Büchi was first validated by using 15 samples of Iberian pig meat. When spectra of the 15 samples were taken, the meat application showed that, except for two samples, the Iberian pig samples did not match to the sample matrix in the calibration. These two ones were identified as similar to the sample matrix in the calibration for fat content only. However, reference values of the two samples mentioned above were not included in the interval (predicted value—2 × *SEP*, predicted value + 2 × *SEP*) for any of the three constituents. The *SEP* values obtained by Büchi for its meat application were 0.38, 0.21 and 0.56 for fat, protein and moisture contents, repectively.[7]

Only some of the samples which differed from the samples in the calibration were predicted correctly for some of the constituents, this happening more times in the case of prediction of the fat content than in the case of protein and moisture contents.

Some reasons could be argued to explain the inability of these equations to predict the Iberian pig samples. These reasons include differences in homogenisation rate, meat cuts, pig breeds and bias in reference and validation laboratory for the wet chemistry.

Development of a specific calibration

Specific calibration equations were obtained for the prediction of fat, protein and moisture content in homogenised Iberian pig meat.

The number of samples, means, ranges and standard deviations for the chemical constituents of the samples are shown in Table 1.

Table 1.Statistical parameters of the sample population. (* Calibration set / Validation set)

Constituent	*n**	Mean* (%)	Range* (%)	*SD**
Fat	60/15	5.94/6.14	2.8–13.4/2.9–10.3	2.43/2.19
Protein	64/15	23.27/23.42	20.6–26.1/21.8–25.0	1.16/0.96
Moisture	61/15	70.53/70.34	64.7–77.44/67.68–73.35	1.93/1.56

Pretreatments, calibration wavelength ranges and regression methods selected and also the statistics obtained for the calibration equations of each constituent are presented in Table 2.

Table 2. Statistics of calibration and validation for Iberian pig meat NIR equations.

	Fat	Protein	Moisture
Pretreatment sequence	1. MSC full.	1.1st derivative BCAP 2.Normalization by closure	1. Kubelka Munk
Calibration wavelength range (cm^{-1})	3999.67–10001.1	4998.62–10001.1	4393.08–4801.91 5392.03–6603.11 7798.77–10001.1
Regression method	PLS	PLS	PLS
Q value	0.76	0.89	0.97
SEE	0.47	0.47	0.44
SEP	0.40	0.45	0.32
C-Set *R*	0.981	0.913	0.974
V-Set *R*	0.984	0.934	0.979

When calibrations are developed working with the NIRCal Software, to define a calibration set and a validation set is always necessary.[9] Calibrations with the minimum number of samples allowed in the validation set (3) were obtained in order to build equations with the maximum number of available samples. The different number of samples, means, ranges and standard deviations of the different constituents are given in Table 3.

Table 3. Statistical parameters of the sample population. (* Calibration set / Validation set).

Constituent	*n**	Mean* (%)	Range* (%)	*SD**
Fat	76/3	5.81/8.07	2.1–13.4/5.8–9.6	2.35/2.00
Protein	76/3	23.31/22.97	20.6–26.1/21.8–24.0	1.13/1.11
Moisture	76/3	70.41/69.47	64.08–77.44/68.02–70.97	2.00/1.48

Table 4 shows how the statistical parameters are improved when the number of samples used in the calibrations set is increased.

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Table 4. Statistics of calibration and validation for Iberian pig meat NIR equations.

	Fat	Protein	Moisture
Pretreatment sequence	1.Kubelka Munk	1.1st derivative BCAP 2.Normalisation by closure	1. Normalisation by closure 2. 1st derivative BCAP
Calibration wavelength range (cm^{-1})	4998.62-7146.94 7397.65-10001.1	4998.62–10001.1	4393.08-4801.91 5392.03-6603.11 7798.77-10001.1
Regression method	PLS	PLS	PLS
Q value	0.88	0.93	0.99
SEE	0.32	0.36	0.26
SEP	0.28	0.39	0.21
C-Set *R*	0.991	0.948	0.991
V-Set *R*	0.991	0.992	0.991

Figure 1 represents the predicted values against the reference values for fat, protein and moisture contents.

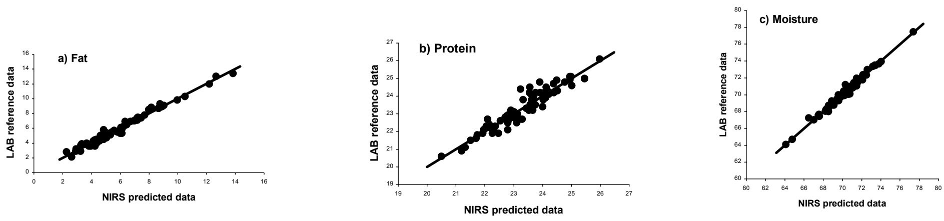

Figure 1. Relationship between reference and predicted data for fat (a), protein (b) and moisture (c) content.

Values of the C-Set *R* obtained by Büchi for its Meat Application were 0.999, 0.977 and 0,993 for fat, protein and moisture contents respectively[7] which compare very well with the C-set *R* values shown in Table 4. The differences observed between them could be mainly explained by variations in the calibration ranges. Thus, calibration ranges for the meat application (8.7–35.2%, 10.1–17.6% and 51–79% for fat, protein and moisture, respectively[7]) were wider than the used in this work (Table 3). The *SEP* values obtained in this study for fat and particularly for moisture were lower than those obtained by Büchi. However, this was not the case for the prediction of the protein content. In absolute values, the *SEP* for the protein meat application (0.21) was lower than the *SEP* given in Table 4. The difference could be explained when SEPs are standardised by dividing each one by the corresponding mean. Then the variation coefficient of the former was similar to the value calculated for our calibration (1.7)

Conclusion

Calibrations from Büchi evaluated in this study must be enlarged with Iberian pig meat samples or a specific calibration must be developed for that product. Preliminary specific calibrations for

Iberian pig meat have been built but further work must be done to develop the definitive ones. Firstly, an increase in the number of samples and an even distribution of the reference values along the calibration range must be considered.

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