

Prediction of sensory properties of espresso from roasted coffee samples by near-infrared spectroscopy

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Abstract

Thirty-five representative and suitably selected roasted coffee samples were characterised by near-infrared (NIR) spectroscopy and used to prepare the corresponding espresso samples to be subsequently subjected to sensory evaluation by trained panellists. The main purpose was to investigate the relationships between certain crucial sensory attributes of espresso coffees, including perceived acidity, mouthfeel, bitterness and aftertaste, and near-infrared spectra of original roasted coffee samples, in such a way that non-destructive near-infrared reflectance measurements would be used to predict all these sensory properties with a decisive influence from a quality assurance standpoint. Separate calibration models based on partial least squares regression (PLS), correlating NIR spectral data of roasted coffee samples with each sensory attribute of espresso samples studied, were developed. Wavelength selection was also performed applying iterative predictor weighting–PLS (IPW–PLS) in order to take into account only significant and characteristic spectral features, in an attempt to improve the quality of the final regression models constructed. Using IPW–PLS regression, prediction of the four sensory responses modelled was performed with high accuracy, with root mean square errors of the residuals in cross-validation (RMSECV) ranging from 4.7 to 7.0%. Thus, the results provided by the high-quality calibration models proposed in the present study, comparable in terms of accuracy to the evaluations provided by a trained sensory panel, are promising and prove the feasibility of using a similar methodology in on-line or routine applications to predict the sensory quality of unknown espresso coffee samples via their respective NIR roasted coffee spectra.

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1. Introduction

Over the years brewing espresso has certainly been made easier with the advancement of more automated and sophisticated machines. However, preparing the ‘perfect’ cup of espresso can still be considered a true ritual, a combination of art and science. A cup of well-prepared fine espresso should taste bitter sweet with an initial slightly acidic note, it should have a strong body and an intense aroma and should be pleasantly persistent [1]. But underlying all these desirable sensory properties that suggest a complex sensory perception system exists a profound chemical complexity affected by a huge number of factors, including bean production, coffee type,

roasting process and cup preparation [2–14]. Thus, being able to enjoy a great-quality cup of espresso is the result of a very delicate process that requires an in-depth understanding of a huge number of determining factors.

Quality is the ultimate criterion of the desirability of any food product, and to that effect, sensory analysis has been extensively used as a valuable tool to evaluate food quality, covering a broad spectrum of specific purposes (quality assurance, consumer acceptance and preference, product development and improvement, process modification, quality control, etc.) [15–19]. In fact, in the coffee industry sensory profiling is still the most widespread technique employed to evaluate the final quality of both raw material and finished products. Nevertheless, traditional sensory panels are expensive to maintain, since such a practice is time-consuming and takes months of specialised training to become remotely

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adept. Moreover, although ‘cupping’ (the act of tasting coffee) adheres to a specific set of detailed guidelines, sensory analysis is subject to multiple potential error sources (e.g., lack of training, habituation, mutual suggestion, false expectations, and lack of reproducibility between separate or consecutive cupping sessions) because the assessment of sensory attributes is necessarily subjective and can consequently lead to inconsistent conclusions [15,20].

In recent times, taking into account the complexities associated with using sensory panels for on-line or routine applications, a major thrust in the food and beverage industry has focused on implementing analytical instrumental techniques in sensory evaluation. Thus, the development of fast, non-destructive and accurate techniques suitable for on-line application, and which could provide information highly correlated to sensory properties (i.e. reliable information about food quality), is desirable in order to replace or enhance a subjective approach to quality control such as sensory profiling. Near-infrared spectroscopy has received special attention to form the basis for such techniques, and it has been widely used for the characterisation and quality evaluation of many food products [21–34].

With regard to coffee characterisation, several important factors (including coffee origin, processing method, and degree of roasting or conditions of cup preparation) have been analysed, investigating their influence on espresso coffee physicochemical composition and their possible correlations to sensory attributes and to the quality of the beverage [35–40]. In this way, it has been proven that certain sensory attributes such as espresso taste, smell, mouthfeel or aftertaste are closely related to carboxylic acids, fats, oils, esters, proteins, aromatics and/or carbohydrates present in coffee.

The aim of this study was to examine the potential of NIR spectroscopy for predicting four relevant and highly influential sensory attributes from an espresso quality assurance standpoint: perceived acidity, mouthfeel (body), bitterness and aftertaste. Thus, once a traditional sensory evaluation study was performed on a representative subset of espresso coffees suitably selected by a panel of trained tasters, separate PLS regression models were constructed based on the corresponding NIR roasted coffee spectra in order to model each sensory property studied, by taking advantage of the fact that the specific scores obtained for each espresso sample in the sensory analysis were the direct consequence of the particular chemical composition of the roasted coffee used as raw material, which was precisely profiled (fingerprinted) by NIR spectroscopy. The main reason for applying a wavelength selection method such as IPW–PLS [41] was to test the hypothesis that a low number of NIR absorption bands corresponding to certain compounds strongly related to a specific sensory attribute can predict it with at least the same accuracy or even improved reliability as using the whole NIR wavelength range. The resultant high-quality calibration models developed on the basis of NIR spectral data might be used for on-line quality control purposes, allowing a straightforward, reproducible and objective future determination of sensory

properties of unknown espresso samples. The promising results reported here may serve to support the feasibility of replacing conventional sensory analysis with analytical instrumental systems.

2. Materials and methods

2.1. Coffee samples

Five green coffee samples (four arabica coffees and one robusta coffee) were selected from a comprehensive green coffee set containing 38 samples of varied origins and varieties (22 arabica and 16 robusta coffees) as the most representative for subsequent roasting and use to prepare the espresso samples serving as the basis for the present study. These five representative green coffees were processed under various roasting conditions, in such a way that seven resultant roasted coffee samples were obtained from each green coffee used as raw material, generating a total number of 35 different roasted coffee samples. The degree of roasting for each sample could be controlled by means of two significant parameters: roasting colour and quantity (kg) placed in the roaster. Thus, the roasted coffee samples were obtained as a result of individual roasting processes in which the quantity of roasted coffee ranged from 12 to 16 kg, working at five loading levels, whereas roasting colour ranged from 50 to 92 (arbitrary units). See Section 3.2 for more details on the selection of the representative green coffee samples subset.

2.2. Sensory analysis of green coffee

The selection of a subset of representative green coffee samples represented a crucial step prior to carrying out a suitable sensory evaluation study of espresso coffee samples, since the huge complexity and considerable effort involved in such a sensory analysis made it necessary to reduce as much as possible the number of espresso coffee samples for tasting at a later stage. A total of 38 green coffee samples, representing a wide range of coffee varieties, were subjected to sensory analysis. The panel, consisting of 11 suitably trained tasters, with ample experience in the sensory evaluation of coffee, were chosen to participate in the study, using a sensory terminology list appropriate for evaluating green coffee [42,43]. The term list included five primary sensory attributes selected for evaluation: aroma, body, acidity, bitterness (tasting properties) and appearance (visual perception). The green beans were lightly roasted (roasting colour varied from 90 to 105 a.u.) in order to enable the panellists to investigate more accurately the sensory potential of each coffee. Then, 10 g of ground coffee were placed directly in each cup at the cupping table and 100 mL of freshly boiled water was poured over them. Since a single bad bean can change the sensory profile of a cup, three separate samples of each coffee were tasted simultaneously; this also allowed the tasters to get a feel for the consistency of the beans. At this stage of the cupping

procedure aromatic characteristics were identified ('breaking the crust'). Next, the coffee was allowed to cool and was then tasted. For attributes such as body, acidity and bitterness, a 10-point scale (0: none; 9: very high) was used to evaluate the sensory score corresponding to each tasted sample, whereas for the other two parameters (aroma and appearance) a more restricted 5-point scale was adopted.

2.3. Espresso coffee samples

The 35 espresso coffee samples were prepared to later undergo sensory evaluation from 6.6 to 7.5 g of finely ground roasted coffee (the dosage varied slightly between samples) for a volume of 30 mL using an espresso coffee machine (Saeco Espresso Classico SS, Italy). Fixed espresso coffee preparation conditions were followed using a pressure in the espresso machine pump equal to 9 atm, a water temperature of 91 °C and extraction times ranging from 20 to 30 s.

2.4. Sensory analysis of espresso

All 35 espresso coffee samples were evaluated under the same conditions by a panel of 11 tasters. The espresso coffee samples were tasted in triplicate over six sessions with a duration of about 1.5 h each on three different days. First, the panellists were briefed on the protocols for the sensory evaluation of espresso. Group discussions and training sessions were held to select the attributes to be judged, define the score sheet and reach a consensus on the rating score of every attribute. Thus, for the four sensory attributes selected for evaluation (perceived acidity, body, bitterness and aftertaste intensities) 10-point scales were adopted, in such a way that each of the adjectives describing the degree of sensory magnitude perceived were given corresponding scale points, e.g. the words 'not perceptible' (0) and 'extremely strong' (9) defined the extreme scores on the rating scale. Each espresso coffee was prepared immediately before tasting and served in a white porcelain coffee cup. The presentation order was randomised among tasters and sessions. Water was provided for rinsing between individual samples.

2.5. Recording of NIR spectra

Reflectance spectra were obtained directly from untreated ground roasted coffee samples. Due care was taken to ensure that the same amount of sample (2.5 g approximately) was always used to fill the NIRS standard sample cup (5 cm in diameter). Each spectrum was obtained from 32 scans performed at 2 nm intervals within the wavelength range 1100–2200 nm, with five replicates for each individual sample. The samples were decompacted between recordings. An average spectrum was subsequently computed from the collected replicates.

2.6. Apparatus and software

NIR spectra were recorded on a near-infrared spectrophotometer NIRSystems 5000 (Foss NIRSystems, Raamsdonksveer, The Netherlands) equipped with a reflectance detector and a sample transport module. The light spot size of the instrument was 1 cm in diameter, which delimits an area smaller than a standard sample cup. However, sample transport device was precisely designed to increase the sample area scanned. The instrument was controlled by a compatible PC, and Vision 2.22 (Foss NIRSystems, Raamsdonksveer, The Netherlands) was used to acquire the data.

Data pre-processing treatments, principal component analysis, PLS and IPW–PLS regressions were carried out with V-PARVUS 2004 (M. Forina et al., Dipartimento di Chimica e Tecnologie Farmaceutiche ed Alimentari, Università di Genova, Italy). ANOVA analysis was performed using Statistical Package for Social Sciences (SPSS, version 9.0, Chicago, IL).

2.7. Data processing

In order to study the repeatability and the discrimination ability of the panellists, all subject data were treated by an analysis of variance (ANOVA) at a confidence level of $\alpha = 0.01$, applying the same procedure for both sensory data matrices obtained (green coffee and espresso evaluations).

A principal component analysis (PCA) was performed on the data corresponding to the sensory evaluation of green coffee samples for objective sample selection based on the most representative green coffees of the whole sample matrix.

Likewise, the data matrix containing NIR spectra of roasted coffee samples and sensory evaluations from the corresponding espresso coffees was subjected to preliminary studies in order to investigate the presence of possible outlier data that could have a detrimental effect on the quality of the results. None of the diagnostic tools applied (PCA, residual and leverage plots) revealed the existence of anomalous data.

Partial least squares (PLS) [44,45] and iterative predictor weighting–PLS (IPW–PLS) [41] were used as multivariate regression methods in the construction of the calibration models. Firstly, an initial PLS model was built for each espresso coffee sensory attribute using the whole NIR wavelength range 1100–2200 nm corresponding to the original roasted coffee NIR spectra. Then, IPW–PLS was used to select a subset of significant NIR absorption bands to be used in the subsequent development of a simplified regression model for predicting each sensory property studied, in such a way that it would be possible to compare the results obtained with those resulting from conventional PLS and to discuss the appropriate assignment of the selected NIR wavelength to particular compounds closely related to the specific sensory response being modelled. The data were always centered before use. In addition, in an attempt to minimise physical contributions incorporating irrelevant information into spectra, two spectral treatments, first derivative and standard normal variate

(SNV), were also applied to NIR spectral data in order to test their effect on the quality of the final regression models. Because cross-validation [46–49] has demonstrated to be a very useful tool for estimating the predictive ability of a regression model for future samples and considering the limited number of representative samples selected, no attempts were made to perform additional external validation. Thus, all the regression models were constructed by cross-validation, using five cancellation groups in all cases. When applying IPW–PLS, after usual PLS, the regression model is iteratively computed many times (IPW cycles), in such a way that in each cycle the predictors are weighted according to their importance. Thus, in the final steady states useless predictors are cancelled out (those having an importance value less than a fixed cut-off value). Therefore, two additional parameters had to be defined prior to developing IPW–PLS calibration models: the number of IPW-cycles (equal to 10) and the importance cut-off value (equal to 0.001).

The quality of the results provided by the different regression models tested was evaluated by several parameters, including the root mean square error (RMSE) of the residuals obtained (termed RMSEC in calibration and RMSECV in cross-validation); the RMSE expressed as a percentage (in both calibration and prediction) taking into account the response range in its calculation, the percentage of variance explained by the model in both calibration and cross-validation, and the corresponding plots showing measured versus predicted sensory attributes values.

3. Results and discussion

3.1. Two-way analysis of variance

The two-way ANOVA performed on the data obtained, in the case of both green coffee (Table 1) and espresso coffee sensory evaluations (Table 2), showed that inter-sample differences were statistically significant for all the evaluated attributes and no significant inter-panellist differences were observed. The fact that the rating of a given attribute was significantly different between samples showed that the panellists demonstrated good agreement after receiving the proper training. The differences between replications of any given attribute rated by the same assessor were not significant, evidencing an acceptable repeatability. In this way, once the lack of significant intra- and inter-panellist differences was confirmed, mean panellist ratings of green and espresso coffee samples were separately computed for all the attributes so that two ‘average’ sensory data matrices were obtained for later use in the selection of representative samples and in the development of regression models. In order to provide a more complete statistical analysis, Table 3 summarizes some relevant quality parameters corresponding to each one of the sensory attributes studied for green coffee and espresso coffee samples. The mean relative standard deviation (R.S.D.) values among panellists were also computed to obtain an ob-

Table 1

Two-way analysis of variance for green coffee sensory evaluation

| Source | Sum of squares | Degrees of freedom | Mean squares | F |
|------------------------|----------------|--------------------|--------------|----------|
| Body | | | | |
| Sample ^a | 2694.370 | 37 | 72.821 | 2637.391 |
| Panellist ^b | 0.640 | 10 | 0.064 | 2.314 |
| Residual | 23.083 | 836 | 0.028 | |
| Total | 2728.611 | 1253 | | |
| Acidity | | | | |
| Sample ^a | 8512.390 | 37 | 230.065 | 3249.519 |
| Panellist ^b | 1.481 | 10 | 0.148 | 2.093 |
| Residual | 59.188 | 836 | 0.071 | |
| Total | 8595.723 | 1253 | | |
| Bitterness | | | | |
| Sample ^a | 294.263 | 37 | 7.953 | 1234.662 |
| Panellist ^b | 0.145 | 10 | 0.015 | 2.253 |
| Residual | 5.385 | 836 | 0.006 | |
| Total | 301.829 | 1253 | | |
| Aroma | | | | |
| Sample ^a | 915.296 | 37 | 24.738 | 1827.270 |
| Panellist ^b | 0.309 | 10 | 0.031 | 2.279 |
| Residual | 11.318 | 836 | 0.014 | |
| Total | 931.139 | 1253 | | |
| Appearance | | | | |
| Sample ^a | 1545.215 | 37 | 41.763 | 3495.184 |
| Panellist ^b | 0.266 | 10 | 0.027 | 2.225 |
| Residual | 9.989 | 836 | 0.012 | |
| Total | 1559.201 | 1253 | | |

^a F-value of Fisher–Snedecor for the samples, $F(37,836) = 1.64$, $\alpha = 0.01$.

^b F-value of Fisher–Snedecor for the panellists, $F(10,836) = 2.34$, $\alpha = 0.01$.

Table 2

Two-way analysis of variance for espresso coffee sensory evaluation

| Source | Sum of squares | Degrees of freedom | Mean squares | F |
|------------------------|----------------|--------------------|--------------|----------|
| Acidity | | | | |
| Sample ^a | 9616.779 | 34 | 282.846 | 3517.733 |
| Panellist ^b | 1.671 | 10 | 0.167 | 2.078 |
| Residual | 61.913 | 770 | 0.080 | |
| Total | 9701.043 | 1154 | | |
| Body | | | | |
| Sample ^a | 3314.112 | 34 | 97.474 | 946.554 |
| Panellist ^b | 2.126 | 10 | 0.213 | 2.064 |
| Residual | 79.293 | 770 | 0.103 | |
| Total | 3435.991 | 1154 | | |
| Bitterness | | | | |
| Sample ^a | 4272.903 | 34 | 125.674 | 2835.037 |
| Panellist ^b | 0.970 | 10 | 0.097 | 2.188 |
| Residual | 34.133 | 770 | 0.044 | |
| Total | 4320.739 | 1154 | | |
| Aftertaste | | | | |
| Sample ^a | 3707.169 | 34 | 109.034 | 1614.443 |
| Panellist ^b | 1.407 | 10 | 0.141 | 2.083 |
| Residual | 52.003 | 770 | 0.068 | |
| Total | 3786.25 | 1154 | | |

^a F-value of Fisher–Snedecor for the samples, $F(34,770) = 1.64$, $\alpha = 0.01$.

^b F-value of Fisher–Snedecor for the panellists, $F(10,770) = 2.34$, $\alpha = 0.01$.

Table 3
Sensory attributes of green coffee and espresso coffee samples

| Attribute | Mean | Standard deviation | R.S.D. ^a |
|-------------------------|------|--------------------|---------------------|
| Green coffee samples | | | |
| Body | 3.49 | 1.50 | 4.00 |
| Acidity | 4.49 | 2.65 | 5.25 |
| Bitterness | 1.71 | 0.49 | 4.15 |
| Aroma | 2.50 | 0.87 | 4.12 |
| Appearance | 2.52 | 1.12 | 3.90 |
| Espresso coffee samples | | | |
| Acidity | 5.06 | 2.94 | 4.52 |
| Body | 5.38 | 1.73 | 5.80 |
| Bitterness | 4.69 | 1.96 | 4.05 |
| Aftertaste | 4.95 | 1.82 | 5.23 |

^a Mean of the R.S.D. values computed for each sample, taking into account the individual score provided by each panellist.

jective measurement of the accuracy of the sensory panel for each studied attribute.

3.2. Selection of representative green coffee samples

The use of the sensory data obtained from the evaluated green coffee samples jointly with principal component analysis (PCA) provided an effective and easy-to-implement tool for selecting representative coffee samples from arabica and robusta varieties. Thus, a PCA was performed on the data corresponding to sensory analysis in the green coffee data set (Table 4). Malinowski's factor indicator function [50,51] was used for determining the correct number of significant PCs, in such a way that only one component was considered relevant, accounting for 71.3% of the variance in the data. Fig. 1 shows a bidimensional representation of PC1 and PC2 scores for the green coffee samples, labelled according to their coffee variety (arabica and robusta coffees). Two sample groups appeared clearly separated along the second bisectrix of the two component axes, confirming the presence of two different clusters just associated with the two varieties considered. Consequently, the direction of maximum intra-variety variability observed would be defined by the first bisectrix, in such a way that this was precisely the direction later considered to select the most representative samples of each class. The centroid of each cluster was identified and selected as the most representative sample of each variety: Kenya_1 for arabicas (A4) and Laos for robustas (R8). Two additional samples corresponding to the most extreme coffees within the arabica cluster were also selected in order to carry out a more in-depth study of this variety due to its greater economic relevance (arabica still accounts for between 70 and 80% of total coffee production worldwide): Brazil (A3) and Kenya_2 (A22). Lastly, a last coffee sample, Colombia (A5), was se-

Table 4
PCA performed on the sensory properties of green coffee samples

| Component | Eigen value | Explained variance (%) | Cumulative (%) |
|-----------|-------------|------------------------|----------------|
| 1 | 3.567 | 71.34 | 71.34 |
| 2 | 0.998 | 19.96 | 91.30 |

lected only due to the particular interest that it arouses in the international coffee market. As noted previously, the application of this sample selection procedure was directly related to the need to reduce as far as possible the number of final espresso coffee samples undergoing sensory analysis. In this way, the results obtained from these selected representative coffees (once roasted and characterised both sensorially and spectroscopically) could be extrapolated to any other coffee by simply taking into account its variety and NIR spectrum without the need to perform sensory evaluation and with all the advantages that this methodology entails.

3.3. Observations on NIR spectra

The overall shape of the raw roasted coffee NIR spectra was qualitatively examined in order to illustrate the influence of two crucial factors such as coffee variety and roasting degree on the spectral profiles.

The SNV average NIR spectra of the selected arabica and robusta coffees are shown in Fig. 2. As an attempt to minimize the spectral variations between coffee samples derived from different roasting processes and to, therefore, better investigate the effect of coffee variety, only similar roasting degrees (roasting colour ranged from 50 to 60 a.u.) were taken into account when computing the average spectra. The shape of the spectra was particularly dominated by the broad water absorption bands at approximately 1450–1940 nm. Nevertheless, no significant differences between both varietal spectra due to different moisture contents were expected to be observed, since this was precisely the purpose of considering a restricted range of roasting degrees. The main differences between spectra of roasted coffee samples belonging to different varieties appeared around 1100–1200, 1700–1850 and 1900–2000 nm, these being wavelength areas indicative of particular bands that might be assigned to certain compounds present in coffee showing a marked inter-variety difference. Thus, when considering the robusta spectrum, the increase in spectral intensity near 1150 nm (second overtone of C–H vibration in CH₃ groups) and in the peak at 1920 nm (second overtone of C=O vibration in functional groups of CONH) were likely correlated with a higher caffeine content. Likewise, there appeared to be a clear change in the observed trend of spectra around the wavelength region corresponding to 1700–1850 nm, in such a way that higher spectral intensities were observed in arabica variety. This finding can be easily explained, since arabica and robusta coffees contain different level of lipids (considerably higher in arabica), and the major NIR absorption bands in fat are due to long-chain fatty acid moiety, which give rise to CH₂ first overtones at 1725 and 1765 nm (double band observed).

The SNV average NIR spectra of the arabica coffees, grouped together into four virtual categories defined according to their particular roasting colour (inversely proportional to roasting degree), are shown in Fig. 3. Robusta coffees were not considered in order to avoid, to some extent, information related to roasting degree to be masked by va-

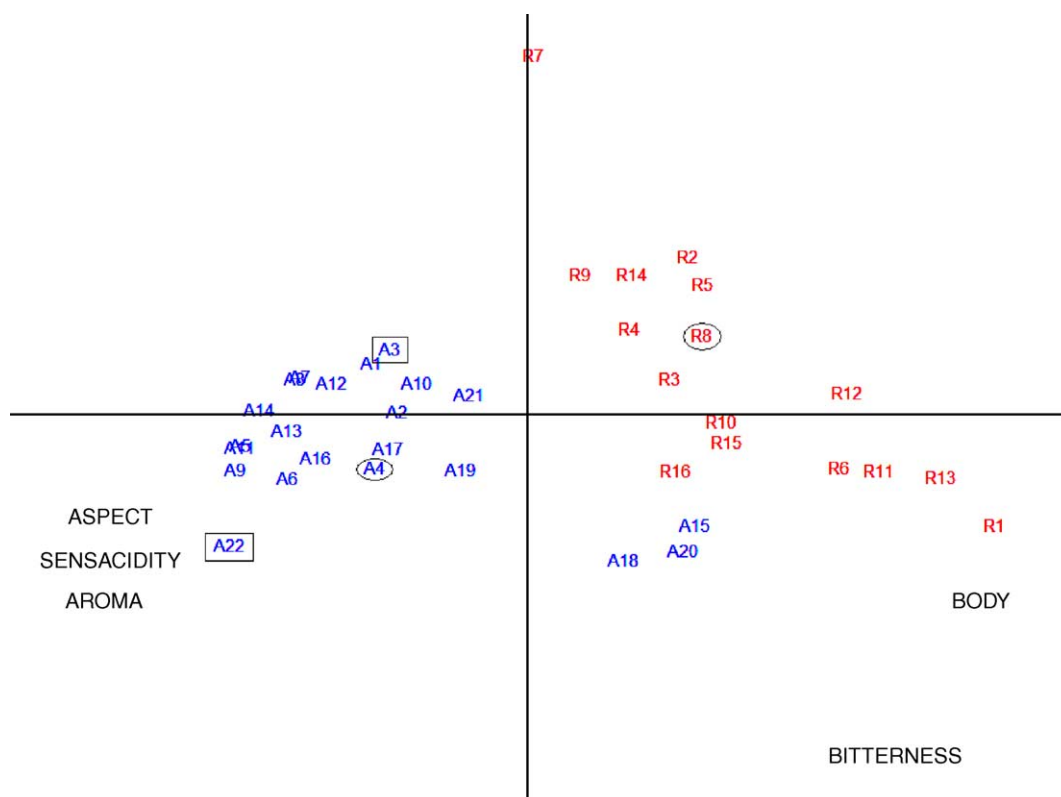


Fig. 1. Scores of the green coffee samples on the first two principal components explaining the variability in sensory data. Loadings of sensory properties on PC1 and PC2 are also shown.

rietal factors. The most significant spectral differences observed when considering diverse roasting degrees appeared around 1100–1250, 1450–1700, 1780–1850, 1920–2000 and 2050–2200 nm. It would be possible to correlate such spectral variations detected with certain changes in chemical composition occurring during roasting, i.e., with the formation or degradation of certain compounds responsible for partic-

ular absorptions that strongly affect the final spectral profile observed. As was expected, water band intensity at 1450 (first overtone of O–H stretching) and at 1940 nm (combination band of O–H stretching and O–H deformation) decreased gradually when coffees were roasted darker, since during roasting the major degradation product is precisely water (its loss is proportional to the degree of roasting). Although all spectra had a similar shape, the whole spectrum

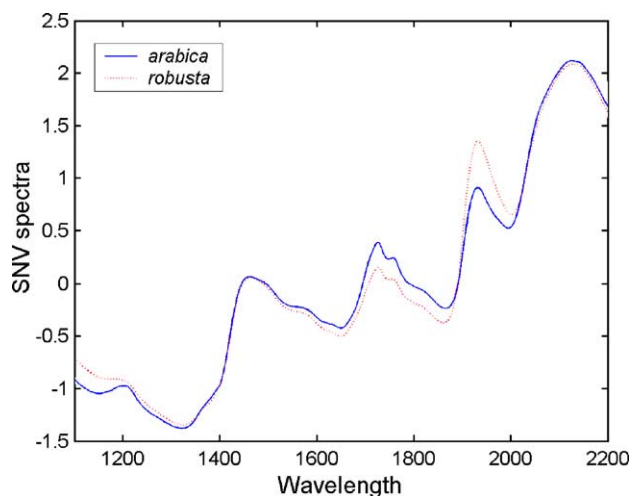


Fig. 2. SNV average NIR spectra representing separately arabica and robusta varieties. Only samples processed under similar roasting conditions (roasting colour ranged from 50 to 60 a.u.) were considered.

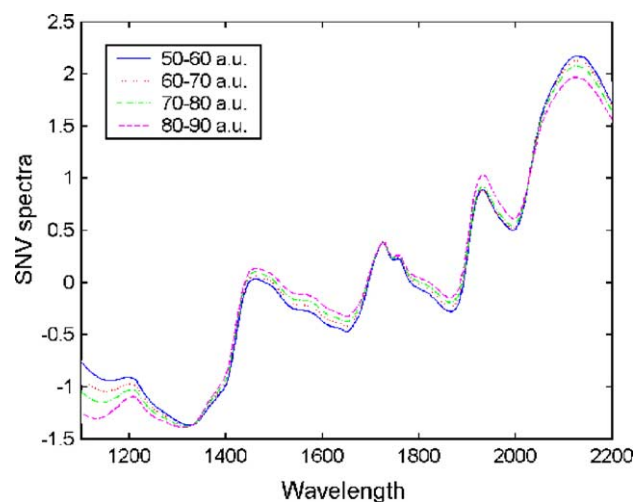


Fig. 3. SNV average NIR spectra of arabica coffees, grouped together according to their roasting degree.

Table 5

Results corresponding to the PLS-calibration models developed from roasted coffee NIR spectra for predicting perceived acidity of espresso samples after selecting the suitable number of latent variables to be included

| | PLS-LVs | RMSEC (%) | Explained variance (calibrated %) | RMSECV (%) | Explained variance (cross-validation %) | |
|------------------------------|---------------------|-----------|-----------------------------------|-----------------------------------|---|---|
| PLS regression | | | | | | |
| Column centering | 6 | 7.2915 | 93.84 | 9.2030 | 90.02 | |
| SNV + centering | 6 | 6.7021 | 94.80 | 8.1701 | 92.13 | |
| First derivative + centering | 5 | 7.2613 | 93.89 | 8.6237 | 91.23 | |
| | Selected predictors | PLS-LVs | RMSEC (%) | Explained variance (calibrated %) | RMSECV (%) | Explained variance (cross-validation %) |
| IPW-PLS regression | | | | | | |
| Column centering | 9 | 8 | 6.1839 | 95.57 | 7.6652 | 93.07 |
| SNV + centering | 8 | 6 | 6.0885 | 95.71 | 6.7675 | 94.60 |
| First derivative + centering | 6 | 4 | 8.2191 | 92.18 | 9.1991 | 90.03 |

Table 6

Results corresponding to the PLS-calibration models developed from roasted coffee NIR spectra for predicting mouthfeel (body) of espresso samples after selecting the suitable number of latent variables to be included

| | PLS-LVs | RMSEC (%) | Explained variance (calibrated %) | RMSECV (%) | Explained variance (cross-validation %) | |
|------------------------------|---------------------|-----------|-----------------------------------|-----------------------------------|---|---|
| PLS regression | | | | | | |
| Column centering | 4 | 8.3249 | 76.42 | 8.8969 | 72.92 | |
| SNV + centering | 10 | 4.9591 | 91.63 | 7.3450 | 81.54 | |
| First derivative + centering | 9 | 5.2509 | 90.62 | 8.3391 | 76.21 | |
| | Selected predictors | PLS-LVs | RMSEC (%) | Explained variance (calibrated %) | RMSECV (%) | Explained variance (cross-validation %) |
| IPW-PLS regression | | | | | | |
| Column centering | 9 | 8 | 5.9764 | 87.84 | 7.0117 | 83.18 |
| SNV + centering | 8 | 7 | 6.1367 | 87.18 | 7.2366 | 82.08 |
| First derivative + centering | 3 | 3 | 7.0200 | 83.23 | 7.6632 | 79.91 |

Table 7

Results corresponding to the PLS-calibration models developed from roasted coffee NIR spectra for predicting bitterness of espresso samples after selecting the suitable number of latent variables to be included

| | PLS-LVs | RMSEC (%) | Explained variance (calibrated %) | RMSECV (%) | Explained variance (cross-validation %) | |
|------------------------------|---------------------|-----------|-----------------------------------|-----------------------------------|---|---|
| PLS regression | | | | | | |
| Column centering | 4 | 6.4382 | 89.17 | 7.2115 | 86.13 | |
| SNV + centering | 3 | 7.2944 | 86.10 | 7.7250 | 84.08 | |
| First derivative + centering | 4 | 6.6681 | 88.38 | 7.2926 | 85.81 | |
| | Selected predictors | PLS-LVs | RMSEC (%) | Explained variance (calibrated %) | RMSECV (%) | Explained variance (cross-validation %) |
| IPW-PLS regression | | | | | | |
| Column centering | 13 | 9 | 4.5792 | 94.52 | 5.9847 | 90.45 |
| SNV + centering | 12 | 7 | 4.0217 | 95.77 | 4.7364 | 94.02 |
| First derivative + centering | 5 | 3 | 6.9145 | 87.51 | 7.4135 | 85.34 |

was shifted upwards at two main wavelength regions (corresponding to 1100–1250 and 2050–2200 nm) when roasting degree increased. This specific trend may be explained by the strong degradation that chlorogenic acids undergo during roasting and the subsequent release of quinic acid, in such a way that several peaks in the above-mentioned ranges could be assigned to absorptions by this latter compound: 1215 and 1225 nm (second overtones of C–H vibration in CH₂ and CH groups, respectively), 2080 nm (com-

bination band of O–H stretching and O–H deformation in ROH groups) and 2150–2180 nm (C–H vibration in aromatic structures). Finally, the fact that as darker roasts were applied less intense spectral absorption were observed around 1500–1700 and 1780–1850 nm could be associated with a number of bands resulting from certain classes of substances subjected to very important transformations (degradation) at roasting, such as chlorogenic acids (1685 nm—first overtone of C–H vibration in aromatic structures), carbohy-

Table 8

Results corresponding to the PLS-calibration models developed from roasted coffee NIR spectra for predicting aftertaste of espresso samples after selecting the suitable number of latent variables to be included

| | PLS-LVs | RMSEC (%) | Explained variance (calibrated %) | RMSECV (%) | Explained variance (cross-validation %) | |
|------------------------------|------------------------|-----------|--------------------------------------|--------------------------------------|--|--|
| PLS regression | | | | | | |
| Column centering | 4 | 7.6131 | 82.53 | 8.4513 | 78.07 | |
| SNV + centering | 3 | 7.7328 | 81.98 | 8.2261 | 79.23 | |
| First derivative + centering | 3 | 7.9730 | 80.84 | 8.3385 | 78.66 | |
| | Selected predictors | PLS-LVs | RMSEC (%) | Explained variance (calibrated %) | RMSECV (%) | Explained variance (cross-validation %) |
| IPW-PLS regression | | | | | | |
| Column centering | 8 | 7 | 5.4214 | 91.14 | 6.5683 | 86.76 |
| SNV + centering | 5 | 3 | 8.0382 | 80.53 | 8.3487 | 78.60 |
| First derivative + centering | 3 | 3 | 8.1715 | 79.88 | 8.4410 | 78.13 |

drates (1584 and 1780 nm—first overtones of O–H stretching, 1830 nm—combination band of O–H and C–O stretching) or amino acids (1510 nm—first overtone of N–H stretching in protein).

3.4. Regression models of espresso sensory properties from roasted coffee NIR spectra

The results obtained when using PLS and IPW-PLS to model each one of the four sensory properties of espresso coffee samples considered on the basis of the NIR spectra corresponding to the original roasted coffee samples, once selected the most suitable complexity of each model constructed, are summarized in Tables 5–8. Several pretreatments of the NIR spectra (mean centering, first derivation and SNV) were tested to find the best relation between the NIR data and the sensory scores. Examination of the resultant

errors in both calibration and prediction clearly indicated that the best regression models for all analysed sensory responses were achieved when applying IPW-PLS to reduce the number of predictor variables so that only significant wavelengths were taken into account in each model development. For all the sensory responses studied, high-quality IPW-PLS regression models were obtained, all of them exhibiting a very high predictive ability (%RMSECV always was lower than 7%) and suitable robustness and reliability confirmed by the agreement between calibration and prediction results. Moreover, Fig. 4 shows graphically the results provided by the optimal IPW-PLS models representing the corresponding measured versus computed (●), predicted (△) values for each of the modelled responses, in such a way that it can be used as an additional tool to display the goodness of the final regression models selected. In order to objectively evaluate the real quality of the NIR calibrations developed in the present study,

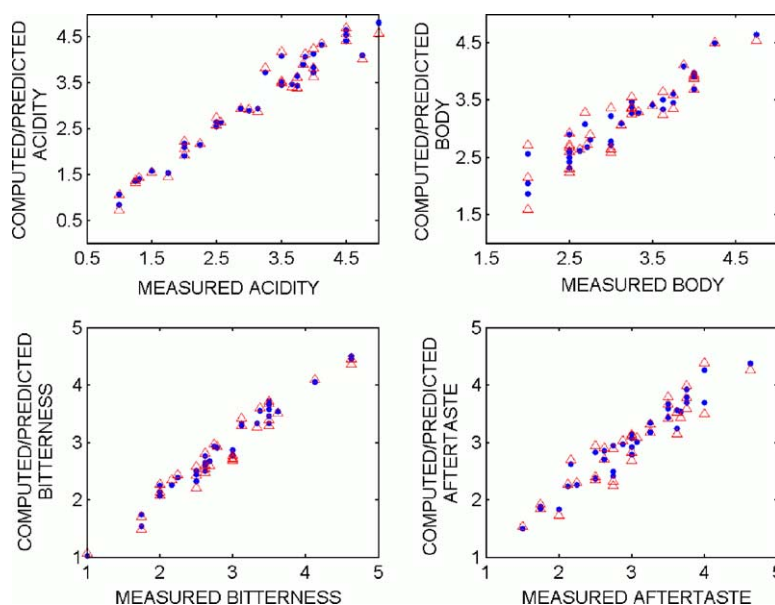


Fig. 4. Measured vs. computed (●)/predicted (△) values of all the studied sensory properties of espresso coffees provided by the final IPW-PLS models developed from NIR spectra of the original roasted coffee samples.

their prediction abilities were compared with an analogous accuracy measurement computed on the basis of the reference method used (i.e., the sensory panel accuracy). For this purpose, mean R.S.D. values among panellists were computed for all the attributes analysed (Table 3). These precision measurements are extremely important, as one has to keep in mind that the prediction error provided by a calibration model can never be lower than the experimental error derived from the reference method. Thus, the comparison between the accuracies associated with both methods (sensory panel and NIR calibrations) for each attribute evaluated served to emphasize the feasibility of NIR spectroscopy to predict sensory attributes of espresso coffee samples, since in all cases, quite similar magnitude errors were obtained. The particular nature of the modelled responses (sensory properties) should not be forgotten when evaluating the goodness of the results. For this reason, the low magnitude of the resulting prediction errors further enhanced the success of the constructed calibration models. On the other hand, it may seem strange that pre-processing of the NIR spectra was not a determinant factor, since their application did not always prompt any improvement of final models. Nevertheless, it must be remembered that the main objective when applying IPW-PLS technique was to select a subset of individual variables closely related to a certain sensory attribute to be predicted. For this reason, the potential beneficial effects derived from the application of some pretreatment to the whole spectra lost relevance, as can be verified in the case of responses such as body or aftertaste, since even better results were obtained when working on original (only mean centered data) spectra. The use of IPW-PLS to model a certain sensory property not only fostered a substantial reduction in the number of predictors with a notable decrease in prediction errors but also offered an interesting advantage from an interpretation standpoint, since when considering a restricted number of wavelengths it was possible to argue the chemical sense of the selected NIR absorption bands by assigning them to certain compounds strongly related to the particular property studied.

3.5. IPW variable subset selection: chemical assignments of selected near-infrared absorption bands

The variable subset selection carried out by IPW-PLS was based on statistical criteria, i.e. neither spectroscopic nor chemical considerations were taken into account in order to constitute the final subset of wavelengths considered as significant and most suitable for modelling each sensory property. However, apart from confirming the suitability of the IPW regression models developed in the present study, it was possible to determine the chemical assignments of the near-infrared bands previously selected by IPW for predicting all the four sensory attributes analysed [23]. The following discussion does not intend to be an exhaustive compilation of all the potential wavelength regions and the related compounds that could contribute to each sensory property studied, but

only a chemical reasoning focused on the final variable selection provided by IPW.

3.5.1. Perceived acidity

After applying IPW, working on SNV-NIR spectra, eight wavelengths were selected as relevant for developing a subsequent high-quality calibration model for modelling the perceived acidity of espresso coffee. Table 9 provides an overview of all these significant absorption bands, including both the identification of the bond vibrations involved and the respective chemical assignments. The selection of certain absorption bands characteristic of caffeine structure for inclusion in the perceived acidity regression model can be easily explained bearing in mind the capacity of caffeine as an inter-variety discriminant parameter and thus its inevitable association with other coffee constituents (e.g. acids). Cup acidity was obviously expected to depend on carboxylic acids, as reflected by the contribution of the C–O vibration near 1900 nm, attributable to functional groups of –COOH. From a quantitative standpoint, the major acids in espresso coffee, despite severe destruction on roasting, are chlorogenic acids, although their contribution to perceived acidity is secondary. The influence of chlorogenic acids on perceived acidity, i.e. the observed relevance of some NIR absorption related to CGA structures, could be justified taking into account the possible use of the decomposition of these acids during roasting as an index of roasting degree and the decisive effect of roasting degree on the relative amounts of many groups of compounds with sensory implications in perceived acidity. Likewise, this close relationship between roasting degree and perceived acidity also serves to justify the selection of a water band at approximately 1940 nm (water is the main degradation product after roasting) and the importance shown by several bands of carbohydrates (fibre content is inversely proportional to roasting temperature) on this considered sensory property.

3.5.2. Mouthfeel (body)

The nine wavelengths considered important for prediction of espresso mouthfeel as selected by IPW on the basis of mean centered NIR spectra are summarized in Table 10. Robusta coffees generally have a fuller body associated with a higher caffeine content; this may explain the assignment of several selected bands to characteristic absorptions of caffeine. The NIR band at 2142 nm may be attributed to *cis* unsaturation in fatty acids (fats), which serves to underline the well-established fact that lipids are important for the perceived body of espresso coffee, since this sensory sensation is prompted by the presence of oil droplets, which not only dissolve important flavour components but also increase viscosity and decrease the overall density of the brew. On the other hand, it is quite possible that certain lipid compounds are thermally labile, meaning that roasting conditions may influence the body of the beverage. This latter assumption seems to be confirmed in view of the considerable importance attached to certain selected wavelengths, which can be

Table 9

Chemical assignments of significant near-infrared bands selected by IPW–PLS for modelling perceived acidity of espresso

| Selected wavelength (nm) | Bond vibration | Assignment |
|--------------------------|---|--|
| 1100 | C–H stretching second overtone (Ar) | CGA |
| 1212 | C–H stretching second overtone | Caffeine Carbohydrates (fibre content) |
| 1710 | C–H stretching first overtone (CH ₃) | Caffeine |
| 1718 | C–H stretching first overtone (CH ₂) | Carbohydrates (fibre content) |
| 1860 | O–H stretching + 2 × C–O stretching | Carbohydrates (fibre content) |
| 1914 | C=O stretching second overtone (–CO ₂ H) C=O str. second overtone (CONH) | Carboxylic acids Caffeine |
| 1944 | O–H stretching + O–H deformation C=O stretching second overtone (–CO ₂ R) | H ₂ O CGA |
| 2112 | O–H stretching + O–H deformation 2 × O–H deformation + 2 × C–O stretching | CGA (ROH) Carbohydrates (fibre content) |

assigned to typical vibrations of compounds strongly affected by the degree of roasting, such as water, chlorogenic acids or carbohydrates (fibre content). Moreover, apart from the fact that the potential use of CGA as a roasting degree index may have determined the contribution from C–O vibration in functional groups of –CO₂R as influencing mouthfeel characterisation, an additional contribution of CGA in relation to their astringent taste (particularly when considering dichlorogenic acids) should also be taken into account when explaining cup body. Lastly, the influence of protein and fibre contents on the coffees body and the observed assignment of various selected bands to both of them can be explained by considering that viscosity (a fundamental sensation constituting perceived body) represents a direct measurement of both relevant parameters.

3.5.3. Bitterness

The assignments carried out in accordance with the 12 significant NIR absorption bands selected by IPW from SNV–NIR spectra when considering the perceived bitterness of espresso as sensory response are summarized in Table 11. Bitterness is intimately correlated with the total dissolved solids of a coffee. Accordingly, soluble carbohydrates and emulsified lipids are included in this property, which means that the contribution of certain bands assignable to both types of compounds can be consistently justified. It has also been shown that colloids can substantially reduce the perception

of bitterness by receptor blockage, and droplets of emulsified oil in espresso behave exactly like colloids; consequently, this fact serves to highlight even more clearly the huge relevance of lipids with respect to this particular sensory attribute. Moreover, roasting level can be used to change the bitterness-to-acidity ratio to some extent because total solids content strongly depends on roasting degree. Thus, the selection of various wavelengths attributable to water or CGA for determining the perceived bitterness of espresso may be explained by considering their common use as practical indexes of actual roasting degree. Likewise, quinic acid (a degradation product of CGA) is present in coffee at 20 times its threshold value and is partly responsible for the perceived bitterness in espresso, and the presence of O–H vibration between selected bands could be indicative of quinic acid influence on bitterness. Lastly, the influence displayed by several vibrations that might be assigned to caffeine structure may be due mainly to the varietal information included in caffeine content and its influence on perceived bitterness (robusta is usually more bitter than arabica), since, despite its bitter taste, the amount of caffeine present in a cup of espresso at best only accounts for less than 10% of its bitterness.

3.5.4. Aftertaste

In this case, when applying IPW on mean centered NIR spectra, a subset comprising eight wavelength bands was selected as significant for constructing a suitable regres-

Table 10

Chemical assignments of significant near-infrared bands selected by IPW–PLS for modelling mouthfeel (body) of espresso

| Selected wavelength (nm) | Bond vibration | Assignment |
|--------------------------|---|---|
| 1340 | 2 × C–H stretching + C–H deformation | Caffeine Carbohydrates (fibre content) |
| 1938 | O–H stretching + O–H deformation | H ₂ O |
| 1968 | C=O stretching second overtone (–CO ₂ R) | CGA |
| 1972/1978 | N–H asymmetric stretching + amide II | Protein |
| 1998/2008 | 2 × O–H deformation + C–O deformation | Carbohydrates (sucrose) |
| 2124 | N–H stretching + C=O stretching | Amino acids |
| 2142 | =C–H stretching + C=C stretching (HC=CH) | Caffeine Fatty acids (<i>cis</i> -unsaturation) |

Table 11

Chemical assignments of significant near-infrared bands selected by IPW–PLS for modelling bitterness of espresso

| Selected wavelength (nm) | Bond vibration | Assignment |
|--------------------------|---|--|
| 1116/1120/1122 | O–H stretching second overtone (ArOH) | CGA |
| 1124/1126 | 2 × C–H stretching + 2 × C–H deformation+(CH ₂) _n C–H stretching second overtone (Ar) | Fatty acids CGA |
| 1154 | C–H stretching second overtone (CH ₃) | Caffeine |
| 1730 | C–H stretching first overtone (CH ₂) | Fatty acids |
| 1838 | O–H stretching + 2 × C–O stretching | Carbohydrates (fibre content) |
| 1948 | O–H stretching + O–H deformation C=O stretching second overtone (–CO ₂ R) | H ₂ O CGA |
| 2066/2096 | O–H stretching + O–H deformation | Carbohydrates (fibre content) CGA/quinic acid (ROH) |
| 2148 | =C–H stretching + C=C stretching (HC=CH) | Caffeine Fatty acids (<i>cis</i> -unsaturation) |

Table 12

Chemical assignments of significant near-infrared bands selected by IPW–PLS for modelling aftertaste of espresso

| Selected wavelength (nm) | Bond vibration | Assignment |
|--------------------------|--|---|
| 1724/1728 | C–H stretching first overtone (CH ₂) | Fatty acids |
| 1908 | C=O stretching second overtone (–CO ₂ H) | CGA |
| 1916 | C=O stretching second overtone (CONH) | Caffeine |
| 1934 | O–H stretching + O–H deformation | H ₂ O |
| 2104 | O–H stretching + O–H deformation 2 × O–H deformation + 2 × C–O stretching | Carbohydrates (fibre content) |
| 2150 | =C–H stretching + C=C stretching (HC=CH) | Caffeine Fatty acids (<i>cis</i> -unsaturation) |
| 2170 | 2 × amide I + amide III CH ₂ asymmetric stretching + C= stretching (HC=CH) | Protein Fatty acids |

sion model for quantifying the aftertaste of espresso coffee (Table 12). The quality of aftertaste is directly related to the quality of original coffee, thus explaining the influence of certain caffeine vibrations due to its varietal distinctive ability. Another crucial factor affecting aftertaste is the ability to properly develop the flavour profile during roasting, in such a way that the inter-dependence of CGA, water and carbohydrates on roasting degree accounts for the presence of several characteristic vibrations of these types of compounds among selected NIR bands. Moreover, the contribution of CGA to aftertaste could have an additional justification, since certain perceptions involving a lingering ‘metallic’ aftertaste may be correlated with the relative quantities of these types of acids. As regards lipids, the assignment of a number of selected bands to fatty acids vibrations and, consequently, their influence on aftertaste could be easily explained by considering the extremely low surface tension presented by the ‘crema’ and caused by the presence of emulsified oils and solid fragments, which is largely responsible for a phenomenon such as aftertaste. Espresso concentration is responsible for high density and viscosity, and fundamentally determines the intense taste and long-lasting aftertaste sensations. Therefore, taking into account the huge influence on density and viscosity of the brew of both coffee lipids dispersed as an emulsion and protein content, it is hardly surprising that wavelength bands

attributable to them were suggested for modelling espresso aftertaste.

4. Conclusion

The high-quality results obtained in the present study confirm that non-destructive NIR spectroscopy measurements can be successfully applied for sensory quality estimation of espresso coffee. The use of the reliable regression models developed for predicting certain sensory properties makes the sensory characterisation of future espresso coffee samples easier, enabling not only more objective and faster determination, compared with that achieved when running repeated sensory panels, but also a more economical assessment, introducing a very promising tool for quality assurance purposes. All the advantages that could be derived from using NIR measurements as an alternative to sensory evaluation would not imply a significant decrease in the accuracy of the determinations, since both methods (NIR regressions and sensory panel) have showed quite similar capabilities in terms of reliability. The relationship between the sensory attributes studied and the significant wavelengths selected for modelling each property was shown to be based on the effect of coffee variety and roasting degree on both the sensory

attributes and physicochemical parameters recorded in NIR spectra.

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