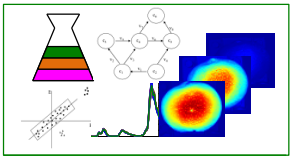

Prediction of olive oil sensory descriptors using instrumental data fusion and partial least squares (PLS) regression

Eva Borràs, Joan Ferré, Ricard Boqué, Montserrat Mestres, Laura Aceña, Olga Busto
Dpto. Química Analítica y Química Orgánica, Universitat Rovira i Virgili, Tarragona. eva.borras@urv.cat, joan.ferre@urv.cat, ricard.boque@urv.cat

Abstract

Three instrumental techniques, headspace-mass spectrometry (HS-MS), mid-infrared spectroscopy (MIR) and UV-visible spectrophotometry (UV-vis) have been combined to quantify virgin olive oil sensory descriptors. The reference sensory values were provided by an official taste panel. Different data fusion strategies were studied to improve the predictions. Best PLS regression models were obtained for musty and fruity attributes. For all the attributes data fusion strategies shown an improvement of the predictions compared to individual techniques.

Keywords:*.Olive oil, sensory attributes, data fusion, PLS regression*

Introduction

Virgin olive oil is a highly appreciated vegetable oil with unique nutritional and organoleptic properties. Its sensory and chemical quality characteristics depend on olive variety, environmental factors, agronomic techniques and cultivation, production and storage conditions. The European Community (EC), the Codex Alimentarius and the International Olive Oil Council (IOOC) have accorded maximum values of specific parameters to guarantee olive oil quality.

To determine olive oil quality categories (extra-virgin, virgin or lampante) different physico-chemical and sensory parameters are evaluated. The only homologated method to assess olive oil sensory attributes is the evaluation by an official taste panel. However, subjectivity, human variability, lack of standards and low throughput per day are some inherent problems associated to this methodology.

Sensory attributes of olive oil are classified into ‘positive’ and ‘negative’. Positive attributes are mainly fruity, bitterness and pungency notes, as well as green grass, sweetness and astringency. The negative ones describe the defects of olive oil, and include fusty (along

with muddy sediment), musty-humidity, winey-vinegary, rancid and metallic. These sensory descriptors depend on the content of volatile and non-volatile minor components.

Alternative solutions to taste panels have been proposed, most of them using instrumental techniques, which offer advantages in terms of fastness, automation and precision. Volatile compounds can be analized by electronic noses (gas sensors or mass spectrometers) using different pre-concentration methods. Non-volatile compounds can be analyzed by electronic tongues (liquid sensors or vibrational spectroscopic techniques such as mid-infrared). Color, although not considered in the evaluation by the taste panel, may influence the quality of the olive oil and color measurements, i.e. by UV-vis spectrophotometry, can provide helpful information.

As olive oil sensory attributes are perceived as a mixture of gustative and olfactive sensations, the combination of data from different instrumental sources can provide complementary information and simplify the sensorial evaluation. Different data fusion approaches of the 'spectral fingerprints' obtained by different instrumental techniques can be applied to correlate to human sensory responses using multivariate pattern recognition techniques. In this study the main olive oil sensory attributes were quantified combining an electronic nose based on headspace mass spectrometry (HS-MS), an electronic tongue based on MIR spectroscopy and an electronic eye based on UV-vis spectrophotometry. Partial least-squares (PLS) was used to correlate sensory data provided by a human taste panel following the official method of the Olive Oil Council (COI/T20/Doc15).

Experimental part

Sensory analysis. Ten sensory attributes, six positive (fruity, bitter, pungent, green grass, sweet and astringent) and four defects (fusty, musty, winey and rancid) were evaluated by the panel for 343 olive oil samples from Catalonia during four harvests (2010-2014). Descriptors were scored in a scale between 0 and 10.

Instrumental analysis. The 343 samples were analyzed with three instrumental techniques: an MS based e-nose and MIR based e-tongue and UV-vis based e-eye. The e-nose consisted on collecting the sample headspace with a solid phase micro-extraction (SPME) fiber and transferring it to an HP5973N MS detector (avoiding chromatographic separation). The m/z range was 50-350 amu. The e-tongue was a FT-MIR Nexus (Thermo Nicolet) spectrometer using a ZnSe crystal ARK multi-bounce over the range 4000–600 cm^{-1} and at 4 cm^{-1} resolution. The e-eye was a UV-Visible Helios Gamma spectrophotometer (Thermo) acquiring within 300 – 1000 nm at 2 nm resolution.

Multivariate analysis. To remove the seasonal variation between samples, a preliminary orthogonalization of the HS-MS and MIR data was applied

To find the optimal prediction model for each attribute, different spectral regions were considered along with different pre-processing options. PLS regression models were built and leave-one-out cross-validated. The lowest root mean square error (RMSECV) was the criterion used to select the optimal number of factors. The final models' performance was confirmed by a test set validation. The average of ten different models was calculated using a random split into a training and test set, with 65% and 35% of the samples, respectively, in order to avoid test results depending on the particular split.

PLS regression models were built for the individual data blocks (MS, MIR and UV-vis), for two-block fused data (MS + MIR) and for three-block fused data (MS + MIR + UV-vis), using low- and mid-level data fusion strategies. In low-level fusion raw data from individual techniques were simply concatenated before model calculation and in mid-level fusion relevant features (independent scores from each individual PLS model) were extracted from the different data blocks and were concatenated into a single matrix.

Results and discussion

The best prediction models for each attribute, considering one-, two- and three-blocks, are summarized in Table 1, together with the detailed PLS results for a specific range of sensory intensities and a final relative root mean square error of prediction (rRMSEP). Best models were obtained for musty and fruity attributes, with R^2 higher than 0.6 and relative errors around 11%. Among the three instrumental techniques, in general, the best results were obtained with mass spectrometry, except for bitterness and fustiness. Good results with MS prove that volatile compounds may potentially contribute to aroma perception. In the case of bitterness the best one-block results were obtained by MIR, confirming the studies that have shown the relationship between this attribute and the polyphenol (non-volatile) content. However, for all the attributes, the best prediction results were obtained when applying data fusion, although in some cases the three-block data fusion only showed a slight improvement. Low-level data fusion was the best option to predict bitterness, pungency and astringency with only MS and MIR. Mid-level data fusion enhanced the prediction of the rest of the attributes, using two-blocks (MS + MIR) for mustiness and three-blocks (MS + MIR + UV-vis) for fruity, green grass, sweet, fusty, winey and rancid attributes.

Table 1. Test-validation PLS regression results (*) for all the attributes studied. Highlighted techniques are the best strategies selected for each attribute.

Attributes	Data Fusion	Technique	Range	R^2p		RMSEP		rRMSEP (%)
				mean	SD	mean	SD	
Positive attributes								
Fruity	One-block	MS	0 – 7	0.55	0.05	0.89	0.07	13.1
	Two-blocks[a]	Low-level		0.63	0.04	0.79	0.04	11.6
	Three-blocks[b]	Mid-level		0.62	0.09	0.77	0.04	11.3
Bitter	One-block	MIR	1 – 7	0.50	0.05	0.67	0.04	11.2
	Two-blocks[a]	Low-level		0.56	0.06	0.62	0.04	10.3
	Three-blocks[b]	Low-level		0.54	0.06	0.64	0.03	10.7
Pungent	One-block	MS	2 – 6.5	0.26	0.08	0.63	0.05	16.2
	Two-blocks[a]	Low-level		0.47	0.07	0.53	0.04	13.6
	Three-blocks[b]	Low-level		0.45	0.06	0.53	0.03	13.6
Green grass	One-block	MS	0 – 5	0.47	0.06	0.83	0.04	17.3
	Two-blocks[a]	Mid-level		0.54	0.07	0.77	0.06	16.0
	Three-blocks[b]	Mid-level		0.58	0.06	0.75	0.05	15.6
Sweet	One-block	MS	3.5 – 5.5	0.36	0.06	0.32	0.02	16.0
	Two-blocks[a]	Low-level		0.41	0.05	0.31	0.01	15.5
	Three-blocks[b]	Mid-level		0.44	0.07	0.30	0.00	15.0
Astringent	One-block	MS	0 – 4	0.40	0.07	0.78	0.04	19.0
	Two-blocks[a]	Low-level		0.56	0.05	0.66	0.03	16.1
	Three-blocks[b]	Low-level		0.53	0.03	0.68	0.03	16.6
Negative attributes								
Fusty	One-block	UV-vis	0 – 6.5	0.54	0.09	0.95	0.11	15.1
	Two-blocks[a]	Mid-level		0.54	0.10	0.92	0.10	14.6
	Three-blocks[b]	Mid-level		0.64	0.05	0.84	0.09	13.3
Musty	One-block	MS	0 – 7	0.64	0.06	0.93	0.09	13.5
	Two-blocks[a]	Mid-level		0.71	0.03	0.82	0.08	11.9
	Three-blocks[b]	Mid-level		0.71	0.06	0.82	0.07	11.9
Winey	One-block	MS	0 – 4	0.58	0.06	0.70	0.05	17.9
	Two-blocks[a]	Mid-level		0.59	0.05	0.69	0.04	17.7
	Three-blocks[b]	Mid-level		0.63	0.06	0.67	0.05	17.2
Rancid	One-block	MS	0 – 7	0.36	0.07	0.82	0.08	12.2
	Two-blocks[a]	Mid-level		0.46	0.09	0.79	0.11	11.8
	Three-blocks[b]	Mid-level		0.51	0.07	0.74	0.09	11.0

(*) Results presented as mean and SD (standard deviation) of the 10 models
R^2p: coefficient of determination of prediction; RMSEP: root mean square error of prediction (test-set); rRMSEP: relative RMSEP
MS: headspace-mass spectrometer; MIR: mid-infrared spectroscopy; UV-vis: ultraviolet-visible spectrophotometer
Two-blocks[a]: MS + MIR; Three-blocks[b]: MS + MIR + UV-vis

References

[1] Apetrei, C., Apetrei, I.M., Villanueva, S., de Saja, J.A., Gutierrez-Rosales, F., Rodríguez-Méndez, M.L., 2010. *Combination of an e-nose, an e-tongue and an e-eye for the characterisation of olive oils with different degree of bitterness*. Anal. Chim. Acta 663, 91–7.

[2] Borràs, E., Ferré, J., Boqué, R., Mestres, M., Aceña, L., Busto, O., 2015. *Data fusion methodologies for* food *and beverage authentication and quality assessment – A review*. Anal. Chim. Acta. doi:10.1016/j.aca.2015.04.042

[3] Escuderos, M.E., García, M., Jiménez, A., Horrillo, M. del C., 2013. Edible and non-edible olive oils discrimination by the application of a sensory olfactory system based on tin dioxide sensors. Food Chem. 136, 1154–9.

[4] Ferré, J., Brown, S.D., 2001. Reduction of Model Complexity by Orthogonalization with Respect to Non-Relevant Spectral Changes. Appl. Spectrosc. 55, 708–714

[5] International Olive Council, 2013. COI/T.20/Doc. No 15/Rev. 6 - Sensory analysis of olive oil. Method for the organoleptic assessment of virgin olive oil. COI.

[6] Monteleone, E., Langstaff, S., 2014. Olive Oil Sensory Science, John Wiley. ed. John Wiley & Sons, Ltd, Chichester, UK.

[7] Sinelli, N., Cerretani, L., Egidio, V. Di, Bendini, A., Casiraghi, E., Di Egidio, V., Bendini, A., Casiraghi, E., 2010. Application of near (NIR) infrared and mid (MIR) infrared spectroscopy as a rapid tool to classify extra virgin olive oil on the basis of fruity attribute intensity. Food Res. Int. 43, 369–375.