ELSEVIER

Carbohydrate Polymers 49 (2002) 83–90

Carbohydrate Polymers

www.elsevier.com/locate/carbpol

Recognition of starches by Raman spectroscopy

N. Dupuy*, J. Laureyns

Laboratoire de Spectroscopie Infrarouge et Raman (LASIR), Centre d'Etudes et de Recherches Lasers et Applications (CERLA), CNRS, Bât C5, Université des Sciences et Technologies de Lille, F-59655 Villeneuve d'Ascq Cedex, France

Received 20 September 2000; revised 19 March 2001; accepted 9 July 2001

Abstract

This paper describes the use of Raman spectroscopy to identify modified starches with regard to their origin and type of modification. Using Principal Component Analysis, natural groupings of similarly modified samples can be obtained on a two dimensional plane. Such mapping provides the expert with the possibility of analyzing the distribution of samples by using their relative position with respect to the existing clusters. On the basis of the available information in the Raman spectra, a Partial Least Squares calibration was built with the intensities of the derivative Raman spectra as input and the starch modifications as output, allows the user to identify the modified starches present in a sample.

Keywords: Modified starches; Raman; Chemometric

1. Introduction

The importance of starches in the food industry has long been recognized. They are commonly available, easy to use, and provide an important source of energy. Starch comes from many sources — from cereals such as corn, wheat and rice, and from root plants such as potatoes or tapioca. Since these crops can be planted every year, starch is an abundant and naturally renewable resource. Modified starches have been developed that preserve the main nutritional features of starch with improved functional properties (Forrest & Cove 1992; Radley 1976). The economic value of starch increases according to the degree and type of modification. It is important to be able to determine the type and modified starch in a sample.

Various types of structural information can be used to identify modified starches. In recent years, several vibrational spectroscopy studies of starch have been reported (Dolmatova, Ruckebusch, Dupuy, Huvenne & Legrand, 1998; Dupuy, Wojciechowski, Ta, Huvenne & Legrand, 1997; Van Soest, Tournois, de Wit & Vliegenthart, 1995). We have selected Raman spectroscopy as the basic source of information because it offers advantages in comparison with other methods. The most important one is the flexibility of sampling (Giles, Gilmore & Bonner Denton, 1999). Solids can be analyzed without any special sample preparation, and the spectra may be recorded through a conventional glass bottle or window without requiring a fixed path-length cell. Furthermore, micro-Raman spectroscopy offers the ability to analyze very small amount of sample non-destructively (Lewis, Daniel, Chaffin & Griffiths, 1994). The advent of high sensitivity, low noise detectors (such as CCD), and improvement in laser technology allows the use of Raman spectra to classify starches (Schuster, Ehmoser, Gapes & Lendl, 2000). The derivative spectra of 39 starch samples were calculated between 200 and 1800 cm^{-1} and for each of them the 4086 values were used as the input vector for a chemometric analysis. Chemometrics is the science relating measurements made on a chemical system or process to the state of the system via the application of mathematical or statistical methods. Initially different modifications were grouped using Principal Component Analysis (PCA). The essential restriction of modeling using unsupervised methods is that it allows only qualitative analysis of the data. It was necessary to model the set of modifications more precisely; therefore a Partial Least Square (PLS) calibration method was used. The calibration was build with a set of 26 samples and the prediction ability was tested on a set of 13 samples, which contained patterns not included in the calibration set.

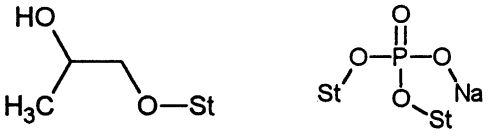
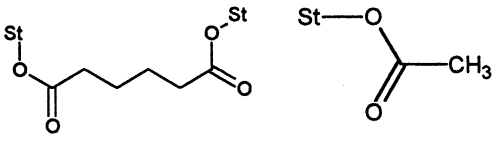
2. Materials and methods

The Raman spectra were measured with a Jobin Yvon

* Corresponding author. Tel.: +03-20-43-66-59; Fax: +03-20-43-65-57.
E-mail address: nathalie.dupuy@univ-lille1.fr (N. Dupuy).

0144-8617/02/$ - see front matter
PII: S0144-8617(01)00304-6

Table 1
Definition of the modifications applied to the studied starch samples (St = starch)

Property or modification	Code	Structure
Hydroxypropyl distarch phosphate	R	
Acetylated distarch adipate	H	
Waxy	C	Pure amylopectin
Pregelatinized	P	
Non Modified corn sample	N	
Manioc sample	Ma	

(Horiba group) LABRAM spectrometer supplied with an OLYMPUS BX40 microscope accessory. The excitation line was a red radiation from a He–Ne laser emitting at 632.8 nm. The sample powders were put on glass slides and analyzed through a × 100 U.L.W.D. microscope objective (numerical aperture: 0.80) and an irradiation power of a few mW at the sample was used. The spectra were recorded in the 200–1900 cm^{-1} spectral range with an integration time of 60 s and were averaged over three scans. Because of the inhomogeneity of the starch powder, the total intensity of the spectra varied, but the relative intensity of the bands in the spectra of the same sample are nearly the same, so all the spectra are normalized at two arbitrary units on the basis of the band at 480 cm^{-1}. In this case the information relative to the degree of crystallinity of the starch was not lost.

Table 2
Description of the 39 starch samples studied

Sample number	Modification	Sample number	Modification
1	CPH	21	CH
2	CH	22	MaR
3	CR	23	CH
4	N	24	CH
5	C	25	CH
6	Ma	26	N
7	MaR	P1	MaR
8	P	P2	CH
9	N	P3	N
10	CP	P4	CPH
11	CPH	P5	CH
12	P	P6	CR
13	CR	P7	CH
14	CH	P8	C
15	P	P9	N
16	CR	P10	CH
17	C	P11	CPH
18	N	P12	P
19	N	P13	CH
20	CH		

This work was performed on 39 starches of corn and manioc (cassava), which are classified with respect to five possible modifications or properties as shown in Tables 1 and 2. The samples were collected by CREALIS (Danone, Brive-la-Gaillarde, France).

To code the starch properties, the five modifications are arbitrarily classified in the order of the vegetable origin, P, H, R, C. So for each sample a five-dimensional output vector may represent the combination of modifications with 1 at the positions corresponding to observed modifications and 0 at other positions. For instance the sample numbered 1, which is CPH-modified, will be coded as 1,1,1,0,1. For a manioc sample the first term of the vector is 0 (non-corn origin), the non-modified samples of manioc origin are represented by 0, 0, 0, 0, 0. The non-modified cornstarch is just called N (Non modified).

3. Chemometric method

3.1. Principal Component Analysis

PCA is a method for the extraction of the systematic variations in one data set (Martens & Naes, 1989). The method can be used for classification as well as for description and interpretation. PCA is oriented towards modeling the variance/covariance structure of the data matrix into a model which represents the significant variations and which considers noise as an error. The components are extracted sequentially and each principal component, called loading, represents the main systematic variation in the data set, which can be modeled after the extraction of the previous ones. The common characteristic of all the spectra are modeled in one or several principal components for which the scores are not significantly different according to the species. On the contrary, the information, which differentiates the species, contributes to principal component whose scores are significant (Millar, Robert, Devaux, Guy &

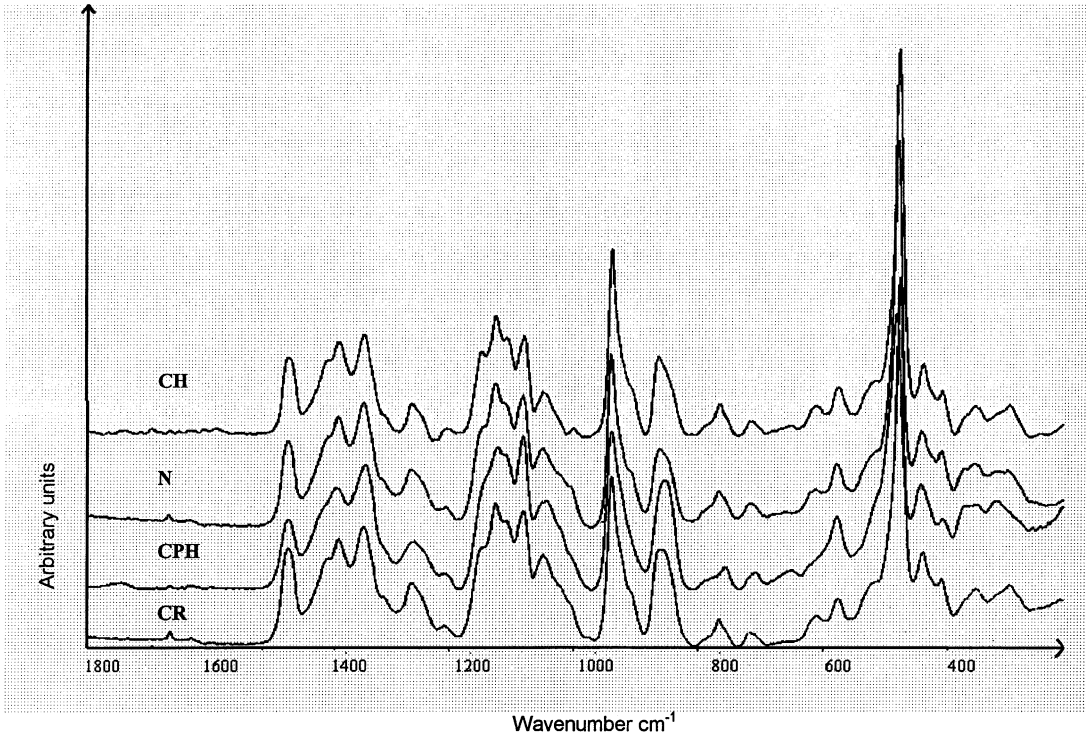


Fig. 1. Examples of Raman spectra of starches obtained for different modifications.

Maris, 1996). The classification may be done on the basis of the scores and the characteristics of each species are established by the interpretation of these specific loadings. PCA is a tool for unsupervised learning, e.g. extracting regularities directly from the input data without referring to classes known earlier.

3.2. Partial Least Square regression

In contrast, the supervised analysis was based on the relation between the signal intensity and the modification of the sample (Martens, 1979). Interference and overlapping of the Raman information may be overcome by using powerful multicomponent analysis such as PLS regression. PLS (Fuller &Griffiths, 1988; Haaland & Thomas, 1988) allowing a sophisticated statistical approach using the full spectral region rather than the unique and isolated analytical bands. The algorithm is based on the ability to correlate mathematically the spectral data to a matrix property of interest while, simultaneously accounting for all other significant spectral factors that perturb the spectrum (Liang & Kvalheim, 1996). It is thus a multivariate regression method that uses the full spectral region selected and is based on the use of latent variables. Samples of known modifications are used as calibration samples and then the modifications of an unknown sample are directly calculated using the resulting equation under the same conditions. In our case, we are only looking for chemical modifications and not real concentrations using the same data processing. We used PLS1 algorithm with mean centered variables.

The evaluation of the calibration performance is estimated by computing the standard error of calibration (SEC) after comparing the real modification with the computed one for each component.

The formula for the standard error of calibration is:

$$\mathrm{SEC} = \sqrt{\left(\frac{\sum_{i=1}^{N}(C_i - C'_i)^2}{N-1-p}\right)} \quad (1)$$

where C_i is the known value, C'_i is the calculated value, N the number of samples and p is the number of independent variables in the regression.

The standard error of prediction (SEP) gives an estimation of the prediction performance during the step of validation of the calibration equation:

$$\mathrm{SEP} = \sqrt{\left(\frac{\sum_{i=1}^{M}(C_i - C'_i)^2}{M-1}\right)} \quad (2)$$

where C_i is the known value, C'_i is the value calculated by the calibration equation, and M is the number of samples in the prediction set.

The reproducibility of the signal at each wavelength is defined by the relative standard deviation according to the formula (Dupuy, Duponchel, Amram, Huvenne &

Table 3
Experimental error (coefficient of variation) calculated at five wavenumbers

Wavenumber (cm^{-1})	946	1073	1469	1347	568	mean
For 10 spectra (%)	11.1	7.7	11	8.8	9.1	9.5
For 10 spectra averaged of 3 (%)	4.6	3.6	4.5	3.7	3.9	4.1

Legrand, 1994):

$$\mathrm{RSD} = \left(\frac{\sigma}{x_m}\right)100 \tag{3}$$

$$\sigma = \sqrt{\frac{\left(\sum_i^N x_i - x_m\right)^2}{N-1}} \tag{4}$$

where x_i represents the intensity of one spectrum, x_m is the average intensity of all spectra of the same sample and N is the number of spectra.

For all the applications, the spectral data were first derived with the algorithm developed by Savitzky and Golay (1964) in order to remove the unwanted spectral variations as offsets and a smoothing with 23 points was performed.

The chemometric applications are performed by the UNSCRAMBLER software version 6 from CAMO (Computer Aided MOdelling, Trondheim, Norway).

4. Results and discussion

The aim of this study is to demonstrate that Raman spectroscopy could be successfully used for the quality control of modified starch in the food industry. All the samples used in this work are commercial products from different manufacturers.

4.1. Raman spectra

With the 39 studied samples, we consider two basic chemical transformations applied to starch:

1. The introduction of the substitution groups such as hydroxy propyl and acetyl on the starch structure carries out a stabilizing reaction, in order to reduce the intermolecular interbranch association.
2. Cross-linking agents such as phosphate or adipate groups are introduced in order to increase the heat resistance.

As shown in Table 1, what is called a modification may be a combination of two basic treatments. For instance, the H modification combines the stabilization and cross-linking transformations. The same observation may be made for the R modification. The waxy starches constitute only amylopectin, but this property was obtained by cultivar selection and not by chemical reaction. So, the waxy starches are in fact unmodified ones, but the waxy property may be regarded as another kind of modification. Under these conditions, the samples may present none, one, two or three single or double modifications as shown in Table 2. This fact increases the difficulty of obtaining a rapid and sure identification. The non-modified cornstarch samples are denoted as N, the cassava starch samples are denoted as Ma if they are non-modified, and MaX, when they are modified (where X, the name of the modification considered).

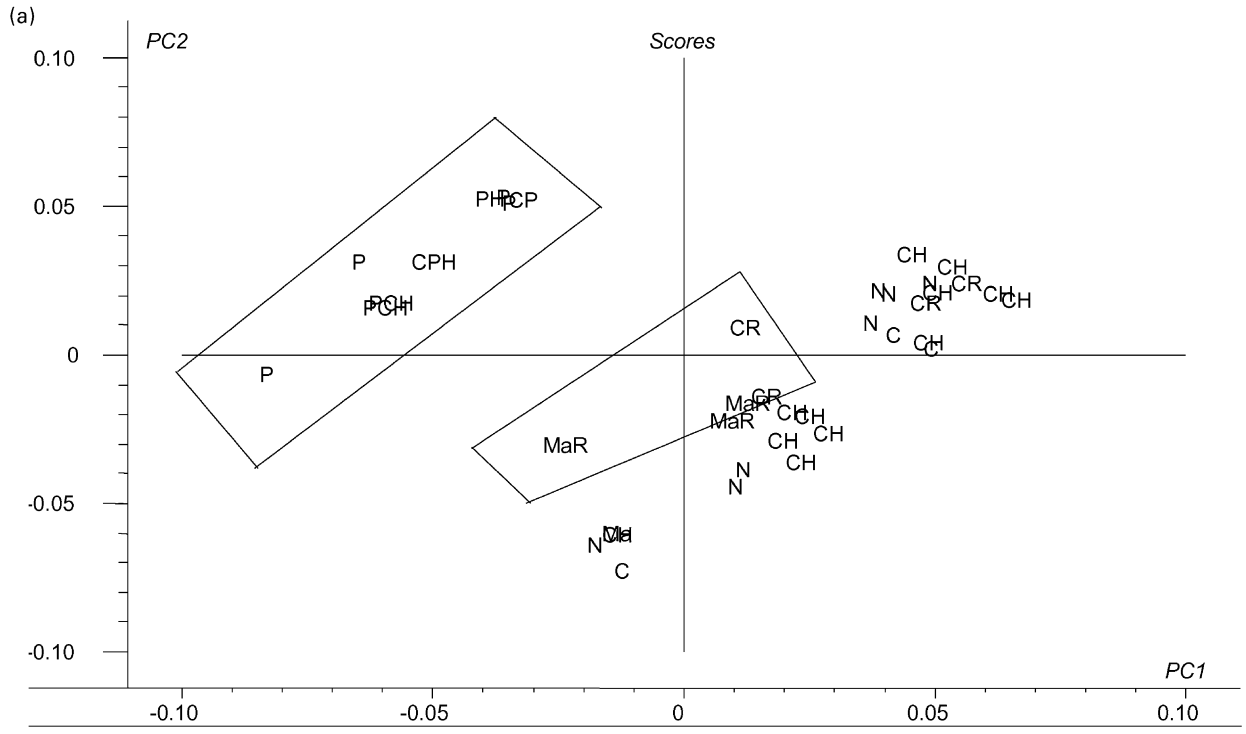
Fingerprint regions of the Raman spectra of some starch samples are shown in Fig. 1. Overall, the spectra seem to be similar because different samples contain the same main components (amylose, amylopectin) and the Raman signal is essentially sensitive to the changes in short-range structure. Nevertheless we can see variations such as the disappearance of the doublet at 600 cm^{-1} for the P modification and some changes in the relative intensity of the bands. The modifications could not affect the spectra more because the R, H and P transformations affect only 1–10% of the total starch according to the European community norm. The situation is even more complex when a combination of several modifications is considered.

4.2. Reproducibility

The spectral reproducibility is expressed in terms of a coefficient of variation. It is computed on 10 spectra of different sheets of the same sample at different wavenumbers. The reproducibility calculated on a non-modified starch (numbered 4 in Table 2) for five different wavelengths is given in the Table 3 with an average result at 9.5%. It is observed that the reproducibility was of the same order of magnitude size at different wavenumbers. This poor result can be related to inhomogeneity in the powder and the samples selected for spectral analysis. In order to minimize this error, for each sample the mean of three different spectra were taken. In which case the coefficient of variation is about 4% as shown in Table 3.

4.3. PCA of the spectral data

The PCA of the data set constituted by the 39 first derivatized spectra explains 85% of the data matrix variance after extraction of four components. The components extracted subsequently contribute less than 2% of the residual variance, and model the non-significant variations as noise. When the spectra are projected (using their scores as coordinates) in the space of the first and second principal components (which explained 45 and 32% of the spectral variance), we obtained groupings of pregelatinized and R modified starches. On the right, we can find all the other



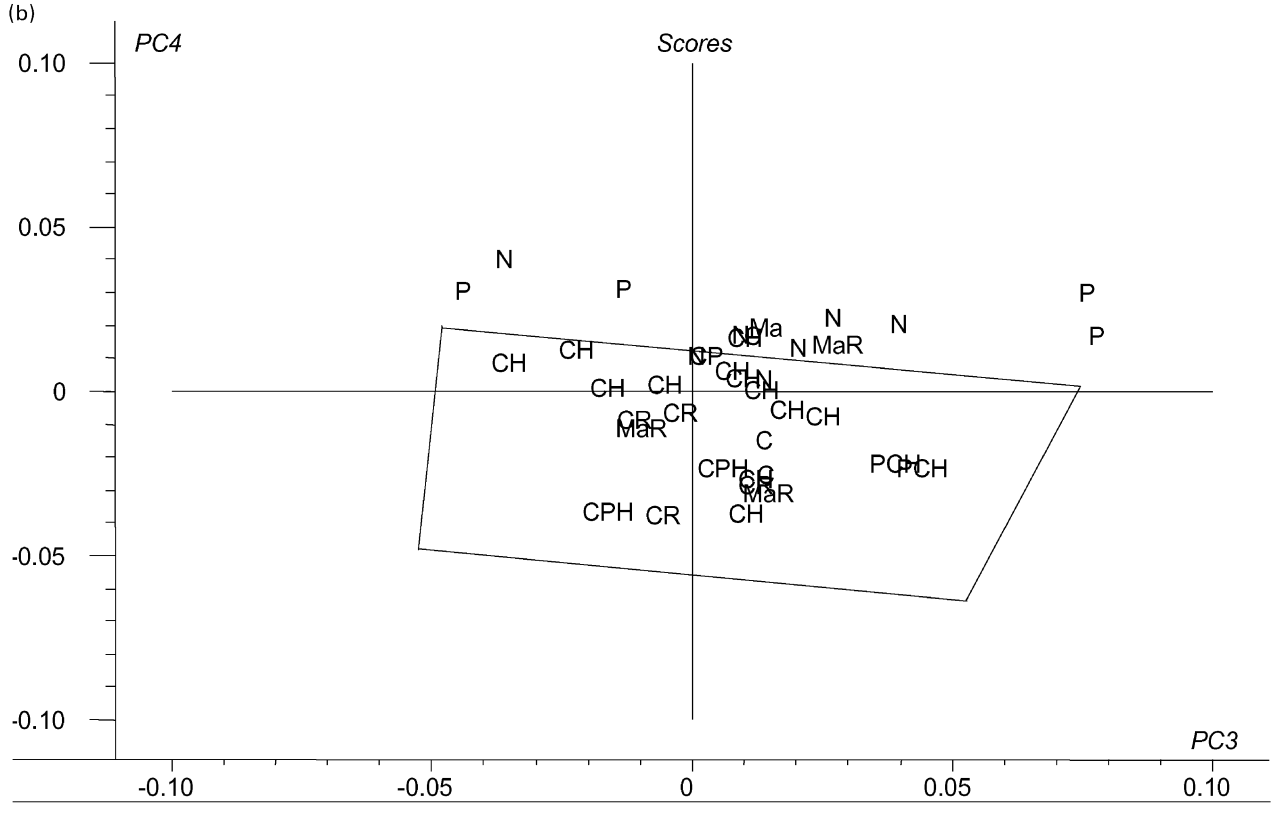


Fig. 2. (a) Distribution of samples in the space of the first and second principal component. (b) Distribution of samples in the space of the third and fourth principal component.

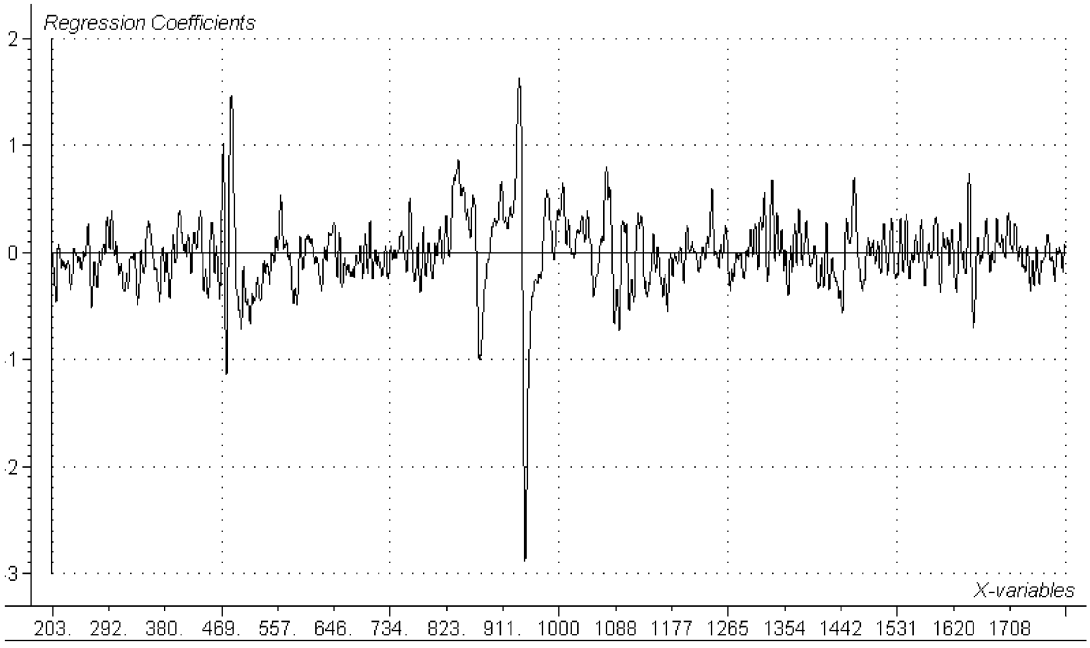
Table 4
Prediction results obtained with PLS multivariate regression for all the predicted samples, for the calibration set (SEC) and for the prediction set (SEP). The theoretical value is called Th and was given as reference

Property		Corn		P		H		R		C	
Sample		Th	PLS	Th	PLS	Th	PLS	Th	PLS	Th	PLS
Factors number		4		2		8		7		6	
P1	MaR	0	0.47	0	− 0.09	0	0.07	1	0.75	0	0.50
P2	CH	1	1.05	0	0.06	1	0.79	0	0.12	1	0.96
P3	N	1	0.97	0	0.10	0	− 0.06	0	0.11	0	0.09
P4	CPH	1	1.08	1	0.86	1	1.07	0	− 0.15	1	1.11
P5	CH	1	0.75	0	− 0.08	1	1.41	0	0.04	1	1.41
P6	CR	1	0.83	0	− 0.05	0	− 0.12	1	1.15	1	1.1
P7	CH	1	0.77	0	0.05	1	1.00	0	0.18	1	1.22
P8	C	1	1.2	0	− 0.07	0	0.45	0	0.44	1	1.12
P9	N	1	0.93	0	0.05	0	0.14	0	− 0.04	0	0.35
P10	CH	1	1.02	0	0.02	1	0.90	0	0.04	1	1.04
P11	CPH	1	1.01	1	1.08	1	1.08	0	0.18	1	1.16
P12	P	1	1.12	1	0.88	0	0.09	0	0.02	0	0.03
P13	CH	1	0.98	0	− 0.12	1	0.77	0	0.14	1	0.86
SEC		0.17		0.06		0.10		0.07		0.15	
SEP		0.19		0.09		0.21		0.18		0.24	

samples (Fig. 2), nevertheless, it was not possible to see the fine structures inside this group. Inside the P zone (pregelatinized starches) PCH modification could be distinguished. In the space of the third and fourth principal component (which explained 5 and 4% of the spectral variance) we observed that all the waxy samples are projected in the same space group with two outliers (the MaR samples). Nevertheless, these results demonstrate that there is sufficient information in the Raman spectra to establish a non-supervised classification of some groups of samples. This led us to build supervised methods to recognize modifications.

4.4. Partial Least Squares analysis

In order to predict the modifications applied to the different starches, we used PLS regression on the Raman data. The results obtained for all the samples and the five



Vector regression calculated for the C property

Fig. 3. Vector regression calculated for the waxy (C) property for six factors loading.

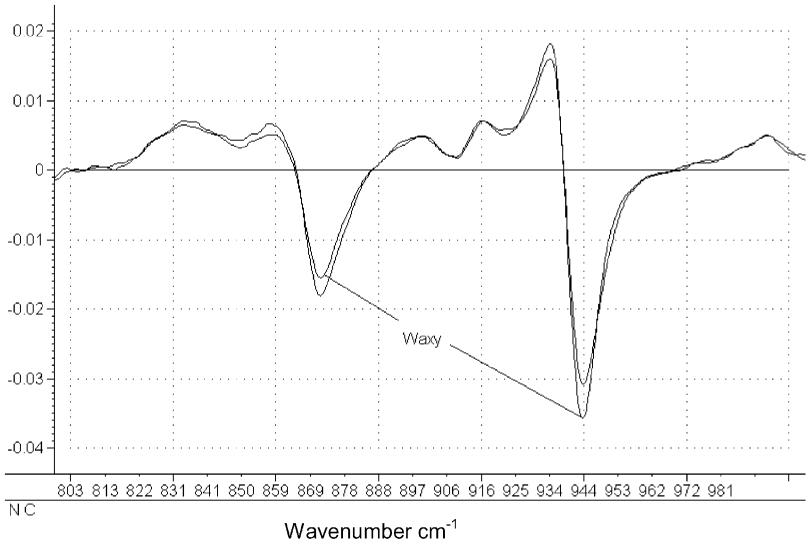


Fig. 4. First derivative spectra of the samples P8 and P9 in the [800–1000 cm^{-1}] spectral region.

variables are given in Table 4. According to the PCA classification the P and R modifications led to the best predictions. The predicted modifications never gave 0 or 1 results but this result was justified by the different levels of modification of the sample. As a matter of fact a sample chemically transformed at 1% would be expected to lead to a predicted modification less intense than the sample modified at 9%. Considering the difficulty in obtaining the real value, it was necessary to discriminate the result between the initial value of 0 or 1. If we consider that all the values between a negative value and 0.49 relate to a non-modified sample, and between 0.51 and a high positive value to a modified sample, all the properties are well predicted. But the results obtained for corn (0.47) and waxy property (0.50) for the sample P1 and for H (0.45) and R (0.44) for the sample P8, seem not to be very reliable. In this case chemical analysis would be done to confirm the previous result. It was also interesting to see that the waxy property and the vegetal origin were well predicted. In a previous study with infrared spectroscopy (Dolmatova, Tchistiakov, Ruckebusch, Dupuy, Huvenne, &, Legrand et al., 1999) these two modifications were difficult to predict. The investigation of the regression coefficients for the waxy prediction (four loading factors) showed four major information at 480, 870, 950 and 1468 cm^{-1} (Fig. 3). These large absolute *B*-values must be seen in relation to the variance of *X*. Large absolute *B*-value indicate important variables. The information mentioned above are, respectively, attributed to the skeletal mode, the CH and CH_2 deformation, the skeletal mode involving α(1–4) linkage and the CH_2 deformation (Corbett, Zichy, Goral & Passingham, 1991; Kim, Yeh, Zhao & Wang, 1989; Santha, Sudha, Vijayakumari, Nayar & Moorthy, 1990).

Table 5
Dispersion of the prediction results calculated on 10 spectra (1–10), on 10 averaging of 3 independent spectra (mean 1–10)

Property	Corn	P	H	R	C
Real predicted	1	0	0	0	0
1	0.92	0.15	0.29	0.05	0.12
2	1.32	0.01	− 0.08	− 0.11	0.09
3	1.17	0.03	− 0.19	− 0.19	0.116
4	1.12	0.11	− 0.02	− 0.15	0.01
5	0.71	− 0.02	0.32	− 0.22	0.01
6	0.40	0.08	− 0.51	− 0.21	0.141
7	1.18	0.09	0.15	− 0.09	0.11
8	1.03	0.37	0.24	− 0.01	0.08
9	0.98	0.02	0.03	0.15	− 0.01
10	0.93	− 0.04	− 0.09	− 0.02	0.05
σ1	0.26	0.12	0.25	0.12	0.05
Mean 1	0.96	0.08	0.21	− 0.04	0.02
Mean 2	1.07	− 0.05	0.40	− 0.02	0.035
Mean 3	1.19	− 0.02	0.34	0.06	0.03
Mean 4	1.15	0.09	0.28	− 0.04	0.02
Mean 5	1.17	0.02	0.31	0.03	0.025
Mean 6	1.12	0.08	0.41	0.01	0.033
Mean 7	1.05	0.01	0.27	0.08	0.03
Mean 8	0.92	0.08	0.22	0.01	− 0.01
Mean 9	1.04	0.119	0.17	0.08	− 0.05
Mean 10	1.01	0.04	0.12	0.07	0.02
σ2	0.09	0.05	0.10	0.05	0.03

In Fig. 4 an example of the difference in 780–1000 cm^{-1} region between the P8 and P9 samples was seen in the prediction set. It was observed that the waxy samples exhibit differences in this region in comparison to the unmodified starches according to the data processing in the regression coefficient. This spectroscopic interpretation justified the high correlation between the Raman spectra and the waxy property.

In order to study the reproducibility of the method, and the importance of averaging the spectra to obtain a good signal to noise ratio, and to minimize the inhomogeneity of the powder, the results obtained on the 10 spectra used in the first part of the discussion were calculated, and also on 10 spectra obtained from an average of three measurements on the same sample. The sample was a non-modified

cornstarch and the predictions are reported in Table 5. The samples numbered 1–10 are relative to individual spectra and the sample numbered mean 1–10 are the averaged spectra. When we consider the predictions obtained on the individual spectra, we note a large dispersion of the results. The standard deviation varied between 0.26 for the vegetal origin and 0.05 for the waxy characteristic, and an incorrect prediction was obtained for the corn origin of the sixth sample. In this case manioc origin was found. On the contrary, for the average spectra all the modifications are well recognized and the standard deviation decrease for all the properties was less than 0.10. These results justified the spectral procedure. Then the mean of three spectra seems to be a good compromise between the time for analysis and the reliability of the results.

5. Conclusion

The studies in this paper have shown that the method of recognition of modified starches by PLS processing of Raman spectra can be a reliable and effective tool for classifying the samples and for identifying modifications. With the use of an unlabeled data set that contains only input data directly from derivative spectra, the principal component analysis provides good clustering on the first and second component projection. The essential restriction of modeling using principal component analysis is that it allows only partial qualitative analysis of the data. Therefore, it is necessary to apply supervised learning to available data in order to predict quantitatively the modifications of starches and the combinations of these modifications. The PLS method allows us to obtain a recognition model for a large range of modifications.

Acknowledgements

The Laboratoire de Spectrochimie Infrarouge et Raman is 'Unité Mixte de Recherche de l'université de Lille1 et du CNRS'. The Centre d'Etudes et de Recherches Lasers et Applications (CERLA) is supported by the ministère chargé de la recherche, the Région Nord-Pas-de-Calais and the Fonds Européen de Développement Economique des Régions.The authors wish to thank CREALIS (Centre de Recherche et d'Etudes Alimentaires), Danone, Z. I. du teinchurier, 19100 BRIVE, France, for supporting this research.

References

Corbett, E. C., Zichy, V., Goral, J., & Passingham, C. (1991). Fourier transform Raman studies of materials and compounds of biological importance-II. The effect of moisture on the molecular structure of the α and β anomers of glucose. *Spectrochimica Acta*, *47* (9/10), 1399–1411.

Dolmatova, L., Ruckebusch, C., Dupuy, N., Huvenne, J. P., & Legrand, P. (1998). Identification of modified starches using infrared spectroscopy and artificial neural network processing. *Applied Spectroscopy*, *52* (3), 329–338.

Dolmatova, L., Tchistiakov, V., Ruckebusch, C., Dupuy, N., Huvenne, J. P., & Legrand, P. (1999). Hierarchical neural network modeling for infrared spectra interpretation of modified starches. *Journal of Chemistry and Information. Computer Science*, *39*, 1027–1036.

Dupuy, N., Duponchel, L., Amram, B., Huvenne, J. P., & Legrand, P. (1994). Quantitative analysis of latex in paper coating by ATR–FTIR analysis. *Applied Spectroscopy*, *8*, 337–347.

Dupuy, N., Wojciechowski, C., Ta, C. D., Huvenne, J. P., & Legrand, P. (1997). Mid-infrared spectroscopy and chemometrics on corn starch classification. *Journal of Molecular Structure*, *410*, 551–554.

Forrest, B., & Cove, L. (1992). Identification and quantification of hydroxypropylation of starch by FTIR. *Starch*, *44* (5), 179–183.

Fuller, M., & Griffiths, P. R. (1988). Diffuse reflectance measurements by infrared Fourier transform spectrometry. *Analytical Chemistry*, *50*, 1906–1910.

Giles, J. H., Gilmore, D. A., & Bonner Denton, M. (1999). Quantitative analysis using Raman spectroscopy without spectral standardization. *Journal of Raman Spectroscopy*, *30*, 767–771.

Haaland, D. M., & Thomas, E. V. (1988). Partial least squares methods for spectral analysis. In relation to other quantitative calibration methods and the extraction of qualitative information. *Analytical Chemistry*, *60*, 1193–1202.

Kim, I., Yeh, A., Zhao, B. L., & Wang, S. S. (1989). Gelatinization kinetics of starch by using Raman spectroscopy. *Biotechnology Progress*, *5* (4), 172–174.

Lewis, I. R., Daniel, N. W., Chaffin, N. C., & Griffiths, P. R. (1994). Raman spectrometry and neural network for the classification of wood types-1. *Spectrochimica Acta*, *50* (11), 1943–1958.

Liang, Y. -L., & Kvalheim, O. M. (1996). Robust methods for multivariate analysis — a tutorial review. *Chemometrics and Intelligent Laboratory Systems*, *32*, 1–10.

Martens, H. (1979). Factor analysis of chemical mixtures. *Analytica Chimica Acta*, *112*, 423–442.

Martens, H., & Naes, T. (1989). *Multivariate calibration*, Wiley: New York.

Millar, S., Robert, P., Devaux, M. F., Guy, R. C. E., & Maris, P. (1996). Near-infrared spectroscopic measurements of structural changes in starch-containing extruded products. *Applied Spectroscopy*, *9*, 1134–1139.

Radley, J. A. (1976). In J. A. Radley, *Starch production technology* London: Applied Science Publishers Ltd.

Santha, N., Sudha, K. G., Vijayakumari, K. P., Nayar, V. U., & Moorthy, S. N. (1990). Raman and infrared spectra of starch samples of sweet potato and cassava. *Proceedings of Indian Academic Sciences*, *5*, 705–712.

Savitzky, A., & Golay, M. J. E. (1964). Smoothing and differentiation of data by simplified least squares procedures. *Analytical Chemistry*, *36*, 1627–1679.

Schuster, K. C., Ehmoser, H., Gapes, J. R., & Lendl, B. (2000). On-line FT-Raman spectroscopic monitoring of starch gelatinization and enzyme catalyzed starch hydrolysis. *Vibrational Spectroscopy*, *22*, 181–190.

Van Soest, J. G., Tournois, H., de Wit, D., & Vliegenthart, J. F. G. (1995). Short-range structure in (partially) crystalline potato starch determined with attenuated total reflectance Fourier transform IR spectroscopy. *Carbohydrate Research*, *279*, 201–214.