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Near infrared hyperspectral imaging: recent applications in the oenological and viticultural sectors

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In the wine sector, it is really important to know the critical parameters and attributes of grapes, and it is necessary to get this information quickly and accurately. Among others, grape variety, maturity or sugar content are typically analysed in order to determine grape quality, set a grape price and classify grapes for a range of commercially-produced wines. Hyperspectral imaging is an emerging and green chemistry technique for non-destructive and rapid food analysis, and has become an interesting option to measure these parameters without sample destruction or reagent consumption. The number of studies that have used this novel technique to characterise oenological products is increasing (Figure 1). Recent and novel applications, both qualitative and quantitative, that have been carried out in our laboratory will be reviewed and discussed as examples of these developments.

Hyperspectral imaging has only been applied to characterise grape skin for a few years. However, several studies have applied hyperspectral imaging to this matrix with the aim of predicting different parameters in grapes. There are some features that make grape skin ideal for hyperspectral analysis: it is not necessary to destroy the berry, whole grapes are used in order to develop grape skin hyperspectral analyses; grape skin contains some important secondary metabolites, such as anthocyanins or flavonols; grape skin thinness allows the use of hyperspectral imaging also for measuring pulp metabolites; grape skin shows essential physiological changes in grape (i.e. veraison and ripeness). Hyperspectral imaging has been applied to grape skin with the goal of predicting tthe echnological maturity of grapes and the total phenolic compounds, total anthocyanins and extractable polyphenols of grape skin.

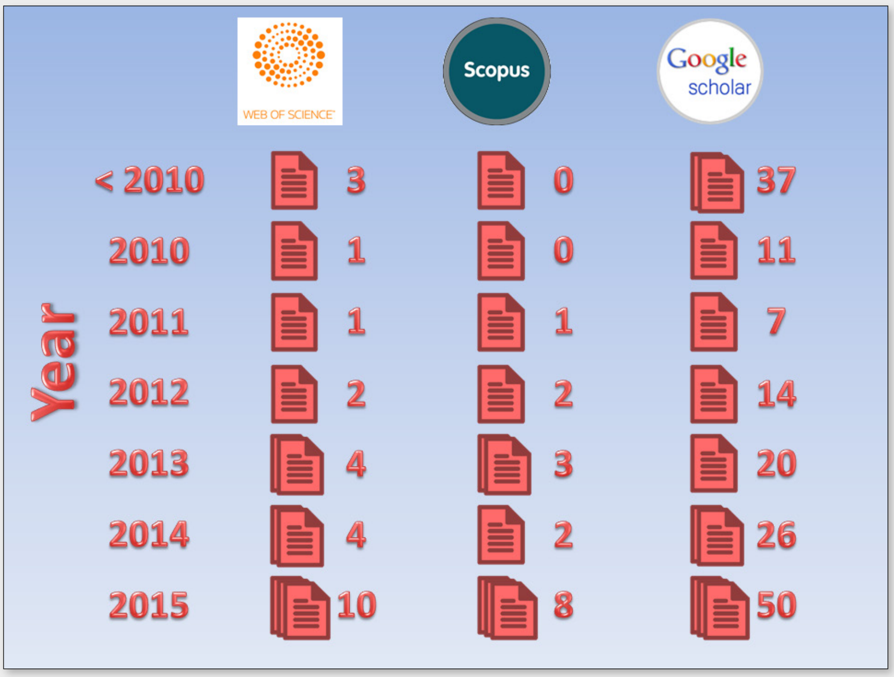

Figure 1. Number of documents found in different data bases using hyperspectral imaging AND (grape OR grape seed OR wine) keywords.

Furthermore, another application of this tool applied to whole grapes is to discriminate between grape varieties. In all these studies hyperspectral systems have been carried out in reflectance mode.

Technological maturity of grape and total phenolic compounds of grape skin have been predicted by Nogales-Bueno *et al.*[1] In this work, hyperspectral images of intact grapes were recorded using a near infrared (NIR) hyperspectral imaging system (900–1700 nm). *Vitis vinifera* L. cv. Zalema, Tempranillo and Syrah grapes were collected from four vineyards located in the Condado de Huelva Designation of Origin (Andalusia, Spain). Grape samples were collected from the 2012 vintage, at different stages of maturity (about 30 grapes per sample). Ninety-nine red and 114 white grape samples were recorded and those spectral data were correlated with grape skin total phenolic concentration and with sugar concentration, titratable acidity and pH of the grape must. Calibrations were performed by modified partial least squares regression (MPLS) using a number of spectral pre-treatments and developed models were tested by an external validation procedure.

The aforesaid work compared the results obtained using different calibration and validation sets. Models developed from red grape samples generated the best results. However, models developed from global sets (using red and white grape samples) also generated good results and have a wider applicability. The results obtained [coefficient of determination (*RSQ*) and standard error of prediction (*SEP*), respectively] for the model developed from red grape samples were 0.89 $mg\,g^{-1}$ and 1.23 $mg\,g^{-1}$ of grape skin for total phenolic concentration, 0.99°Brix and 1.37°Brix for sugar concentration, 0.98 $g\,L^{-1}$ and 3.88 $g\,L^{-1}$ for titratable acidity and 0.94 and 0.12 for pH.

Anthocyanins are important secondary metabolites in grape skins. They provide the colour of red wine, the red and blue colours found in the skins of red or black grapes[2,3] and they also influence the antioxidant activity of red wines.[4] Hyperspectral imaging provides non-destructive, fast, efficient and green chemistry methods to screen anthocyanin content in grape skin.

Hernández-Hierro *et al.* have used a hyperspectral system with a spectral range from 900 nm to 1700 nm to measure total anthocyanin and non-acylated anthocyanin content.[5] Both total and non-acylated anthocyanin contents have also been determined using single grapes from different grape varieties (Garnacha, Graciano, Mazuelo and Tempranillo) as described elsewhere.[6]

In a further step, Nogales Bueno *et al.*[7] used hyperspectral tools for the screening of extractable polyphenols in red grape skins. In particular, extractable total phenolic content, extractable anthocyanin content and extractable flavanol content were determined as reference parameters in Syrah and Tempranillo grapes. Two hundred single berries were collected at harvest time, immediately carried to the laboratory, tempered and subjected to hyperspectral analysis. An unsupervised pattern recognition technique was used in order to select representative samples from the spectral data set. For each selected sample, extractable polyphenols were extracted in a model wine hydroalcoholic solution, then reference parameters were determined and PLS regressions were performed for each parameter. Results (*RSQ* and *SEP*, respectively) for the developed models were: 0.82 mg g^{-1} and 0.92 mg g^{-1} of grape skin for extractable total phenolic content, 0.79 mg g^{-1} and 0.63 mg g^{-1} of grape skin for extractable anthocyanin content, 0.82 mg g^{-1} and 0.45 mg g^{-1} of grape skin for extractable flavanol content. These show good potential for the screening of extractable polyphenols in grape skin. Moreover, developed methods were used in order to predict the extractable polyphenols in the remaining samples and the heterogeneity of extractable polyphenols within the same ripeness stage was studied.

Furthermore, hyperspectral imaging can be used as a tool to discriminate between red grape cultivars. Nogales-Bueno *et al.*[8] investigated the use of three independent methodologies to achieve the differentiation of red grapes from different grape varieties (Garnacha, Graciano, Mazuelo and Tempranillo) collected from five vineyards located in the D.O.Ca. Rioja. Anthocyanin chromatographic analysis, colour image analysis and NIR hyperspectral imaging were carried out on the grapes. A stepwise linear discriminant analysis (SLDA) was developed for each data set in order to discriminate grapes according to their grape variety. As a result, using anthocyanin profile, colour image analysis and NIR hyperspectral imaging, respectively, 88%, 54% and 100% of the samples were correctly classified in the internal validation process and 86%, 52% and 86% were correctly classified in the leave-one-out cross-validation procedure.

Figure 2. Grape seed samples.

Hyperspectral imaging has also been used to record the spectra from other parts of grapes, i.e. grape seeds (Figure 2). Grape seeds are also important because their flavanols have an effect on structure, astringency stability and indirectly on the colour of wine by means of a phenomenon called copigmentation. NIR hyperspectral imaging can also be used to differentiate between varieties using the aforementioned samples. Rodríguez–Pulido *et al.* evaluated seeds belonging to white and red grape varieties.[9] Two red varieties (Tempranillo and Syrah) and one white variety (Zalema) cultivated in two kinds of soil (sand and clay) were considered. In order to monitor the whole development of seeds, sampling began at the beginning of summer, when maturation had not yet started. Seeds were spread in a flat surface and images acquired with a pushbroom hyperspectral imaging system, having a usable spectral range of 914–1715 nm (240 bands). The results obtained using principal component analysis (PCA) revealed that the main variability within the samples set lay in differences of ripeness between seeds (PC1). Regarding PC2 and PC3, it was possible to distinguish between seeds belonging to red or white grapes. Even the kind of soil had repercussions in the spectral information.

Furthermore, hyperspectral imaging has been applied to study not only the content of flavanols, but also the amount that passes to the must during the winemaking process.[10]

Recently, NIR hyperspectral imaging has been used fo evaluate individual phenolic substances in the components of grape marc after freeze-drying. By applying PLS regression to the spectral data, values of R^2 up to 0.98 were obtained for estimating even some minor compounds. Use of this technique could allow winemakers to determine phenolic composition and decide the destination of this by-product that is produced in huge amounts as reported by Jara-Palacios *et al.*[11]

Regarding the use of hyperspectral imaging, all the quantitative results devoted to the oenological sector obtained in our laboratory are summarised in Table 1 for grape[1,5-7] and Table 2 for grape seeds[10] and marc.[11] Further information on the global use of hyperspectral imaging in the

Table 1. Calibration statistical descriptors for the model developed in the NIR zone close to 950–1650 nm for grapes.

Sample	Parameters	Spectral pre-treatments	T outliers	PLS factors	*N*	Est. min	*SD*	Est. max	*SEC*	*RSQ*	*SECV*	*SEP*
Red grapes	Non-acylate anthocyanins (mg g^{-1} skin)	SNV 2,5,5,1	4	5	62	0	3.42	15.61	1.27	0.86	1.70	2.62
	Total anthocyanins (mg g^{-1} skin)	SNV 2,5,5,1	3	5	63	0	4.95	22.82	1.84	0.86	2.41	3.05
Grapes (red and white)	Total phenols (mg g^{-1} skin)	SNV 2,5,5,1	1	9	140	0	2.87	16.34	1.37	0.77	1.77	1.97
	°Brix	MSC 1,5,5,1	8	10	133	0	1.01	31.40	1.01	0.97	1.23	1.61
	Titratable acidity (g L^{-1})	MSC 0,0,1,1	7	10	134	0	11.32	45.06	2.33	0.96	2.72	3.89
	pH	MSC 2,5,5,1	2	8	139	2.17	0.35	4.30	0.10	0.92	0.13	0.18
Red grapes	Total phenols (mg g^{-1} skin)	SNV and Detrend 0,0,1,1	3	6	63	0	2.99	16.69	1.01	0.89	1.07	1.23
	°Brix	None 2,5,5,1	4	6	62	0	5.98	34.61	0.73	0.99	1.04	1.37
	Titratable acidity (g L^{-1})	SNV 0,0,1,1	5	8	61	0	13.39	53.08	1.72	0.98	2.24	3.88
	pH	SNV and Detrend 1,5,5,1	0	8	66	2.08	0.36	4.23	0.09	0.94	0.13	0.12
White grapes	Total phenols (mg g^{-1} skin)	SNV 2,5,5,1	2	7	73	0	2.64	15.49	1.18	0.80	1.76	2.29
	°Brix	SNV and Detrend 2,10,10,1	6	7	69	0.62	4.20	25.79	0.91	0.95	1.10	1.89
	Titratable acidity (g L^{-1})	Detrend 2,5,5,1	5	6	70	0	7.22	30.02	1.89	0.93	2.60	2.21
	pH	SNV 2,5,5,1	4	7	71	2.27	0.34	4.32	0.08	0.94	0.11	0.18
Red grapes	EPC (mg g^{-1} skin)	SNV and Detrend 1,5,5,1	1	5	33	0	1.53	6.86	0.65	0.82	0.92	0.92
	EAC (mg g^{-1} skin)	MSC 1,5,5,1	1	6	33	0	0.92	4.50	0.42	0.79	0.62	0.63
	EFC (mg g^{-1} skin)	Detrend 2,5,5,1	2	4	32	0	0.64	3.21	0.28	0.82	0.50	0.45
Red grapes	Non-acylate anthocyanins (mg per grape)	SNV and Detrend 0,0,1,1	3	6	47	0	0.96	5.37	0.51	0.72	0.78	
	Total anthocyanins (mg per grape)	SNV and Detrend 0,0,1,1	3	6	47	0	0.85	4.63	0.65	0.72	0.70	

EPC: extractable total phenolic content; EAC: extractable anthocyanin content; EFC: extractable flavanols content

oenological and viticultural sectors can be found in Nogales-Bueno *et al.*[12]

In summary, there are several applications in grape skin and seed analysis to which hyperspectral imaging can be applied. Some of them have already been studied while others have not yet been explored and further work is merited. Accordingly, hyperspectral imaging could be applied to the screening of several parameters in grape skin such as total flavanol content, total and extractable flavonol content, total

Table 2. Calibration statistical descriptors for the model developed in the NIR zone close to 950–1650 nm for seeds and marc

Sample		Parameters	Spectral pre-treatments	#LV	R^2_c	RMSEC	R^2_{cv}	RMSECV
Seeds		Stage of maturation	MSC	5	0.96	3.82	0.94	4.58
Seeds	Extraction Model wine	Flavanols (mg catechin per gram of grape seeds)		3	0.82	0.92	0.85	0.88
	Total			3	0.73	4.01	0.75	3.86
Zalema seeds	Model wine	Flavanols (mg catechin per gram of grape seeds)		2	0.83	0.98	0.85	0.92
	Total			1	0.82	2.90	0.82	2.93
Tempranillo seeds	Model wine	Flavanols (mg catechin per gram of grape seeds)		2	0.88	0.67	0.88	0.69
	Total			6	0.94	2.09	0.88	2.89
Marc		Epicatechin (mg/100 g dry mass)		4	0.97	3.70	0.96	4.72
		Total flavanols (mg/100 g dry mass)		6	0.88	48.03	0.78	66.63
		Caffeic acid (mg/100 g dry mass)		6	0.96	0.25	0.92	0.36
		Caftaric acid (mg/100 g dry mass)		6	0.94	2.12	0.91	2.56
		trans-Coutaric acid (mg/100 g dry mass)		6	0.97	0.13	0.95	0.19
		Total phenolic acid (mg/100 g dry mass)		6	0.92	7.04	0.87	9.61
		Kaempferol 3-*O*-galactoside (mg/100 g dry mass)		5	0.99	0.07	0.98	0.11
		Kaempferol 3-*O*-glucuronide (mg/100 g dry mass)		5	0.97	0.04	0.93	0.07
		Kaempferol 3-*O*-glucoside (mg/100 g dry mass)		5	0.99	0.27	0.98	0.41
		Kaempferol (mg/100 g dry mass)		4	0.99	0.01	0.97	0.02
		Total flavanols (mg/100 g dry mass)		6	0.82	10.56	0.70	14.27

and extractable resveratrol content or aromatic potential. Other parameters of interest present in grape seed, such as fat, could also be the target of this new and green analytical methodology. Cell wall structure of the aforesaid matrices and their spectral signature might be also important in order to better understand the release of compounds from tissues to the must or wine and therefore a deep spectral and chemical study should be carried out to examine these issues. Moreover, discrimination tools could be increased in order to discriminate between other grape varieties, detect grape diseases or heterogeneity of samples prior to further analysis. The use of hyperspectral imaging in other matrices such as oenological by-products and the chemical imaging of compounds which present an important or useful commercial role are also two important targets. Furthermore, pilot plant and industrial studies should be developed in order to improve the hyperspectral software and allow automation of the measurements.

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