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Chemometrics and Intelligent Laboratory Systems 74 (2004) 243–251

Chemometrics and intelligent laboratory systems

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Spectrophotometric variable selection by mutual information

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Received 3 December 2003; received in revised form 27 January 2004; accepted 21 April 2004
Available online 24 July 2004

Abstract

Spectrophotometric data often comprise a great number of numerical components or variables that can be used in calibration models. When a large number of such variables are incorporated into a particular model, many difficulties arise, and it is often necessary to reduce the number of spectral variables. This paper proposes an incremental (Forward–Backward) procedure, initiated using an entropy-based criterion (mutual information), to choose the first variable. The advantages of the method are discussed; results in quantitative chemical analysis by spectrophotometry show the improvements obtained with respect to traditional and nonlinear calibration models.

Keywords: Spectrophotometric variable selection; Mutual information; Spectrophotometry

1. Introduction

The infrared spectra of agricultural and food products contain information that presents an analytical interest. However, the extraction of this information is not immediate and requires almost always a rather complex mathematical treatment. Indeed, the spectra are the result of an interaction of light with matter that cannot completely be described from a theoretical point of view.

This paper focuses particularly on the application of chemometrics in the field of analytical chemistry. Chemometrics (or multivariate analysis) consists of finding a relationship between two groups of variables, often called dependent and independent variables. In infrared spectroscopy for instance, chemometrics consists of the prediction of a quantitative variable (the obtention of which is delicate, requiring a chemical analysis and a qualified operator), such as the concentration of a component present in the studied product, from spectral data measured on various wavelengths or wave numbers (several hundreds, even several thousands).

From a chemometric point of view, the spectrum obtained in infrared spectroscopy is a complex function that depends on both the physical and chemical properties of the sample [1], and has remarkable characteristics that require specific methods for their treatment.

The spectrophotometric data may often comprise more independent variables (spectral data) than observations (spectra or samples). This case is rather less encountered in other applications of statistics. Collinearity of the independent variables is typical for spectrophotometric data, that is, certain independent variables can be practically represented as a linear combination of other independent ones; this is the source of many problems in direct application of many statistical methods, such as the multiple linear regression (MLR) [2–6]. Studies have shown that if collinearity is present among variables, the prediction results can get poor (see for example Refs. [4,7]). This limitation has promoted other alternative linear methods to offset the problems generated by the strong redundancy between variables. Several alternatives that are able to adapt to this collinearity were developed, such as stepwise multiple linear regression (SMLR) [3,8–11], principal component regression (PCR) [5,6,10,12,13], partial least square regression (PLSR) [3,6,10,12–16], and so forth.

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doi:10.1016/j.chemolab.2004.04.015

In analytical chemistry, a lot of linear calibration methods (mentioned above) are applied to solve quantitative problems with the argument that the relation between the chemical composition and the measured signal is linear [17]. However, there are many situations where nonlinearity is present. For instance, Miller [18] discusses important sources of nonlinearity in near-infrared spectroscopy, namely

- deviations from the Beer–Lambert law, which are typical of highly absorbing samples;
- nonlinear detector responses;
- drifts in the light source;
- interactions between analytes;
- nonlinearity between diffuse reflectance/transmittance data and chemical data.

When the nonlinearity is significant, one can use truly nonlinear calibration techniques, for example, artificial neural networks (ANN).

The purpose of this study is to predict the concentration (dependent variable) of analyte present in a studied product from independent variables, which are spectral data measured on various wavelengths. Because spectrophotometric data have specific characteristics (a.o. collinearity), it is necessary to select independent variables among the candidates to build a still suitable model with only few variables. The objective of variable selection is three-fold: improving prediction performances, providing faster and more cost-effective prediction, and providing a better understanding of the underlying process that generated the data [19].

In Ref. [20], we proposed a procedure for spectral data selection in infrared spectroscopy based on the combination of three principles: linear or nonlinear regression, incremental procedure for variable selection, and use of a validation set. This procedure allows on one hand to benefit from the advantages of nonlinear methods to predict chemical data (there is often a nonlinear relationship between dependent and independent variables), and on the other hand to avoid the overfitting phenomenon, one of the most crucial problems encountered with nonlinear models. In this paper, we suggest to improve this method by a judicious choice of the first spectral data, which have a very high influence on the selection of other variables and on the final performances of the prediction.

In the first iteration of the incremental procedure, a model is built with only one independent variable. Although the intrinsic dimensionality of the spectra is less than the hundreds of variables used to describe them, one variable is definitely not enough to rightly characterize a spectrum. As a consequence, building a regression model with only one independent variable hardly makes sense; its expected results are very poor and should not be used "as-is" to initiate the incremental procedure. That is why we suggest not to build any model in the first iteration but rather trust a model-independent criterion for the choice of the first spectral variable.

The idea is to use a measure of the mutual information between the spectral data (independent variables) and the concentration of analyte (dependent variable) to select the first variable; indeed, this measure allows to identify the variable (spectral data) having the highest relation to the analyte. Once the first variable is selected the incremental procedure (forward–backward selection, FBS) [20] is used to select the next spectral variables.

If the idea of using a mutual information criterion for the choice of the other spectral data can also seem relevant, its implementation becomes more and more difficult when the number of selected variables increases. Indeed, we will see in the next section that estimating the mutual information between a group of k variables and another one requires the estimation of a $(k+1)$-dimensional joint probability density function (pdf). As k increases, that estimation gets less and less accurate because of the lack of sufficient number of examples and the inherent so-called "empty space phenomenon" [21]. We will thus limit the use of mutual information criterion to the crucial choice of the first spectral variable; we will see in the Results section that it is advantageous to combine the two approaches.

Furthermore, the variable selected by mutual information can have a good interpretation from the spectrochemical point of view and does not depend on the data distribution in the training and validation sets. On the other hand, the traditional chemometric linear methods such as PCR or PLSR produce new variables that do not have an obvious interpretation from the spectrochemical point of view.

In this work, we will first explain how mutual information can be used to assess the importance of each variable (spectral data) with respect to the calibration model. Then, we will propose the new variable selection method based on the combination of two ideas: the mutual information to select the first variable and then the application of the FBS-radial basis function network (RBFN) method [20] to select the next ones. Lastly, we will present a comparison of prediction results between the improved and PCR, PLSR, and FBS-RBFN methods.

2. Mutual information

In this section, we will explain how the mutual information can be used to assess the relevance of an independent variable to predict a dependent variable.

2.1. Definitions

The first goal of a prediction model is to minimize the uncertainty on the dependent variable. A good formalization of the uncertainty of a random variable is given by Shannon and Weaver's [22] information theory. While first developed for binary variables, it has been extended to continuous variables.

The uncertainty of a random variable $\mathbf{y}$ with values v in a finite set D can be measured by its entropy H:

$$H(\mathbf{y}) = -\sum_{v\in D} P(\mathbf{y}=v)\cdot \log P(\mathbf{y}=v). \quad (1)$$

To illustrate this concept, let us suppose that in an extreme case all values $v \in D$ have null probability except one, say $v*$, which has a probability equal to 1, that is,

$$P(\mathbf{y}=v) = \begin{cases} 1 & \text{if } v = v^* \\ 0 & \text{otherwise.} \end{cases} \quad (2)$$

The entropy is thus $H(\mathbf{y})=0$; indeed there is absolutely no uncertainty since $\mathbf{y}$ always has value v^*.

Suppose on the other hand that all values in D are equiprobable:

$$\forall v\in D : P(\mathbf{y}=0) = \frac{1}{\#D} \quad (3)$$

Uncertainty is then maximal since no value is more probable than others. In this case, it is possible to show that the entropy is maximal too: $H(\mathbf{y})=\log \#D$.

When the value of another variable $\mathbf{x}_i$ with values v' in D' is known, one can define the conditional entropy:

$$H(\mathbf{y}\mid \mathbf{x}_i) = -\sum_{v'\in D'} P(\mathbf{x}_i=v') \sum_{v\in D} P(\mathbf{y}=v\mid \mathbf{x}_i=v') \times \log P(\mathbf{y}=v\mid \mathbf{x}_i=v'). \quad (4)$$

This represents the uncertainty on $\mathbf{y}$ when $\mathbf{x}_i$ is known. The difference between the uncertainty on $\mathbf{y}$ and the uncertainty on the same variable knowing $\mathbf{x}_i$ is called the mutual information between $\mathbf{x}_i$ and $\mathbf{y}$:

$$I(\mathbf{y},\mathbf{x}_i) = H(\mathbf{y}) - H(\mathbf{y}\mid \mathbf{x}_i) \quad (5)$$

It represents the decreasing of uncertainty on $\mathbf{y}$ when $\mathbf{x}_i$ is known. Reexpressing $P(\mathbf{y}=v|\mathbf{x}_i=v')$ as $P(\mathbf{y}=v\wedge\mathbf{x}_i=v')/P(\mathbf{x}_i=v')$, one can show that

$$I(\mathbf{y},\mathbf{x}_i) = \sum_{v\in D;v'\in D'} P(\mathbf{y}=v\wedge \mathbf{x}_i=v') \times \log \frac{P(\mathbf{y}=v\wedge \mathbf{x}_i=v')}{P(\mathbf{y}=v)\cdot P(\mathbf{x}_i=v')} \quad (6)$$

This formulation shows that the mutual information between $\mathbf{x}_i$ and $\mathbf{y}$ is zero if and only if $\mathbf{x}_i$ and $\mathbf{y}$ are statistically independent. Furthermore, the mutual information is not affected by any variable transformation and does not make any assumption on the underlying relationship between $\mathbf{x}_i$ and $\mathbf{y}$.

The concepts of entropy, conditional entropy and mutual information, can be extended to the continuous case (set D of infinite size).

The uncertainty of a continuous random variable $\mathbf{y}$ with probability density function (pdf) $f(\mathbf{y})$ is given by:

$$H(\mathbf{y}) = -\int f(\mathbf{y})\log f(\mathbf{y})\mathrm{d}\mathbf{y} \quad (7)$$

and the conditional entropy when $\mathbf{x}_i$ is known:

$$H(\mathbf{y}\mid \mathbf{x}_i) = -\int f(\mathbf{x}_i)\int f(\mathbf{y}\mid \mathbf{x}_i)\cdot \log f(\mathbf{y}\mid \mathbf{x}_i)\mathrm{d}\mathbf{y}\mathrm{d}\mathbf{x}_i. \quad (8)$$

The mutual information between variables $\mathbf{y}$ and $\mathbf{x}_i$ may be expressed by [23,24]:

$$I = \int h(\mathbf{x}_i,\mathbf{y})\cdot \log \frac{h(\mathbf{x}_i,\mathbf{y})}{f(\mathbf{x}_i)\cdot g(\mathbf{y})}\mathrm{d}\mathbf{x}_i\mathrm{d}\mathbf{y}, \quad (9)$$

where $f(\mathbf{x}_i)$ and $g(\mathbf{y})$ are the marginal probability densities of variables $\mathbf{x}_i$ and $\mathbf{y}$, respectively, and $h(\mathbf{x}_i, \mathbf{y})$ is the joint probability density function of $\mathbf{x}_i$ and $\mathbf{y}$.

Since

$$f(\mathbf{x}_i) = \int h(\mathbf{x}_i,\mathbf{y})\mathrm{d}\mathbf{y}, \quad (10)$$

and

$$g(\mathbf{y}) = \int h(\mathbf{x}_i,\mathbf{y})\mathrm{d}\mathbf{x}_i, \quad (11)$$

we only need to estimate $h(\mathbf{x}_i, \mathbf{y})$ to estimate the mutual information between $\mathbf{x}_i$ and $\mathbf{y}$.

2.2. Estimation of the mutual information

As we saw in the previous section, estimating the mutual information between $\mathbf{x}_i$ and $\mathbf{y}$ requires the estimation of the joint probability density function of $\mathbf{x}_i$ and $\mathbf{y}$. This estimation has to be carried on the data set. Histogram- and kernel-based pdf estimations are among the most commonly used [25]. In this study, we used histogram estimation for its reduced computation requirements.

Because we need to estimate the joint density $h(\mathbf{y}, \mathbf{x}_i)$, we must construct a bidimensional histogram $\{\hat{h}_{k,j}\}(1\le k\le m, 1\le j\le n)$ approximating the bidimensional pdf surface with a set of rectangular tiles (cells) $\{[a_k, a_{k+1}]\times[b_j, b_{j+1}]\}$.

The procedure starts by building the set of tiles as a bidimensional grid $[a_1,\ldots, a_{m+1}]\times[b_1,\ldots, b_{n+1}]$ spanning the Cartesian product of the respective ranges of $\mathbf{x}_i$ and $\mathbf{y}$. Then, the number of pairs $(\mathbf{x}_i, \mathbf{y})$ that fall into a particular cell $[a_k, a_{k+1}]\times[b_j, b_{j+1}]$ has to be counted:

$$\hat{h}_{k,j} = \#\{(\mathbf{x}_i,\mathbf{y}) \mid a_k\le \mathbf{x}_i < a_{k+1} \text{ and } b_j\le \mathbf{y} < b_{j+1}\}. \quad (12)$$

The sizes $(a_{k+1}-a_k)$ and $(b_{j+1}-b_j)$ of the cells are important parameters that have to be chosen carefully. If the cells are too large, the approximation will not be precise enough; if they are too small, most of them will be empty and the approximation will not be sufficiently smooth. Even

though heuristics were proposed [26–28] to guide this choice, only experiments can lead to an optimal choice.

Once the histogram has been constructed, it can be used to estimate $h(\mathbf{y}, \mathbf{x}_i)$. Marginal densities $f(\mathbf{x}_i)$ and $g(\mathbf{y})$ can also be estimated using $\hat{h}_{k,j}$ thanks to Eq. (10) and (11):

$$\hat{f}_k = \sum_j \hat{h}_{k,j} \; ; \; \hat{g}_j = \sum_k \hat{h}_{k,j} \tag{13}$$

From there, estimating the mutual information (Eq. (9)) simply consists in computing

$$\hat{I}(\mathbf{y}, \mathbf{x}_i) = \sum_{k,j} \hat{h}_{k,j} \cdot \log \frac{\hat{h}_{k,j}}{\hat{f}_k \cdot \hat{g}_j}. \tag{14}$$

In the next section, we will see how the mutual information can be used in the context of variable selection.

3. Variable selection and validation by nonlinear models

In the Introduction, we highlighted the need for the selection of independent variables, in order a.o., to reduce the problems related to collinearity.

The problem of variable selection can be defined as follows: given a set of candidate variables, select a subset that performs best (according to some criterion) in a prediction system. More specifically, let $\mathbf{x}_i$, $1 \le i \le N$ be the original spectral data variables. The objective is to find a subset of $\mathbf{x}_i$ containing d variables ($d < N$) that will be used to build an adequate model [4,29].

In the literature, often the PCR and PLSR methods are used in near-infrared spectroscopy. These methods make the assumption of the existence of a linear relation between the spectral variables on one hand and the characteristic to be predicted on the other hand. This can obviously not be the case in the reality of certain applications in analytical chemistry, leading to the need for using nonlinear models instead of linear ones.

Given this limitation, in Ref. [20] we proposed a spectral data selection method based on the combination of three principles mentioned in Section 1. The combination of these three principles leads to enhanced calibration capabilities (compared to linear methods), to an efficient compromise between inefficient and exhaustive searches of the variables to select, and to an objective assessment of the performances. It should be noted that the nonlinear model used in the variable selection method is a radial basis function networks (RBFN) [30].

In this study, we suggest to improve this method by combining it with a measure of the mutual information between the dependent and independent variables. A measure of mutual information between the dependent and independent variables is used to select the first variable and the spectral data selection method is then used to select the next variables. We will show that a judicious choice of the first selected variable has a very high influence on the selection of the other variables and on the final performances of the prediction.

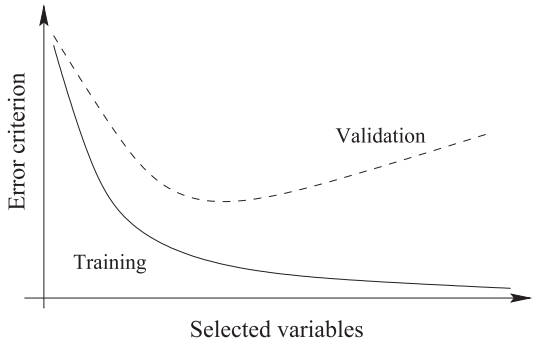


Fig. 1. Typical evolution of the performances of training and validation.

3.1. Selection procedure

The improved variable selection procedure that will be used in the nonlinear prediction model is the following.

First let us imagine that m observations, that is, m spectra, are at disposal. The set of m spectra has to be split into two independent parts: a training set with N_T spectra and a validation set with N_V spectra, so that $N_T + N_V = m$. The reason is a basic principle in modeling: to avoid the overfitting phenomenon, and therefore to avoid an optimistic estimation of the performance of a model, on should never validate a model on the same data used for the learning. Furthermore, Fig. 1 shows that the evolution of the performances of a model versus its complexity can lead to an optimum only when these performances are evaluated on a validation set (on the contrary, an error measured on the learning set always decreases with complexity). The complexity is here measured in terms of the number of selected variables.

More formally, one defines:

$$T = \{(x^j, y^j) \in \Re^n \times \Re, 1 \le j \le N_T, y^i = f(x^j)\} \tag{15}$$

$$V = \{(x^j, y^j) \in \Re^n \times \Re, N_T + 1 \le j \le N_T + N_V, y^j = f(x^j)\}. \tag{16}$$

In this definition, it has been supposed that the first N_T spectra (according to their numbering) have been attributed to the learning set, while the last N_V ones have been attributed to the validation set. In practice, a random draw is performed among the m spectra to select the two sets. As the numbering of the spectra is irrelevant, the above hypothesis is not restrictive.

Then, the following two steps are performed:

1. The first selected spectral data is the one that maximizes the mutual information with the dependent variable,

according to the estimation method detailed in the previous section.

2. Other spectral data are selected according to the forward–backward selection procedure with RBF networks (FBS-RBFN) [20]:
   - Forward selection: once k variables have been selected ($k=1$ in the first iteration), $p-k$ models with $k+1$ variables (the selected k and, respectively, each of the other ones) are built and compared according to an error criterion on a validation set; the variable corresponding to the minimum of the error criterion is added. The 'forward' process is repeated for $k=2, 3,\ldots$, until the value of the error criterion (on the validation set) increases.
   - Backward selection: it consists of eliminating the least significant spectral data already selected in the 'forward' stage. If q spectral variables were selected after the 'forward' stage, q models are built by removing, respectively, one of the selected variables. The error criterion on a validation set is calculated for each of these models, and the one with the lowest error is selected. Once the model is chosen, we compare its error to the error of the model obtained at the preceding stage. If the error criterion corresponding to the new model is lower, then the selected spectral variable is not significant and may be removed. The process is then repeated on the remaining spectral variables. The backward selection is stopped when the lowest error among all models calculated at a specific step is higher than the error at the previous step.

It should be noted that during Step 1, we only need the training set since the computation of the mutual information does not require the estimation and the comparison of models. On the other hand, for Step 2, it is necessary to use other data (validation set) independent from the training set for the computation of the error criterion.

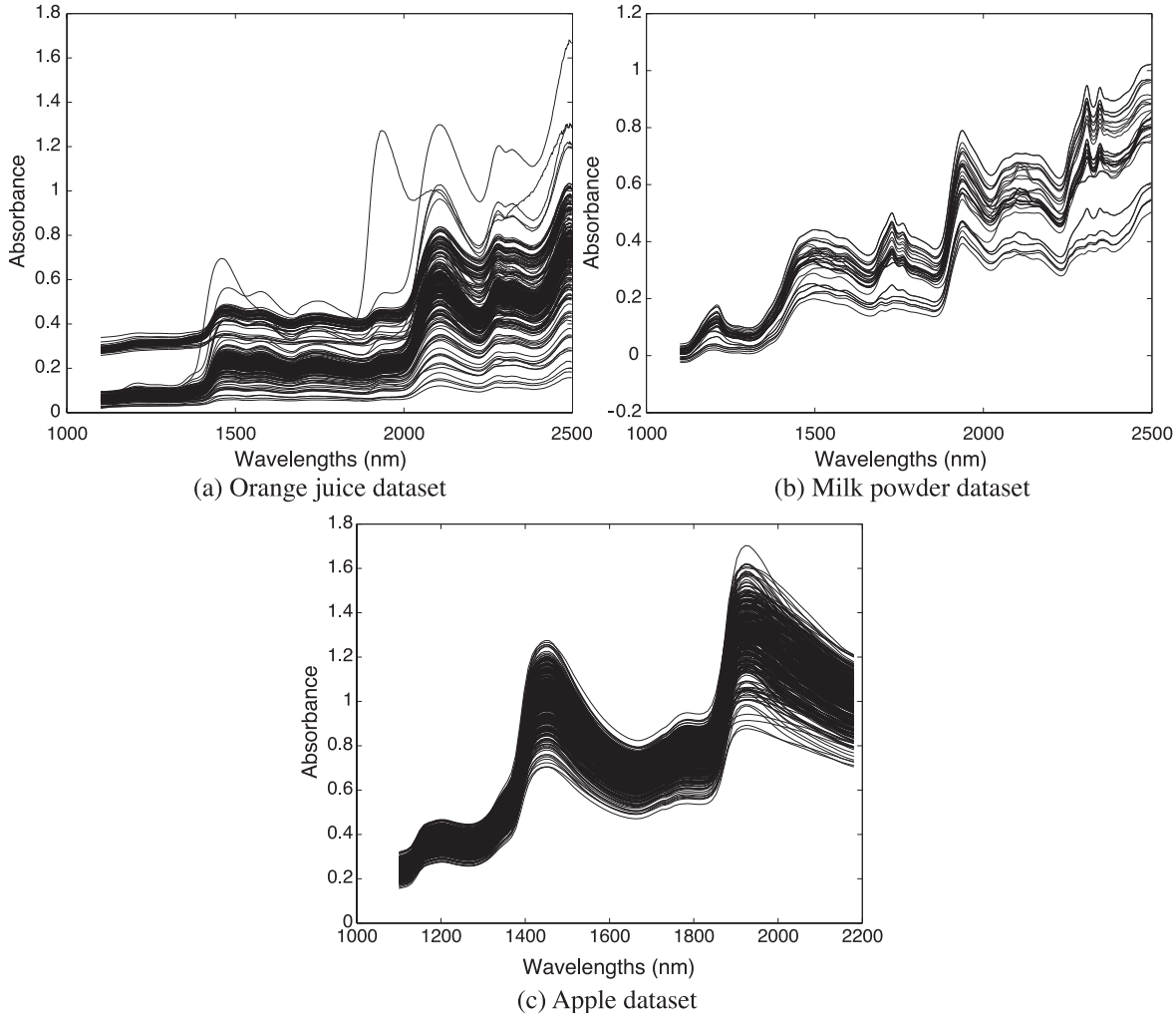


Fig. 2. Near-infrared reflectance spectra of three data sets.

Table 1
Number of selected variables and their corresponding $NMSE_V$ for the three data sets

Data set	Calibration model	Number of variables	$NMSE_V$
Orange juice	PCR	42	0.2596
	PLSR	16	0.2435
	FBS-RBFN	13	0.0703
	MI + FBS-RBFN	36	0.0313
Milk powder	PCR	10	0.9250
	PLSR	7	0.8758
	FBS-RBFN	6	0.5309
	MI + FBS-RBFN	18	0.4816
Apple	PCR	7	0.6721
	PLSR	4	0.6029
	FBS-RBFN	8	0.2787
	MI + FBS-RBFN	12	0.2321

3.2. Error criterion

As mentioned in Step 2 above, the respective errors of several models must be evaluated on data independent from the one used for learning, that is, data from a validation set. The error criterion can be chosen as the normalized mean square error ($NMSE_V$) defined as [31]:

$$\mathrm{NMSE}_V = \frac{\frac{1}{N_V}\Sigma_{j=N_T+1}^{N_T+N_V}(\hat{y}^j - y^j)^2}{\frac{1}{N_T+N_V}\Sigma_{i=1}^{N_T+N_V}(y^i - \bar{y})^2}, \quad (17)$$

where $\hat{y}^j$ is the value predicted by the model and y^j is the actual value corresponding to jth spectrum.

3.3. Data sets

Three data sets were chosen to illustrate this study. The first data set relates to the determination of sugar (saccharose concentration) by near-infrared reflectance spectroscopy in orange juice samples (see Fig. 2a). In this case, the training and validation sets contain 150 and 68 dry extract spectra, respectively, with 700 spectral variables that are the absorbances (log $1/R$) at 700 wavelengths between 1100 and 2500 nm (where R is the light reflectance on the sample surface). The second data set consists of near-

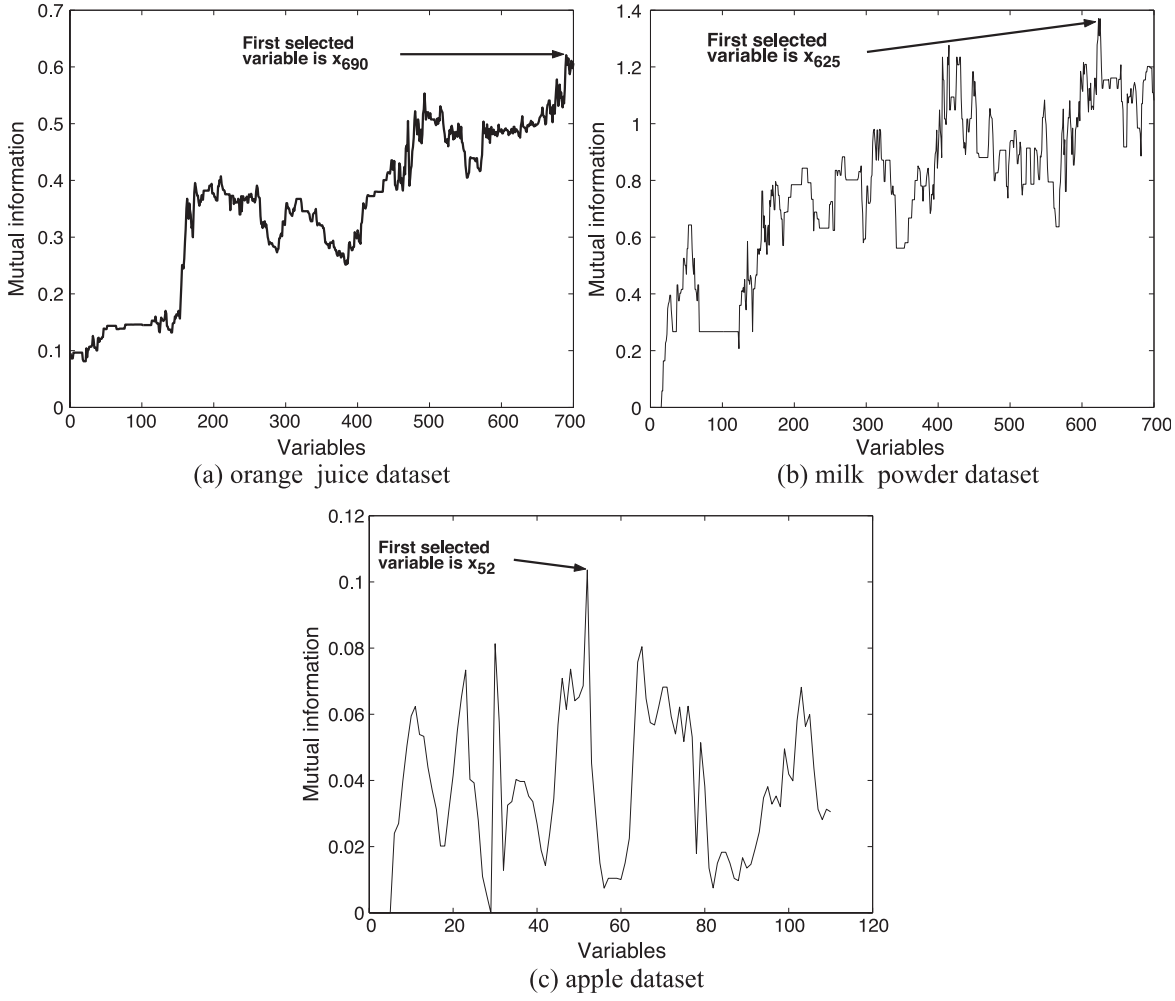


Fig. 3. Spectrum of the mutual information between the independent and dependent variables for the three data sets.

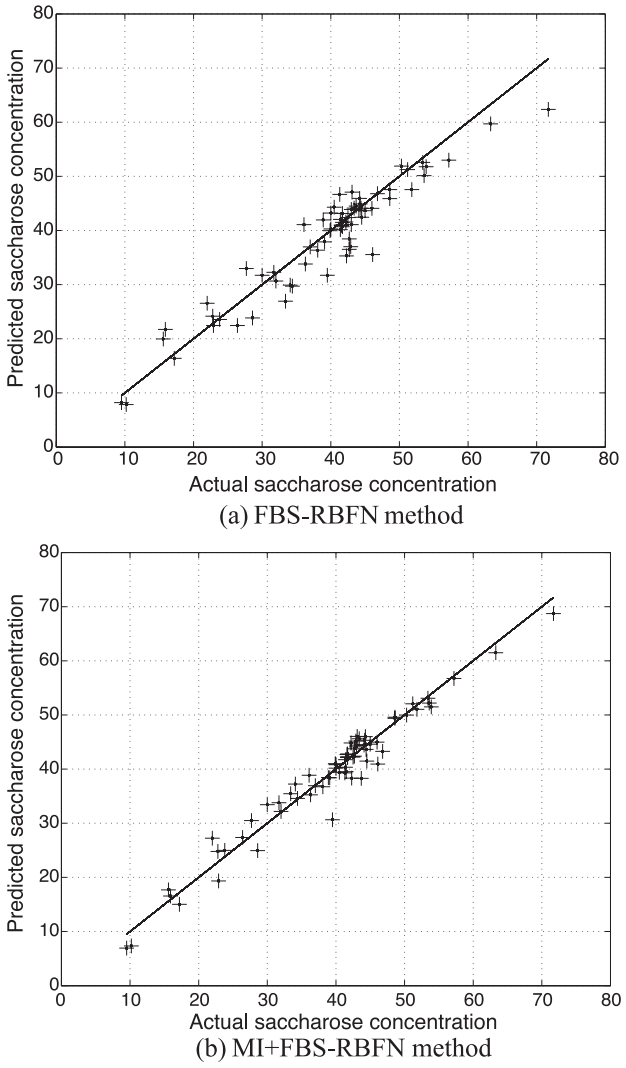


Fig. 4. Predicted value in function of measured value in the orange juice data set.

infrared spectra of milk powder obtained in the wavelength range from 1100 to 2500 nm at regular intervals of 2 nm (see Fig. 2b). The y value to predict is the water content in the milk powder. The training and validation sets consist of 27 and 10 samples, respectively, with 700 spectral variables that are the absorbance (log $1/R$) at 700 wavelengths. The third data set concerns the near-infrared reflectance spectra of apples and the prediction of the crushing force that should be employed to insert an object (stem or marble) in the skin of an apple to determine if it is too ripe or not (see Fig. 2c). This force is proportional to the firmness of the flesh. If an apple is not too ripe and is well crunching, it will be firm and the crushing force will be high. The apple spectra are measured by near-infrared reflectance spectroscopy. The training and validation sets contain 225 and 112 spectra, respectively, with 110 spectral variables that are the absorbance (log $1/R$) at 110 wavelengths between 1100 and 2190 nm.

4. Results and discussion

We applied the new variable selection method described in Section 3 to the three data sets (orange juice, milk powder, and apple).

In Table 1, the predictive ability of the PCR, PLSR, FBS-RBFN, and MI + FBS-RBFN models is compared in terms of normalized mean square error ($NMSE_V$) on a validation set. The new method presented in this paper is denoted MI + FBS-RBFN, for mutual information and forward–backward selection with radial-basis function networks.

Fig. 3 shows the spectrum of mutual information between the independent variables and the dependent one on the training set for the three data sets. In the case of the orange juice data set (see Fig. 3a), the first selected variable by the MI + FBS-RBFN method is $\mathbf{x}_{690}$. This variable corresponds to the end of the spectrum where the absorbance (log $1/R$) is high, that is, where the relationship is less

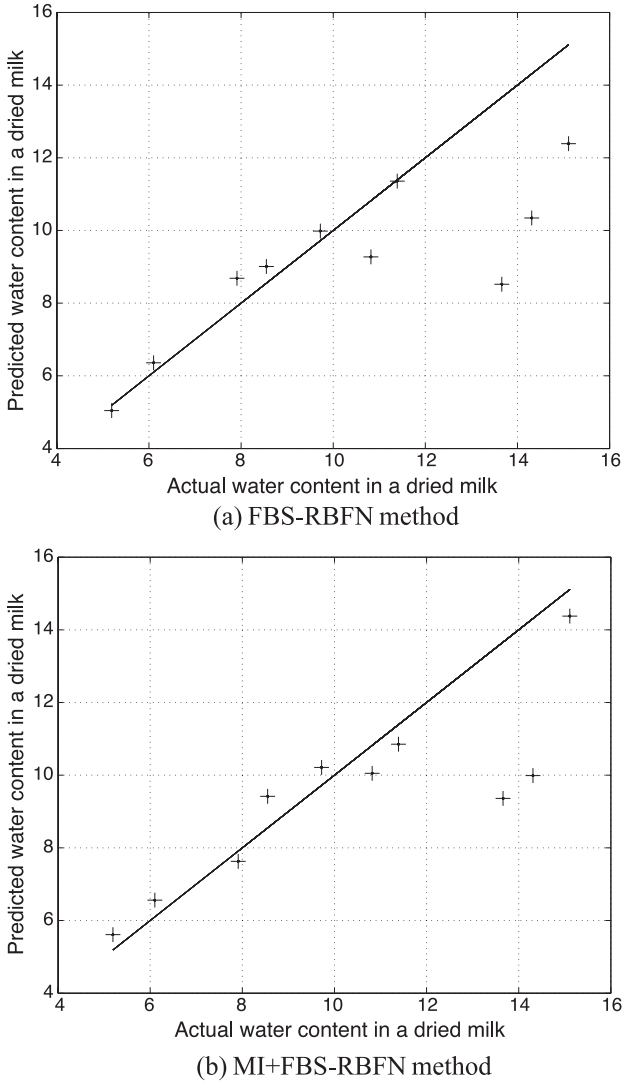
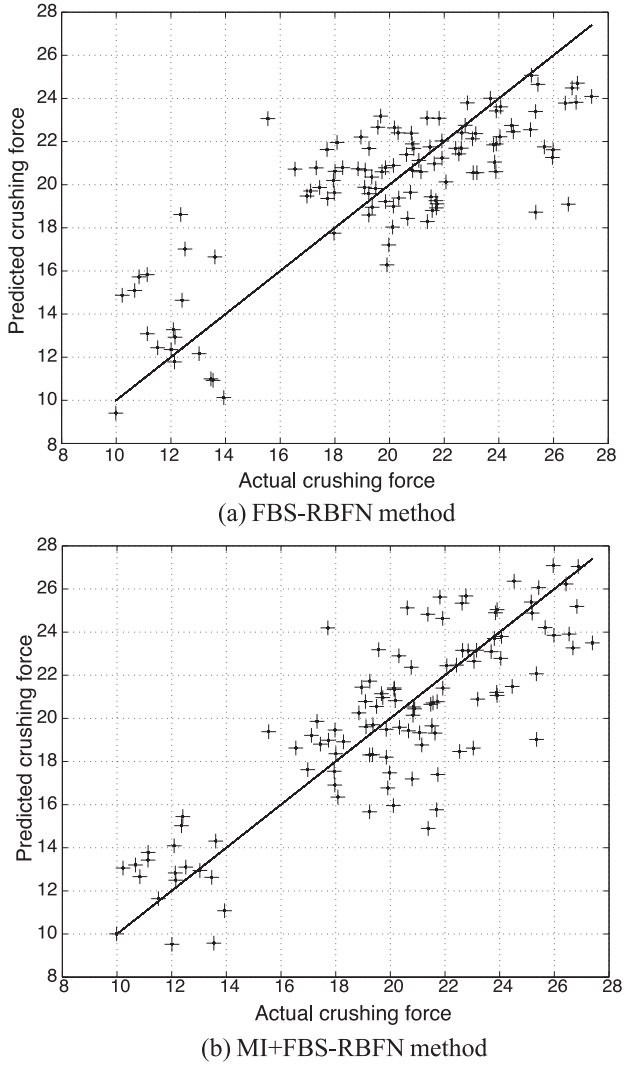


Fig. 5. Predicted value in function of measured value in the milk powder data set.



(a) FBS-RBFN method

(b) MI+FBS-RBFN method

Fig. 6. Predicted value in function of measured value in the apple data set.

linear according to the hypothesis of the shortening of the optical path [32]. In the case of the milk powder (see Fig. 3b), the first selected variable by this method is $\mathbf{x}_{625}$ that corresponds to the fat situated in the last of the spectra shown in Fig. 2b; the specialists know that there is an inverse relationship between the fat and water. The variable selected by the mutual information method corresponding to the fat does not suffer from the spectral interference that undergo the other variables and the other constituents in the spectra of the milk powder. In the case of the apple data set, the first selected variable by the mutual information method is $\mathbf{x}_{52}$ (see Fig. 3c). Concerning this last data set, no spectrochemical explanation is available to justify this choice.

About the MI + FBS-RBFN procedure, after the selection of the first variable, we tested radial-basis function networks [30] with 1 to 20 centers (neurons) for the three data sets in the hidden layer. The best results were obtained with, respectively, 5, 1, and 13 centers in the hidden layer and, respectively, 36, 18, and 12 selected variables for the three data sets.

Fig. 4 shows the relationship between the predicted saccharose concentration in orange juice and the actual concentration with the FBS-RBFN and MI + FBS-RBFN variable selection methods. Fig. 4b shows the improvement obtained with the use of the MI + FBS-RBFN procedure compared to the FBS-RBFN procedure. Figs. 5 and 6 represent the same improvement obtained for the milk powder and apple data sets respectively.

It should be noted that the set of selected variables by MI + FBS-RBFN is different from the set of selected variables by the FBS-RBFN procedure for each of the three data sets.

Finally, we can conclude that the choice of the first selected variable has a very high influence on the performances of the final model, thus showing the interest of the combination of both approaches: the mutual information to select the first variable and the application of the FBS-RBFN method to select the next ones. The first variable selected by the mutual information method does not depend on the data distribution in training and validation sets.

5. Conclusions

In the context of infrared spectroscopy, it has been shown that the use of nonlinear modeling on adequately selected variables can be beneficial for the quality of a prediction based on the spectral variables. In this paper, we suggested a way to improve the incremental FBS-RBFN method by a judicious choice of the first spectral data, which has a large influence on the final performances of the prediction. The idea is to use a measure of the mutual information between the spectral data (independent variables) and the concentration of analyte (dependent variable) to select the first variable; then an incremental method (FBS-RBFN) is used to select the next spectral variables. This combined method is shown to offer enhanced performances compared to the use of the FBS-RBFN method alone and to various linear methods; it also offers a better independence to a specific choice of training and validation sets, and a better interpretability from a spectrochemical point of view.

Acknowledgements

The authors thank Mohamed Hanafi from ENITIAA/INRA (Unit of Sensometry and Chemometrics), Nantes (FRANCE), for having provided the apple data set.

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