# Durum wheat adulteration detection by NIR spectroscopy multivariate calibration

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## Abstract

In the present work, we explored the possibility of using near-infrared spectroscopy in order to quantify the degree of adulteration of durum wheat flour with common bread wheat flour. The multivariate calibration techniques adopted to this aim were PLS and a wavelet-based calibration algorithm, recently developed by some of us, called WILMA. Both techniques provided satisfactory results, the percentage of adulterant present in the samples being quantified with an uncertainty lower than that associated to the Italian official method. In particular the WILMA algorithm, by performing feature selection, allowed the signal pretreatment to be avoided and obtaining more parsimonious models.
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## 1. Introduction

NIR spectroscopy is nowadays a widespread technique used in many fields of analytical chemistry, including the quality control of foodstuffs [1–4]. In comparison with other analytical techniques, such as classical wet analysis, its advantages are essentially rapidity, cheapness and the fact of being a non-destructive method. Furthermore, in the last two decades, the application of NIR spectroscopy as routine quality control analysis has gradually increased thanks to the possibility of its on-line implementation [5–8].

In the field of cereal analysis, NIR spectroscopy in association with chemometrics has been used since the late seventies [9], being successful in modelling many quality variables, such as protein, moisture, dietary fibre contents, and wheat hardness [10–16]. More recently, the applications of NIR spectroscopy on cereals have been focused on the prediction, only partially successful, of functional and technological parameters, such as flour yield, percentage of damaged starch,

water absorption, dough development, time extensibility and loaf volume [9,12].

However, to our knowledge, an interesting composition-related aspect of wheat has not yet been considered. Wheat for human feeding can be essentially distinguished in two species, i.e., durum wheat (*Triticum durum*) and bread wheat (*Triticum aestivum*), which are characterized by different chemical and physical properties that give rise to different quality, nutritional contribution and, consequently, commercial value of the final products [17–20]. Italian law establishes that pasta can be made only by durum wheat semolina and water [21]. The addiction of bread wheat flour is an adulteration that leads to a product with a scarce resistance to cooking and therefore of lower quality. However, since the accidental contamination of semolina with bread wheat during harvesting, transport or storage remains possible, it is allowed the presence of bread wheat flour in percentages not higher than 3% [22]. The problem of durum wheat adulteration with common bread wheat is of particular interest in the Italian, French and Spanish markets, where semolina is the only allowed constituent for pasta, while in the north European countries both bread and durum wheat are allowed.

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Presently, the Italian official method for determining this type of fraud is the Resmini analysis [23,24], which is based on electrophoretical separation of albumins. The Resmini method gives repeatable results for percentages of bread wheat higher than 2% and in the 2–15% range, with an uncertainty of ±1%, while for greater amounts of adulterant the uncertainty is higher. Besides the Resmini method and other similar electrophoretical techniques [20,25], i.e., A-PAGE and SDS-PAGE, other methods are employed, such as real-time polymerase chain reaction (PCR) [26–28] and reverse-phase high performance liquid cromatography (RP-HPLC) of water-soluble proteins [29,30]. These methods provide a high sensitivity and a satisfactory accuracy, but they require specialized personnel, quite long analysis times and high costs. Therefore, frequently, the routine analysis laboratories make use of the immunological Durotest© kit (Rhone Poulenc Diagnostic Ltd.), that allows to detect the non-durum wheat adulteration of semolina using a mono-clonal antibody, which is specific to the protein friabilin, present only in bread wheat. If non-durum wheat is present in the sample, the friabilin and the antibody form a complex that, with the addition of a coloured staining reagent, assumes a blue–purple colour. The intensity of the colour, assessed with respect to a 3% non-durum wheat standard, is proportional to the percentage of adulterant and gives a semi-quantitative response, which is essentially used to estimate the presence or absence of non-durum wheat, rather than giving a quantitative response.

It is therefore clear that all the above described methods show some important drawbacks, and that it could be of great value to develop calibration models based on NIR spectra, able to furnish the percentage of adulterant within short times, in a simple manner, and with very low costs. The potential spreading of this approach could also be high, taking into account that nowadays most of the mills and of the pasta factories are already provided with NIR spectrophotometers, for monitoring process quality control.

At this time, the present work should be considered as a preliminary study in order to verify the potential efficacy of the proposed procedure, but it does not yet constitute a basis for implementing a method to be used in the routine control of commercial wheat samples. In fact, optimal operative conditions have been selected to evaluate if the NIR spectra show sufficient variation going from pure durum wheat semolina to mixtures containing small percentages of bread wheat. In order to eliminate the variability in the percentage of bread wheat flour due to the uncertainty associated with the traditional analytical methods, a set of artificial samples with known content of adulterant has been constructed. Only after the verification of the suitability of the proposed procedure, i.e. after demonstrating that NIR spectra contain relevant information in order to discriminate the two categories of wheat from which the flour is made, it will be possible to plan more realistic designs based on a wide set of commercial samples.

Since chemometrics has a fundamental role in NIRS based calibration, another important aspect to be taken into account is the method performance in deriving the calibration models [31,32]. In general, one of the most powerful chemometric techniques used in NIRS calibration is partial least squares (PLS), since it usually gives very stable regression models. Anyway, changes in the ambient and/or instrumental conditions can lead to modifications in the signal shape (e.g., baseline shift), which often result in a lower predictive capability of the models themselves, furthermore the presence of many uncorrelated/noisy variables can lead to not enough robust models. For this reason, both signal pretreatment techniques [33–35] and/or feature selection techniques coupled to the calibration step [36–38], can give more satisfactory results.

In this context, we propose the use of a novel feature selection/calibration algorithm recently implemented by some of us, wavelet interface to linear modelling analysis (WILMA) [39]. This algorithm makes use of the advantages offered by the wavelet transform [40–42], which is a signal analysis method capable of compressing in few variables (wavelet coefficients) the information contained in the signal, which is relevant to the prediction of the dependent variable (in our case, the percentage of bread wheat flour).

In the present work, PLS and WILMA were applied both on the raw and on the SNV pretreated spectra. The models obtained have been carefully validated both with the cross-validation procedure and with the use of two test sets, paying attention to avoid overfitting.

## 2. Experimental

### 2.1. Instrumentation

All spectra were acquired in reflectance mode using a FOSS NIRSystem 6500 spectrophotometer, equipped with a monochromator and a quartz sample cell, in the range 400–2498 nm with a 2 nm resolution.

### 2.2. Samples

Equal quantities of Italian durum wheat in grains and bread wheat in grains (belonging to the most diffuse national and international varieties) have been separately subjected to:

- a cleaning step using mechanical oscillating sieves to eliminate pebbles, straw and stunted kernels;
- a manual cleaning step for removing extraneous kernels;
- a conditioning step, by addition of distilled water, until they reached 17% of moisture after 24 h. This treatment makes easier the removal of the bran during the milling step.

After conditioning grains have been milled in proper roll mills, with a yield of 75%, and then they have been milled again with an electric mill Fritsch Pulverisette 14, equipped

with a sieve ring with trapezoid perforation 0.080 mm, reaching a more homogeneous particle size, in order to reduce scattering problems during acquisition of the NIR spectra.

The obtained durum and bread wheat flours have then been used to prepare 29 mixtures of durum wheat flour added with different percentages of bread wheat flour, ranging from 0 to 7%, with a step of 0.25%. In order to do that, the following procedure has been adopted:

- weighing at the fourth decimal digit, with a Mettler AE 200 balance, of the flour amounts necessary to furnish a 12 g sample;
- homogenisation in agate mortar for 10 min;
- sampling two replicates of 3 g each, suitable for the cell filling, by coning and quartering procedure, for a total of 58 samples (29 × 2 replicates).

In order to account for day-to-day variability, the first 29 samples have been analysed in a single day and in randomised order, while the respective replicates have been analysed the day after in reverse order.

### 2.3. Data analysis

All PLS calibration models have been calculated on the column-wise mean centred variables, both before and after the SNV pretreatment [33].

As far as WILMA is concerned, a detailed description of the algorithm may be found in the original article [39], while in the present work only its main aspects of interest are briefly explained.

WILMA essentially uses for calibration purposes the possibilities offered by the wavelet transform (WT) [40–42]. The efficacy of WT derives from its ability to represent the signal in an alternative domain as a function both of frequency (scale) and of the original domain. Therefore, WT allows modelling both point and shape characteristics of an instrumental signal. WILMA is based on the fast wavelet transform (FWT) decomposition, which consists in recursively splitting the low frequency content and the high frequency content of the signal into two orthogonal sub-spaces called approximations and details, respectively. The optimal calibration model is automatically selected by WILMA algorithm on the basis of the following procedure:

- each signal is decomposed into the wavelet domain by FWT until its maximum level of decomposition;
- the wavelet coefficients of each decomposition level are ranked either according to their variance ($V$) or to their squared values of the correlation coefficient ($R^2$) or of the squared covariance ($C^2$) with the response variable;
- for each level, the optimal number of wavelet coefficients is iteratively selected by crossvalidation using the leave one out (LOO) procedure either with multilinear regression (MLR, in this case high intercorrelated coefficients are also removed), or PLS;

- finally, the optimal decomposition level is chosen as the one giving the best results in LOO crossvalidation.

Once the optimal regression model (MLR and/or PLS) has been selected, it can be validated by means of an external test set, whose signals are decomposed in the FWT domain until the optimal decomposition level, in order to get the wavelet coefficients corresponding to those previously selected and used as descriptor variables.

Moreover, the wavelet coefficients selected with this procedure constitute a set of descriptor variables, which can be eventually fed also to different regression techniques, including non-linear methods, such as neural networks. In addiction, for interpretative purposes, both the selected wavelet coefficients and the calculated regression coefficients can be reconstructed into the original domain by the inverse FWT. This can help in focusing those signal regions, whose contribution is relevant to model the response variables.

One of the most important aspects when dealing with FWT in regression tasks is the choice of the best wavelet filters. In this work, 21 wavelets belonging to five different families were considered: daubechies (db1/db10); symlet (sym4, sym7, sym8); coiflet (coif1, coif3, coif5); biorthogonal (bior2.4, bior4.4) and reverse biorthogonal (rbio3.1, rbio3.3, rbio3.9). Both MLR and PLS regression techniques with column-wise mean-centering of the original signals have been applied to the wavelet coefficients, ranked according to the three different criteria, $R^2$, $C^2$ and $V$. All the combinations resulting from the parameters listed above have been tested, leading to 126 cycles of calculation.

The performance of the PLS and the WILMA models was evaluated by LOO crossvalidation and by two validation sets. In particular, the 58 samples have been divided in three subsets: a training set, composed by 30 samples; a monitoring set, of 14 samples; a test set, also comprising 14 samples. As far as the PLS models are concerned, the optimal number of latent variables has been chosen on the basis of the monitoring set and then the predictive capability has been evaluated on the test set. Conversely, with WILMA the monitoring set has been used in order to choose the best cycle of calculation among the 126 performed (as previously told, here the number of PCs is selected by LOO crossvalidation), while also in this case the test set has been used to finally evaluate the predictive capability of the selected model. The two replicates of each sample have been kept together in the same set. The subdivision of the samples in three sets has been performed randomly, with the only care of including in the training set samples showing the extreme values of bread wheat flour percentage.

### 2.3.1. Software

WILMA has been written in Matlab© ver. 6.1 language and uses some routines from the Wavelet Toolbox ver. 2.1 for Matlab© [43], and from the PLS Toolbox ver. 2.1.1 [44] for Matlab©, which has been also used to calculate the PLS models.
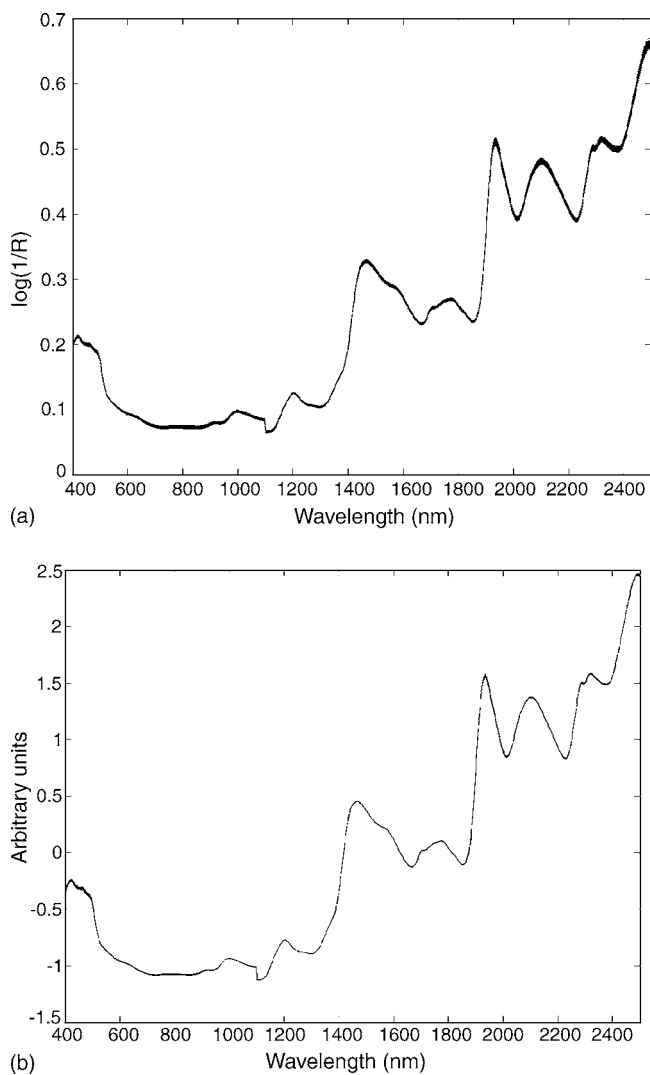
Fig. 1. NIR spectra of all the samples before (a) and after (b) the SNV pretreatment.

## 3. Results and discussion

All the acquired spectra are reported in Fig. 1, which shows the signals before (a) and after (b) SNV normalization. It is possible to notice that the original spectra present a light vertical shift of the baseline, affecting all the spectral region,

which is probably due to little differences in the scattering behaviour of the samples. As it can be seen, this baseline shift can be successfully eliminated pretreating the signals by SNV. The discontinuity of the signal at 1100 nm is caused by the change of the detector, from the silicon diode array to the lead sulphide photoconductor.

Table 1 reports the results of the regression models calculated both on the raw and on the SNV pretreated spectra by PLS and only on the raw spectra by WILMA. In fact, in this case, the results obtained from the SNV pretreated spectra were very similar and showed no improvement with respect to those obtained from the raw spectra. This is a consequence of the fact that the variable selection performed in the wavelet domain removes implicitly the uninformative variability, making the SNV pretreatment unnecessary. As far as WILMA is concerned, only the results relative to the best models obtained for each regression technique and ranking criterion have been reported. The models highlighted in grey are those considered as the best performing ones and are discussed in detail.

As for PLS, it is clear that the spectra pretreatment improves the quality of the model both in calibration and in prediction. The predicted versus experimental plot of the PLS model computed on the normalized spectra, which is reported in Fig. 2, confirms that all the samples are modelled satisfactorily. Furthermore, the root mean squares errors of calculations (RMSEC) and of prediction (RMSEP) values are comparable and around 0.5% (the root mean squared errors are expressed in the same scale as the percentage of bread wheat flour present in the samples), which is lower than the 1% associated with the Italian official method.

The plot of the pseudo-regression coefficients of this model (Fig. 3) provides some indications about the spectral regions that are mainly correlated with the response variable. It is interesting to notice that the model keeps information from most part of the spectral range, but in particular from the visible region, with the exclusion of the 1100–1400 nm region.

As for the WILMA models, they have, in general, a predictive capability similar to that of the SNV–PLS model, using a relatively low number of coefficients. As it can be seen, the different WILMA models present similar performances, hence we decided to discuss the best calibration

Table 1
Performance of the best calibration models developed by PLS and WILMA

| Regression method | Pretreatment | Ranking criterion | Wavelet | n°cfs | n°LV | RMSEC | RMSECV | RMSEP$_{mon}$ | RMSEP$_{test}$ |
|---|---|---|---|---|---|---|---|---|---|
| PLS | None | | | 1050 | 6 | 0.5334 | 0.8126 | 0.5056 | 0.5215 |
| | SNV | | | 1050 | 8 | 0.2903 | 0.7215 | 0.4165 | 0.3974 |
| WILMA–MLR | | $C^2$ | db1 | 7 | – | 0.4627 | 0.6013 | 0.5040 | 0.4863 |
| | None | $R^2$ | coif3 | 4 | – | 0.5790 | 0.6889 | 0.6679 | 0.5602 |
| | | $V$ | db6 | 8 | – | 0.3242 | 0.4569 | 0.7320 | 0.5041 |
| WILMA–PLS | | $C^2$ | db6 | 50 | 7 | 0.3913 | 0.6335 | 0.5889 | 0.4684 |
| | None | $R^2$ | db8 | 60 | 7 | 0.3276 | 0.6264 | 0.5077 | 0.4470 |
| | | $V$ | db8 | 57 | 7 | 0.3138 | 0.8124 | 0.6144 | 0.5141 |

The calibration models selected for discussion are highlighted in grey colour.
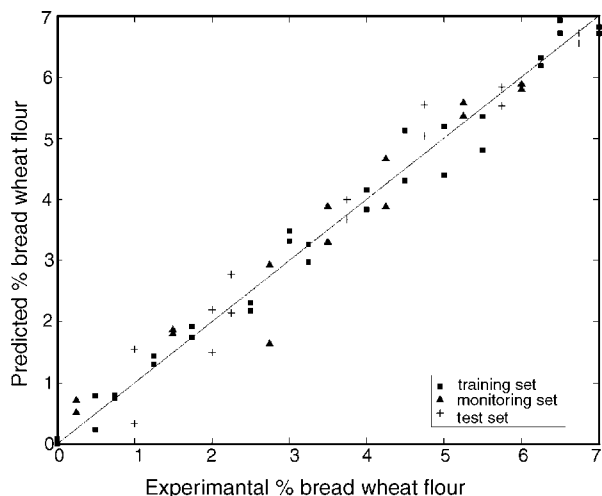
Fig. 2. Predicted vs. measured plot for the PLS model obtained on the normalized spectra.

model obtained using the PLS regression technique (with $R^2$ as ranking criterion and with the db8 wavelet) in order to get direct comparison with the simple SNV–PLS model. Fig. 4 reports the plot of the predicted versus experimental values for the WILMA–PLS model highlighted in grey in Table 1. This calibration model is quite parsimonious both for the number of coefficients (60) and for the number of latent variables (7). The root mean squared errors are still acceptable and remain lower than 1%.

Since only a part of the information contained in the original spectra has been selected, the signals reconstructed in the original domain from the selected wavelet coefficients look very different with respect to the original spectra, as it can be observed in Fig. 5. Comparing the reconstructed signals with the original spectra it is possible to identify the more relevant regions, which contain information correlated with the response variable. According to the PLS pseudo-regression coefficients plot of Fig. 3, WILMA has extracted
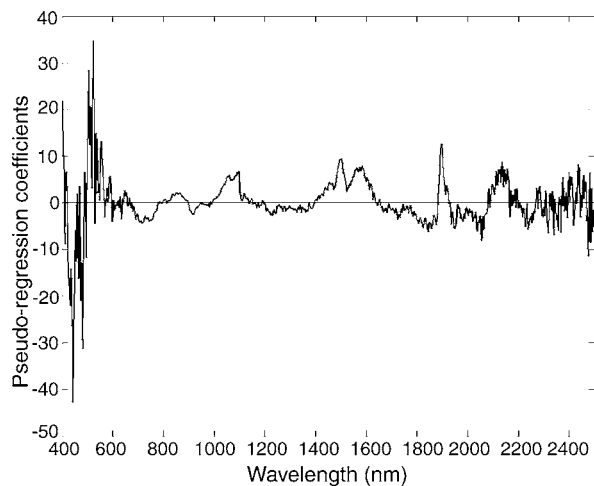


Fig. 3. Pseudo-regression coefficients plot for the PLS model obtained on the normalized spectra.
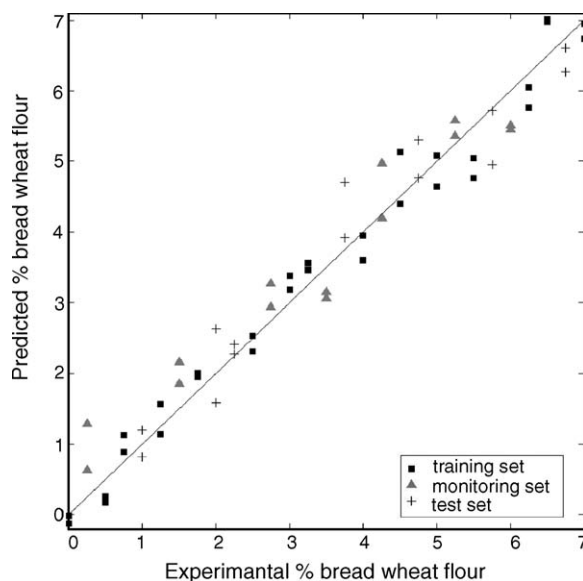


Fig. 4. Predicted vs. measured plot for the WILMA model obtained on the raw spectra with a db8 wavelet, level 7, PLS as regression technique and $R^2$ as the ranking criterion.
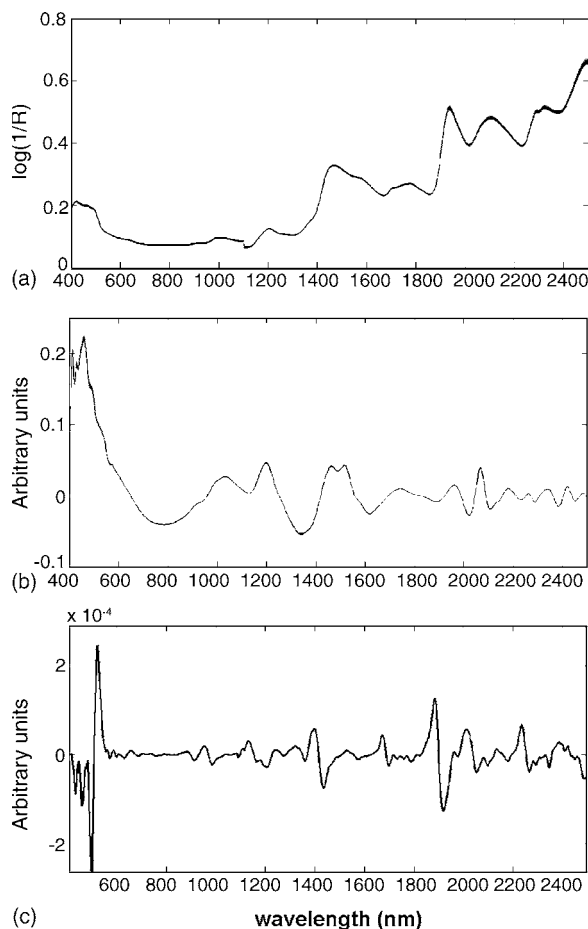


Fig. 5. Comparison between the NIR spectra of all the samples (a); the reconstructed spectra in the original domain on the basis of the wavelet coefficients selected by the WILMA model (b) and the difference spectra, after taking the second derivative, between a pure durum wheat sample and a pure wheat flour sample (c).

useful information along all the spectral range, and particularly in the visible region between 400 and 500 nm. Other relevant regions are those in the ranges 1000–1200, 1400–1600 and 2000–2100 nm, which in the major part have been also selected from the PLS model. It is interesting to notice that the same spectral regions have been also selected by several others among the WILMA calculation cycles reported in Table 1, this convergence confirms the statistical significance of those signal regions.

In the literature [3] different attributions of the NIR bands lying in these spectral regions are cited, relative to agricultural and food products. In particular, the overtones of the C–H bonds of the methylic and methylenic groups between 1170 and 1230 nm, the bands of the O–H bonds due to water and starch at about 1450 and 1940 nm, and the bands of the N–H bonds at about 1500–1570 and 2050–2070 nm are mentioned. The spectral region at higher wavelengths is characterized by the absorptions of constituents like starch, cellulose and protein. Part of this information has been probably used by WILMA also for the baseline correction.

The results obtained in this work suggest that the presence of bread wheat flour in durum wheat one produces a detectable effect on the corresponding NIR spectra.

The raw spectra of a pure durum wheat sample and a pure wheat flour sample are indeed very similar, by their direct comparison it is only possible to observe that the durum wheat spectrum is characterized by higher absorption in the visible frequency range from 400 to about 550 nm and by a lower moisture content, lower absorption at 1940 nm. However, by looking at the difference between the spectra of a pure durum wheat sample and a pure wheat flour sample, after taking the second derivatives (Fig. 5c), which allows to remove background effects and to partially resolve overlapping peaks, differences can be observed generally in the same regions where the reconstructed signals from the selected wavelet coefficients (Fig. 5b) show significant contributions. As discussed above, on the basis of the literature attributions, we may think that the chemical constituents mainly determining the durum wheat/wheat flour discrimination are protein, lipids and moisture. This is in agreement with previous studies [17,18] where a classification between the two categories was achieved on the basis of the content of these components after their extraction by wet methods from the wheat matrix.

Therefore, a method based on NIR spectroscopy coupled with the chemometric analysis of the signals could be possible, in order to individuate this alimentary fraud. Both PLS and WILMA regression models have shown good predictive performance. In fact, the uncertainties associated to this models are about one half with respect to the uncertainty of the Italian official method. As a consequence, NIR spectroscopy, already characterized by the advantages of rapidity, cheapness and accuracy, may find a new application. Even if the use of the WILMA algorithm does not lead to improved quality of the calibration models in terms of predictive capability, it allows obtaining more parsimonious calibration models. Moreover, the signals pretreatment step becomes unnecessary when such a method is used. These results, even if obtained on a limited number of samples can be seen as an exciting starting point for the extension of the procedure to practical applications, even if a lot of work is still needed in this direction. In effect, encouraged from this evidences, it is now possible to consider a wide number of "real" samples from the trade, in order to construct calibration models and to perform extended validation.

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