

MASS SPECTROMETRY-BASED FINGERPRINTING OF WINE

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References to wine date back to biblical times and its production and consumption are characteristic of many cultures [1]. In order to preserve the identity of unique quality traits in wine against fraud or commercial disputes it is mandatory to develop systems able to collect information related to units/batches of wine ingredients and products [2,3]. Moreover, the last third of the twentieth century was marked by an increase in competitiveness among the world wine market. Therefore, there is a growing demand for new fast methodologies that could certify food quality and authenticity.

On this work it was demonstrated that direct white wine analysis based on direct matrix-assisted laser desorption/ionization (MALDI) mass spectrometry can provide a characteristic mass spectrometry-based fingerprint, MS-FP. Together with informatics and statistics tools, the MS-FP could be used for traceability and quality control in the wine industry. This simple and fast method for wine fingerprinting appears to be effective as it allowed the classification of different wines through their content, without any previous chemical sample treatment.

Here we report a simple and fast method for wine fingerprinting based on direct matrix-assisted laser desorption/ionization (MALDI) mass spectrometry analysis of different white wine samples. A representative set of fourteen different wines from Spain and Portugal, Table 1, were used to infer the potential of this approach to be used as a classification tool of wine on the wine industry.

TABLE 1 – SELECTED WHITE WINES SAMPLES

WINE	GRAPE TYPE
VegaVerde	Airén, Macabeo
Lambrusco Dell'Emilia	Lambrusco
L'Antigón	Macabeo, Merseguera
Viña do Val	Macabeo, Palomino, Sauvignon Blanc
Comportilho Rioja	Viura
Coto de Gomariz	Albariño, Godello, Loureira, Treixadura
Vilerma Blanco	Albariño, Godelho, Treixadura
Beade Primacia	Treixadura
Gran Reboreda	Treixadura
Viña Reboreda	Godello, Palomino, Torrontés, Treixadura
Condes de Albarei	Albariño
Castillo de Liria	Sauvignon, Viura
Pazo Blanco	Treixadura
Joaquín Rebolledo	Godello

For each type of wine it was been acquired five bottles from the same vintage. Wine samples were filtered through a cellulose acetate membrane before analysis. The MALDI matrices were prepared with Alpha-cyano-4-hydroxycinnamic acid in acetonitrile/water with TFA. A mixture of analyte and matrix was applied five times for each sample on a ground steel plate.

All mass spectrometry analysis was performed using Ultraflex II MALDI-TOF/TOF instrument from Bruker Daltonics equipped with a 200 Hz Smartbeam laser system. Data was acquired using FlexControl 3.3.92.0 (Bruker Daltonics). Close external calibration was performed with the monoisotopic peaks of the Bradykinin 1-7 (757.3992), Angiotensin II (1046.5418), Angiotensin I (1296.6848), Substance P (1347.7345), Bombesin (1619.8223), renin substrate (1758.9326), ACTH clip 1-17 (2093.0862), ACTH 18-39 (2465.1983), Somatostatin 28 (3147.4710). The mass spectrometer was operated with positive polarity in reflectron mode, spectra were acquired at each spot position at a constant power. The mass spectrum of each sample was used to statistical analysis.

Table 2 – CLASSIFICATION ANALYSIS OF WINE USING DIFFERENT CLASSIFIERS.

	With Intensities		Without Intensities	
	Kappa	Accuracy	Kappa	Accuracy
Bayes Net	0,929	93,43%	0,895	90,29%
C4.5	0,852	86,29%	0,797	81,14%
IBk	0,939	94,29%	0,902	90,86%
Naive Bayes	0,859	86,86%	0,803	81,71%
Random Forest	0,886	89,43%	0,791	80,57%
SMO	0,880	88,86%	0,828	84,00%
Bagging+C4.5	0,834	84,57%	0,775	79,14%
Bagging+IBk	0,855	86,57%	0,840	85,14%
AdaBoost.M1+C4.5	0,874	88,29%	0,815	82,86%
AdaBoost.M1+IBk	0,837	84,86%	0,895	90,29%
Average	0,874	88,34%	0,834	84,60%

Direct MALDI analysis of wine has proven to be an effective method to profile wines for classification purposes. A total of fourteen wines were correctly classified. It has been possible to classify wines with a high accuracy by grape type and winery, including wines done with the same grape but from different wineries. The analysis performed with intensities appear to be more accurate for classification.