Carbohydrate Polymers 287 (2022) 119365

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Feasibility study on the use of ATR-FTIR spectroscopy as a tool for the estimation of wine polysaccharides

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ARTICLE INFO

Keywords:
ATR-FTIR
Polysaccharides
Wine
Chemometrics
GC–MS

ABSTRACT

Polysaccharides are the main macromolecules of colloidal nature in wines. These compounds play a critical role in stabilizing other molecules in solution and thus modifying the wine processing and organoleptic properties. Different analytical techniques have been proposed for their determination. However, most of them are complicated and time-consuming. To overcome these drawbacks, Fourier transform infrared spectroscopy (FTIR) has been evaluated in this study for the estimation of wine polysaccharides in a fast and non-destructive way.

Spectral data have been correlated with wine polysaccharide contents by modified partial least squares regression (MPLS) using different spectral pretreatments. MPLS models developed have revealed the potential of FTIR analysis for the routine screening of polysaccharides rich in arabinose and galactose (PRAG), rhamnogalacturonans types II (RG-II), mannoproteins (MP) and total soluble polysaccharides (TSP) in wine samples, obtaining standard errors of prediction from 6.07 to 8.44%. Monitoring the wine polysaccharides can assist in the elaboration of the wines according to their requirements and improving quality to satisfy consumer preferences.

1. Introduction

Wine represents a complex matrix of molecules with valuable biological and organoleptic properties (Boulet et al., 2016; Quijada-Morin et al., 2014). Among them, polysaccharides coming mainly from grapes, but also from yeasts and bacteria during winemaking, are the main macromolecules of colloidal nature in wines (Apolinar-Valiente et al., 2013). Different factors such as grape variety, stage of maturity, agronomic treatment, or wine-making techniques affect both the profiles and content of these compounds in grape and therefore in wine (Jones-Moore et al., 2021). The main polysaccharides present in wine can be divided into two groups according to their origin. The first of them, originated from grape berry cell walls, comprises polysaccharides rich in arabinose and galactose (PRAG), homogalacturonans (HG) and rhamnogalacturonans types I and II (RG-I and RG-II). The second group of polysaccharides is given to the wine by yeast during the stages of fermentation and aging of wines on lees (Ayestaran et al., 2004; Vidal et al., 2003). Mannoproteins (MP) and glucans (GL) are its main constituents. Different authors have reported in their research the varied and interesting properties of wine polysaccharides. These compounds have the property of being able to stabilize other molecules in solution and therefore modify the wine processing and organoleptic properties. It has been demonstrated that the effect on wine properties depends on the quantity but also on the type of polysaccharide (Guadalupe et al., 2015).

Several analytical techniques have been reported for the determination of wine polysaccharides (Arnous & Meyer, 2009; Ayestaran et al., 2004; Boulet et al., 2007; Coimbra et al., 2005; Doco et al., 1999; Doco et al., 2001; Guadalupe et al., 2012). Gas chromatography coupled with mass spectrometry (GC–MS) after hydrolysis and monosaccharide silylation is reported in the bibliography as one of the most used methods for the determination of individual wine polysaccharides. Moreover, high performance liquid chromatography (HPLC) is widely used for the determination of monosaccharides composition. The high sensitivity of these techniques and their ability to adequately separate complex samples justify the extent of its use. However, they are complicated, demanding expensive and time-consuming techniques because of the

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https://doi.org/10.1016/j.carbpol.2022.119365
Received 17 January 2022; Received in revised form 2 March 2022; Accepted 14 March 2022
Available online 17 March 2022

high number of operations, equipment and reagents that they demands. To overcome these drawbacks, analysis by FTIR has been proposed as an important technique for a fast evaluation of wine components. FTIR is a non-destructive technique that supplies information about the structural features of a wide range of compounds. Its main advantages include response speed, high degree of automation, good resolution, environmentally friendly and cost-effectiveness (Bokobza, 1998). These characteristics, together with the improvements experienced by chemometrics, provide an interesting analytical tool for the routine qualitative and quantitative analysis widely used in many industrial sectors during control processes. In fact, FTIR has proven to be useful and reliable technique in the analysis of a high diversity of samples in different industrial sectors including the agro-food sector (Baca-Bocanegra et al., 2019; Han et al., 2019; Li et al., 2015; Lucarini et al., 2018).

In the oenological industry, FTIR analysis has been reported as a routine procedure for the determination of classical oenological parameters (Cozzolino et al., 2011), organic acids (Mato et al., 2005), aroma precursors (Schneider et al., 2004) and phenolic compounds (Edelmann et al., 2001; Passos et al., 2010; Silva et al., 2014) in grape and wines. In addition, FTIR analyses have been successfully applied to correlate the more characteristic features to phenolic extractability levels in grapes seeds and skins (Nogales-Bueno et al., 2017a; Nogales-Bueno et al., 2017b).

However, although FTIR spectroscopy is widely used in the oenological industry, its use for the analysis of wine polysaccharides has been relatively scarce and mainly restricted for identification. For that matter, Coimbra et al. (2002) described the potential of FTIR to discriminate polysaccharides in purified white wine extracts, allowing the quantification of mannose from MP in the samples. Following the work aforementioned, Coimbra et al. (2005) improved the predictive ability of the developed FTIR model for more complex matrices, such as the whole polymeric material, and from red wine.

The objective of this study is to evaluate the use of FTIR as an analytical technique for the estimation of major wine polysaccharides families in a fast and non-destructive way. To the best of our knowledge, no reference addressing this goal has yet been reported. An understanding of the polysaccharide composition of wines is an important issue in the oenological sector. The quality of wine depends mostly on this aspect either for their role in wine organoleptic properties and their impact on different stages of the winemaking process such as fermentation, filtration and stabilization.

2. Materials and methods

2.1. Wine samples

Red wines from unknown origin, wine-making technique and grape varieties, among others, have been used in this study. The used samples have been analyzed in Instituto de Ciencias de la Vid y del Vino (ICVV) for VIETEC for other confidential purposes and have been provided using blinded codes. A total of 81 wine samples were studied. The heterogeneity found for each polysaccharide family in terms of their contents justifies the usefulness of these samples for the stated objective.

2.2. FTIR data collection

FTIR spectra were recorded using a Cary 600 FTIR (Agilent Technologies, Inc., USA) spectrometer with Attenuated Total Reflectance (ATR) and the Agilent Resolutions Pro as control software. Spectral data were registered using a zinc selenide crystal accessory in absorbance mode from 1 mL of wine. Three spectra were recorded for each sample in the 4000–600 cm^{-1} infrared region, at 2 cm^{-1} resolution and by 16 average scans. Background spectra were acquired in air and automatically subtracted by the software.

2.3. Polysaccharides content

The content of the main polysaccharide families in the wine samples was determined following the procedure previously reported by Guadalupe et al. (2012) and Martinez-Lapuente et al. (2013). In detail, the monosaccharide composition was determined by GC–MS of their trimethylsilyl-ester *O*-methyl glycolsyl-residues obtained after acidic methanolysis and derivatization. GC was controlled by ChemStation software and equipped with a 7653B automatic injector consisting of an Agilent 7890A gas chromatograph (Agilent Technologies, Waldbronn, Germany) coupled to a 5975C VL quadrupole mass detector (MS). Samples were injected in duplicate. The content of each polysaccharide family in the wine samples was estimated from their concentration of individual glycosyl residues which are characteristic of structurally identified wine polysaccharides. PRAGs, representing mainly arabinogalactan-proteins and arabinans in wines, were estimated from the sum of galactosyl, arabinosyl, rhamnosyl and glucuronosyl residues. All the mannose content was attributed to yeast MPs, and all the glucose content was attributed to yeast GLs. The RG-II content was calculated from the sum of its diagnostic sugars (apiose, 2-*O*-methyl-l-fucose, 2-*O*-methyl-dxylose, aceric acid (3-c-carboxy-5-deoxy-l-xylose), Kdo (3-deoxy octulosonic acid), and Dha (3-deoxy-D-lyxo heptusolaric acid)), which represent approximately 25% of the RG-II molecule. For one residue of 2-*O*-methyl fucose, RG-II contains 3.5 rhamnosyl, 2 arabinosyl, 2 galactosyl, 1 glucuronosyl and 9 galacturonosyl residues. Taking into account these molar ratios, it was possible to estimate their respective amounts in the RG-II. The remaining part was attributed to the presence of PRAG in the case of rhamnose, arabinose and galactose; and the remaining galacturonosyl residues was used to estimate the content of oligomers of HG. The content of total polysaccharides was estimated from the sum of PRAG, MP, GL, RG-II and HG.

2.4. Data analysis

Wine spectra were randomly divided into calibration and validation groups by allocating, respectively, 75% and 25% of the total set of samples.

In a first step, a principal component analysis (PCA) was used to explore the latent structure of the spectral matrix constituted for the samples belonging to the calibration set. This method provides information about the spectral outliers evaluating the differences between the spectra of the different samples, the position of samples in the newly-created space but also it is a significant source of information to generate cross-validation groups used in the calibration process (Brereton, 2003; Shenk & Westerhaus, 1995).

After that, a calibration procedure was carried out by modified partial least squares regression (MPLS) to get quantitative prediction models for the evaluated reference parameters. For it, the corresponding GL, HG, MP, PRAG, RG-II and TSP wine content were assigned to the raw spectral data of each sample belonging to the calibration set, and then different spectral pre-treatments were evaluated to try to remove or reduce scattering effects (Dhanoa et al., 1995; Geladi et al., 1985). For each polysaccharide family, the best model was selected. Standard normal variate (SNV), multiplicative scatter correction (MSC), detrend, different derivatives and none pre-treatments were applied in this work. Identification and removal of chemical outliers was carried out using the $T \geq 2.5$ criterion according to which the samples that are predicted with a high residual value are not considered in the MPLS regression. The standard error of cross-validation (SECV) was generated by the combination of the validation errors.

Finally, the goodness of the best MPLS model obtained for each reference parameter was evaluated. For it, the models generated in the calibration process were applied to the samples belonging to the validation set. The results obtained in this way for each evaluated parameter were compared to the reference values obtained by gas chromatography coupled with mass spectrometry to generate the standard error of

prediction (SEP) in external validation.

Data pretreatment, principal components analysis and MPLS models (development and testing) were carried out using the software Win ISI® (v1.50) (Infrasoft International, LLC, Port. Matilda, PA, USA).

3. Results and discussion

3.1. Polysaccharides contents in wine samples

In this study, RG-II, PRAG, HG, MP, GL and TSP have been evaluated as reference parameters. The content of each wine polysaccharide family was obtained from their concentration of individual glycosyl residues determined by GC–MS after hydrolysis, reduction and acetylation. The sum of all of them was estimated as total soluble polysaccharides. Table 1 shows the main statistical parameters for RG-II, PRAG, HG, MP, GL and TSP content of all wine samples and the samples belonging to the validation and calibration sets.

The average content of PRAG and GL in the studied wines were comparable, being the polysaccharides families with the highest representation in this study (mean value of 35.4% and 33.4% respectively) followed by MP (13.2%), RG-II (12.9%) and HG (10.7%). The profile and content of these compounds in grapes and, therefore, in wine depend on factors like grape variety, stage of maturity, agronomic treatment or wine-making techniques (Jones-Moore et al., 2021). So, even though, a similar trend has been reported in the literature for the evaluated parameters, significant differences have been found between the polysaccharide contents in the different published studies depending on the previously mentioned factors (Apolinar-Valiente et al., 2014; Ayestaran et al., 2004; Doco et al., 2007; Ducasse et al., 2010; Martinez-Lapuente et al., 2016). The unknown origin of the wines used in this work prevents a detailed and justified comparison of the obtained results with those published by other authors.

Chemical variability of the calibration and validation sets was found to be homogenous for all parameters. Taking that into account, it can be assumed that these two new sets generated by a random sample selection procedure properly represent all data variability.

Table 1
Main statistical descriptors for reference parameters in calibration and validation sets.

Set	Reference parameter	Maximum	Mean	Minimum	SD[a]
All samples	RG-II[b]	202.28	117.41	2.49	43.12
	PRAG[c]	959.06	564.89	1.74	223.48
	HG[d]	327.29	170.72	0.98	83.75
	MP[e]	341.16	210.73	0.84	70.74
	GL[f]	3771.40	532.08	102.36	445.87
	TSP[g]	4465.26	1595.82	110.44	597.45
Calibration	RG-II[b]	202.28	118.98	2.49	44.57
	PRAG[c]	959.06	568.72	1.74	232.19
	HG[d]	327.29	171.05	0.98	84.98
	MP[e]	341.16	211.59	0.84	72.95
	GL[f]	3771.40	560.44	102.36	508.42
	TSP[g]	4465.26	1630.78	110.44	635.65
Validation	RG-II[b]	151.64	112.60	5.15	39.01
	PRAG[c]	824.32	553.21	2.90	199.61
	HG[d]	304.42	169.69	1.39	82.02
	MP[e]	281.93	208.11	18.16	65.23
	GL[f]	714.20	445.57	188.21	101.52
	TSP[g]	2285.94	1489.18	216.22	459.43

All reference parameters are expressed as mg L^{-1} of wine.
[a] SD: standard deviation.
[b] RG-II: rhamnogalacturonans type II.
[c] PRAG: polysaccharides rich in arabinose and galactose.
[d] HG: homogalacturonans.
[e] MP: mannoproteins.
[f] GL: glucans.
[g] TSP: total soluble polysaccharides.

3.2. Exploratory Analysis of Spectra

Raw average spectrum of analyzed wine in the region of 500–4000 cm^{-1} is shown in Fig. 1. It can be seen that the spectrum shows high absorbance at wavenumbers around 3400 cm^{-1}, 1600 cm^{-1} and 1200–900 cm^{-1} related to OH, carboxylate and carbohydrate respectively and characteristic of cell-wall polysaccharides (Coimbra et al., 1998; Coimbra et al., 1999). The broad wavenumber region between 2900 and 3700 cm^{-1} with very high absorbance intensity could be associated with the absorbance of water. The abundant presence of water in the wine suggests that the absorbance of the OH group will not be very useful to develop a calibration model for polysaccharides quantification. For this reason, only the region between 1900 and 900 cm^{-1}, containing information about polysaccharide features, has been taken into account for multivariate analysis purposes (Boulet et al., 2007).

In order to explore the structure of the calibration spectral matrix, a SNV pretreatment was applied to the calibration spectra and, after that, a principal component analysis was performed. A spectral variability greater than 95% was explained using 13 principal components. Mahalanobis distance (H) was determined for each spectrum, samples were ordered according to their H distance with respect to the mean spectrum of the full sample set, and the samples with $H > 3$ were identified as spectral outliers and, therefore, eliminated. No samples were identified as spectral outlier in this study and, then, the 61 samples belonging to the calibration set were used in the calibration procedure.

3.3. MPLS regression models

Using the 1900–900 cm^{-1} region of the FTIR spectra of wine samples, a MPLS regression procedure were applied for the prediction of the main families of polysaccharides (PRAG, RG-II, MP, HG and GL) and TSP. The wine spectra belonging to the calibration set were used as independent variables while reference parameters previously calculated by CG-MS for wine samples were used as dependent variables. Table 2 shows the main statistical parameters for the obtained models. Pretreatment applied is the best of the different treatment evaluated; number of factors generated by the MPLS algorithm (PLS); N is the number of samples used in the calibration analysis after eliminating chemical outliers (T criterion); standard deviation (SD) and the applicability range of the models (maximum-minimum estimations) allows defining the data that could be used for the external validation; the multiple correlation coefficient (RSQ) evaluates how well the calibration fits between spectral and chemical data and, finally, the standard error of calibration (SEC) and standard error of cross-validation (SECV) are estimates of the prediction capability of the model.

Good RSQ values were obtained for MP, PRAG, RG-II and TSP. However, a poor correlation was observed between the GL and HG content and the FTIR spectrum of the samples. This lack of fit could be related to the strong differences that exist in these parameters for the evaluated wines in this study, especially marked for GL (Table 1). The MPLS models were also evaluated by means of the SECV values. This confirmed the challenges for predicting GL and HG from their 1900–900 cm^{-1} FTIR spectra and the suitability of the models for prediction of the rest of the evaluated parameter in wine samples.

The robustness of each selected model was evaluated by means of external validation. MPLS model obtained in the calibration step was applied to the validation set samples and the predicted values were compared with the values determined by GC–MS. All samples belonging to the validation set presented Mahalanobis distances lower than 3 and adequate reference values to be considered in the obtained models according to their applicability. Therefore, no sample was considered as spectral outlier and all of them could be taken into account in the external validation process. Standard error of prediction (SEP) in external validation were calculated (Table 2). SEP, expressed as percentages with respect to the corresponding mean reference values,

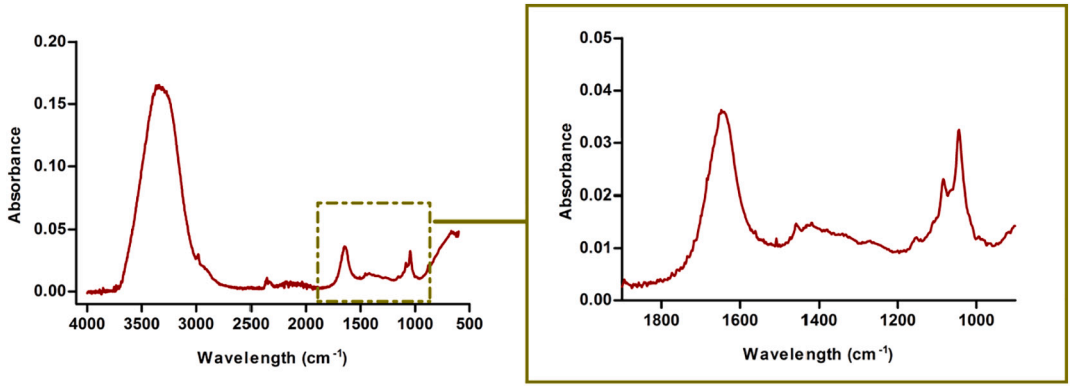

Fig. 1. Raw average FTIR spectra of wine samples in the 4000–500 cm^{-1} and the magnification of the 1900–900 cm^{-1} region.

Table 2
Calibration statistical descriptors for the models developed in the MIR zone close to 1900–900 cm^{-1}.

Reference parameter	Spectral pretreatment	T outliers	PLS factors	N[a]	Est. min.	SD[b]	Est. max.	SEC[c]	RSQ[d]	SECV[e]	SEP[f]	SEP (%)
					(mg L^{-1} wine)					(mg L^{-1} wine)		
RG-II[g]	None 2,5,5,1	0	3	61	0	44.57	252.69	19.23	0.91	22.46	15.33	6.07
PRAG[h]	SNV 1,5,5,1	3	2	58	0	224.35	1224.25	56.88	0.94	75.01	78.67	6.43
HG[i]	Standard MSC 2,5,5,1	0	3	61	0	84.98	426.00	51.47	0.63	56.88	54.61	12.81
MP[j]	Detrend 0,0,1,1	0	1	61	0	72.95	430.44	7.36	0.99	33.45	36.33	8.44
GL[k]	Standard MSC 2,5,5,1	4	1	57	112.25	119.13	827.02	92.30	0.40	105.23	89.06	11.55
TSP[l]	None 2,5,5,1	4	2	57	53.80	497.57	3039.19	237.10	0.77	247.53	188.54	6.25

[a] N: number of samples (calibration set).
[b] SD: standard deviation.
[c] SEC: standard error of calibration.
[d] RSQ: coefficient of determination (calibration set).
[e] SECV: standard error of cross-validation (7 cross-validation groups).
[f] SEP: standard error of prediction (external validation).
[g] RG-II: rhamnogalacturonans types II.
[h] PRAG: polysaccharides rich in arabinose and galactose.
[i] HG: homogalacturonans.
[j] MP: mannoproteins.
[k] GL glucans.
[l] TSP: total soluble polysaccharides.

ranged from 6.07 to 12.81% being the most promising values those obtained for MP, PRAG, TSP and RG-II in decreasing order. Therefore, results obtained for RSQ, SECV and SEP parameters indicate that FTIR spectroscopy possess a great potential for a fast and reasonably inexpensive monitoring of MP, PRAG, RG-II and TSP in wine samples. Coimbra et al. (2002) reported a regression procedure using FTIR spectra for the estimation of the mannose content in purified ethanol polysaccharide fractions from white wines with a good predictive ability. In a later study, Coimbra et al. (2005), improved and successfully extended the previous model to less purified samples from white wines and from red wine (polymeric material and ethanol fractions). However, the studies focused on the estimation of polysaccharides content are very scarce.

Fig. 2 displays the loadings of the MPLS model that led to characterizing the most important wavenumber regarding the prediction of PRAG, RG-II, MP and TSP. Two, three, one and two PLS factors were respectively needed to obtain a predictive ability. The spectral region between 1200 and 900 cm^{-1}, where the C-O-C and C-O-H link band positions are found, showed the most important contribution to all model loadings. The position and intensity of the bands in the 1900–900 cm^{-1} region are characteristics of each purified polysaccharide (Boulet et al., 2007). However, in wine samples it is not easy to assign the specific wavenumber to specific polysaccharides due to underlying spectral bands and vibrational coupling from the high diversity of polysaccharides chemical bonds (Liu et al., 2021). According to the study carried out by Boulet et al. (2007) in purified polysaccharides, the three polysaccharides families have a characteristic peak around 1045 cm^{-1} with different shoulders at 980, 1130 and 1070 cm^{-1} depending on the family. In aqueous solutions, Kacurakova et al. (2000) described bands at 1070 and 1043 cm^{-1} for rhamnogalacturonan, 1072 cm^{-1} for galactan, and 1039 cm^{-1} for arabinan. Two well-defined mannoprotein peaks at 980 cm^{-1} and 1100–1150 cm^{-1} are also described in this work. The discrimination of these compounds could be compromised by their complicated chemical structure and the proximity of their peaks. The 1900–1200 cm^{-1} region is mainly related to minority compounds present in polysaccharides, proteins and uronic acids. The spectrum of proteins is characterized by three bands of different intensity around 1650, 1550 and 1400 cm^{-1}, while uronic acids present three absorbance peaks around 1750, 1620 and 1420 cm^{-1} characteristic of carboxylic acid functional group (Boulet et al., 2007; Manrique & Lajolo, 2002). RG-II are rich in uronic acids while PRAG and MP possess proteins in their composition (Vidal et al., 2003). The presence of these compounds in the three polysaccharides families is directly related to the importance of this region of the spectrum for the correct prediction of their content in wine samples. The high ratio mannose/protein in mannoproteins justifies the relevance of the region of the spectrum related to carbohydrates for the mannoprotein estimation.

4. Conclusions

In this study, FTIR spectroscopy has been evaluated as a technique for the estimation of major wine polysaccharides families. MPLS models

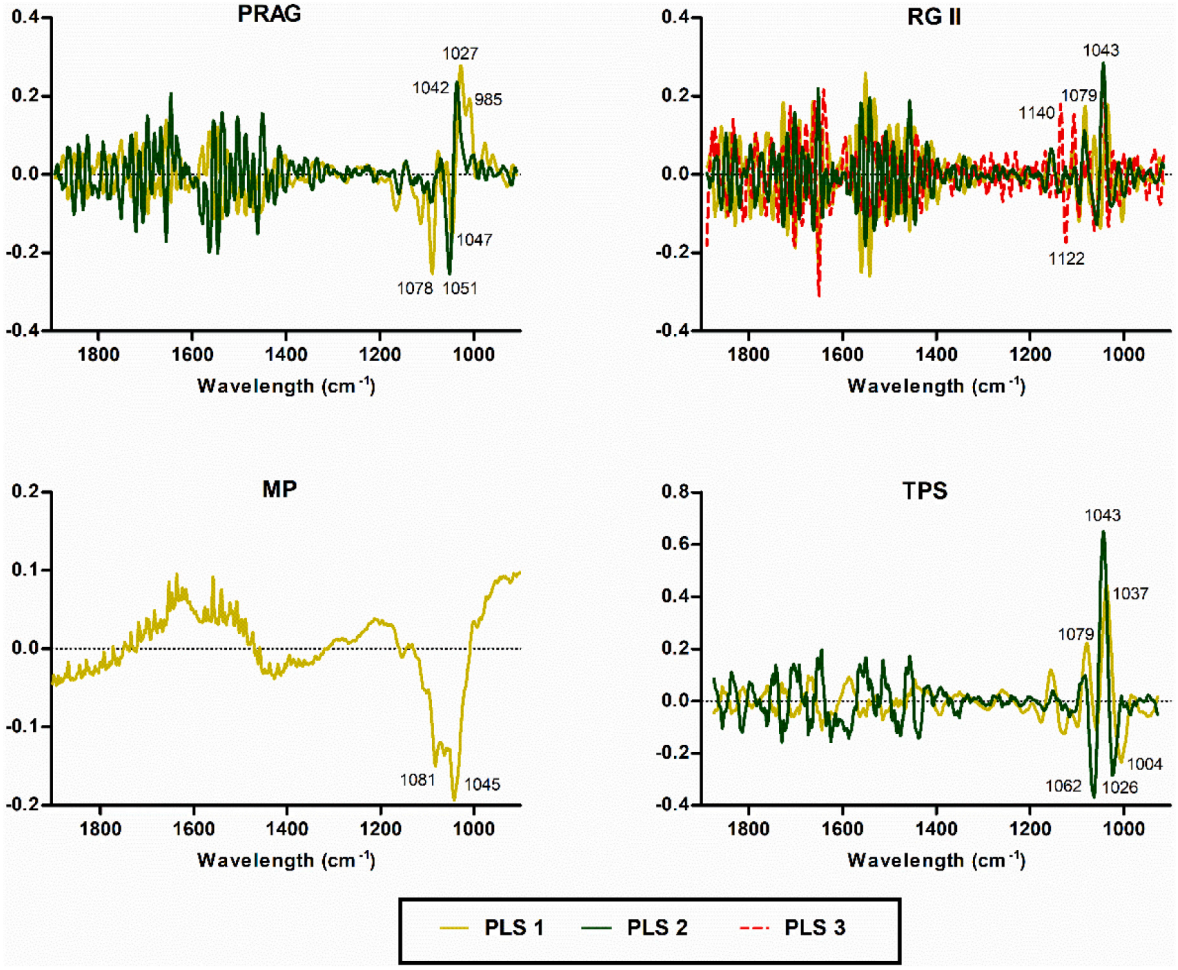

Fig. 2. Loadings plots of the MPLS models for polysaccharides rich in arabinose and galactose (PRAG), rhamnogalacturonans types II (RG-II), mannoproteins (MP) and total soluble polysaccharides (TSP).

developed have revealed the potential of the FTIR analysis in the 1900 and 900 cm^{-1} region as a tool for the daily screening of PRAG, RG-II, MP and TSP in wine samples based on spectral features. Different spectral pretreatments and MPLS calibrations were tested in order to obtain quantitative models for these reference parameters obtaining standard errors of prediction between 6.07 and 8.44%. Moreover, spectral regions with high importance in the adequate estimation of each of these parameters have been identified. GC–MS after hydrolysis and monosaccharide silylation is the most common technique for the polysaccharides determination. However, this analytical procedure requires a great number of operations, equipment and reagents. Taking that into account, the MPLS models developed in this work acquire greater importance. Fast, non-pollutant, non-destructive and cost-effectiveness are properties of FTIR analysis that accentuate its value allowing, especially its speed response, a high versatility and efficiency for the decision-making in the oenological sector. Monitoring the polysaccharides composition of wines in the different stages of the wine-making process is a very important matter in the oenological industry, since it can assist in adapting the wines according to the requirements of the wine and improving quality to satisfy the consumer preferences.

However, more wine samples from different grape varieties, regions, agronomic treatment or wine-making techniques need to be collected in order to obtain more reliable and robust methods especially for those families of polysaccharides that have not been adequately predicted in this work.

Abbreviations

PRAG	Polysaccharides rich in arabinose and galactose
RG-I	Rhamnogalacturonans types I
RG-II	Rhamnogalacturonans types II
MP	Mannoproteins
GL	Glucans
HG	Homogalacturonans
TSP	Total soluble polysaccharides
FTIR	Fourier transform infrared spectroscopy
ATR	Attenuated total reflectance
GC–MS	Gas chromatography coupled with mass spectrometry
PCA	Principal component analysis
MPLS	Modified partial least squares regression
RSQ	Coefficient of determination
SECV	Standard error of cross validation
SEP	Standard error of prediction
SNV	Standard normal variate
MSC	Multiplicative scatter correction

CRediT authorship contribution statement

Berta Baca-Bocanegra: Data curation, Writing – original draft. **Martínez-Lapuente Leticia:** Methodology. **Julio Nogales-Bueno:** Writing – review & editing. **José Miguel Hernández-Hierro:** Writing – review & editing, Supervision. **Raúl Ferrer-Gallego:** Conceptualization, Supervision.

Declaration of competing interest

None.

Acknowledgments

Funding

This work was supported by Spanish Ministerio de Economía y Competitividad [grant number AGL2017-84793-C2] and by Junta de Andalucía [grant number PAIDI-DOCTOR:DOC_00906].

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carbpol.2022.119365.

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