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Matrix assisted laser desorption ionization mass spectrometry linear time-of-flight method for white wine fingerprinting and classification

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ABSTRACT

A fast and simple method for white wine differentiation based on fingerprinting by means of matrix-assisted laser desorption/ionization mass spectrometry (MALDI) combined with linear time-of-flight (TOF) mass spectrometry (MS) and statistical interpretation of the obtained data using principal component as well as cluster analysis is presented. A systematic development was performed to allow a direct comparison and classification of 33 Croatian white wines based on MALDI linear TOF mass spectra ("assuming protein/peptide fingerprints") in the positive ion mode. α-Cyano-4-hydroxycinnamic acid as a MALDI matrix in solution mixed with the unmodified (without any dilution or preconcentration or purification/isolation) white wine sample in a volume ratio 1:1 was applied at ambient conditions and this volume sample preparation technique provided the highest mass spectral information content and optimal reproducibility. Several MALDI matrices, solvents and preparation techniques were evaluated with the selection of the above mentioned as the optimum, prior to large scale investigations. Data obtained by statistical analysis of the aligned mass spectrometric data are shown to provide an efficient way to differentiate white wines of Croatian origin.

1. Introduction

Many traditional food products, including wines, are subject to European Community directives and laws concerning a set of rules and directives for product properties descriptions and declarations, e.g. Regulation (EC) No 178/2002. of the European Parliament and of the Council. The geographical origin is considered one of the most important quality parameters for many wines as it provides added value to the product as well as improved marketing opportunities for producers (Di Stefano et al., 2012; Herrero, Símo, Garcia-Canas, Ibáñez, & Cifuentes, 2012). Frauds and adulterations in similar, yet inferior, products, have become a raising problem in the last decades (Aung & Chang, 2014). Indeed, consumers ask for authentic products with certain characteristics, including standard production procedures.

Assessment of authenticity is therefore of high importance even though presently analytical protocols still have to be developed to accomplish this complex issue. Standard methods including high pressure liquid chromatography (HPLC) or capillary gas-chromatography (cGC) coupled to mass spectrometry (MS) play the key role in research and quality control in viticulture and enology (Antignac et al. 2011; Castro-Puyana & Herrero, 2013; Villiers, Alberts, Tredoux, & Nieuwoudt, 2012). These techniques and their appropriate protocols have been accepted by international quality control organizations as official reference methods and contain laborious sample preparation in combination with sophisticated instrumental measurements. A number of studies report on hundreds of components identified in wines responsible for flavour, taste and colour (Bosch-Fusté et al., 2007; Gruz, Novák, & Strnad, 2008; Jaitz et al. 2010; Welke, Manfroi, Zanus, Lazzarotto, & Alcaraz Zini, 2013). Although the classification is at the moment subjected to proper selection of analytical marker molecules and elements, a more holistic approach based on the measurement and evaluation of several compounds or compound classes in parallel, e.g. fingerprinting, is favourable as the most rationale approach (Capuano & Ruth, 2012).

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Matrix-assisted laser desorption/ionization (MALDI) as a "soft" desorption/ionization technique allows sensitive detection of small as well as large, non-volatile and thermolabile molecules by mass spectrometry (Hillenkamp & Peter-Katalinić, 2014). In the MALDI process the matrix-embedded analyte molecules are desorbed from the solid and ionised, both steps by means of a UV laser beam in a complex process mediated by the solid or liquid MALDI matrix (Karas & Hillenkamp, 1988).

Nevertheless, only two studies have been published so far that deal with fast and reliable molecular fingerprinting of wines using MALDI MS alone. Carpentieri, Marino, and Amoresano (2007) reported on a simple and fast method for red wine fingerprinting using MALDI MS-based analysis as a first application of an efficient wine profiling that was not limited to the detection of anthocyanins. This approach proved useful in particular for the batch-to-batch analysis and for detection of key compounds present in trace amounts and subject to vintage variation. Only one paper reports an attempt of developing a MALDI-MS protocol for origin classification of Spanish white wines (Nunes-Miranda et al. 2012), however the authors until now did not show any results that the presented protocol can be applied for wine classification purposes.

Croatia is a country with a long tradition of grape growing and wine production with about 200 grape-wine varieties registered in the Croatian Ministry of Agriculture's official list of cultivars (detailed lists are given in Croatian official bulletin "Narodne novine" No 53/14.). According to the main register of the grape varieties in Croatia the cultivar Graševina is a dominating wine while autochthonous Istrian Malvazija is the second cultivar. Istrian Malvazija is particularly important for the Croatian Istria where the label 'Istrian Quality (IQ) designation', referring to the wine Istrian Malvazija, is used for high-quality wines made exclusively from Istrian Malvazija grapes. In extensive studies of Croatian wine polyphenols and metal content it was shown that molecular and elemental profiling provide useful tools for differentiation and classification of wine samples according to the type and geographical origin (Fiket, Mikac, & Kniewald, 2011; Kruzlicova, Fiket, & Kniewald, 2013; Rastija, Srečnik, & Medić-Šarić, 2009).

The aim of the present study was to develop a fast and reliable method for white wine differentiation by means of fingerprinting based on MALDI linear TOF MS measurements in combination with subsequent statistical interpretation of the obtained mass spectrometric data, applicable for high-throughput profiling in the future. For that final purpose of Croatian wine fingerprinting comparison and differentiation of MALDI MS based white wine fingerprints, between Istrian Malvazija and four other Croatian white wines, namely Žlahtina, Graševina, Chardonnay and Sauvignon Blanc was performed.

2. Materials and methods

2.1. Chemicals

The α-cyano-4-hydroxycinnamic acid (CHCA), ferulic acid (FA), sinapinic acid (SA), trifluoracetic acid (TFA) and peptide standards (Angiotensin I, Angiotensin II, ACTH 7-38, Cytochrome C and Apomyoglobin) were obtained from Sigma (St. Louis, MO, USA), acetonitrile (ACN) from Fluka (Buchs, Switzerland). All solvents were analytical grade and ultrapure water ($\Omega_m \leq 18$ S/cm) was obtained by Simplicity System (Millipore, MA, USA).

2.2. Wine samples

33 bottles of white wines available from Croatian registered wine producers and two samples of non-filtrated wine samples (IM_A_6 and IM_A_7) purchased from a local registered wine cellar were used in this study. A list of all wines employed in the presented study including vintage year is given in Table 1.

2.3. Sample preparation experiments for MALDI linear TOF MS

Preliminary experiments were done using wine sample IM_A_5 to determine the most appropriate MALDI matrix and sample deposition technique. For sample preparation, three MALDI matrices, FA, SA and CHCA, were separately dissolved in different solvents. Moreover, binary combinations of MALDI matrix solutions were examined. A detailed summary of all studied MALDI matrices and solvents is given in Table 2. Four matrix/wine sample deposition techniques were evaluated, namely volume, dried droplet, two-layer and sandwich technique (Kussmann et al., 1997). For the dried droplet technique, 0.5 μL wine sample was applied onto the stainless steel MALDI target. Additional 0.5 μL of MALDI matrix solution were immediately added to the wine droplet using the pipette tip for mixing. For the two-layer technique the wine sample and matrix solution were mixed in a sample tube (volume ratio 1:1, v/v). After vortexing, 0.5 μL of the mixture was deposited onto the MALDI target. After drying at room temperature 0.5 μL matrix solution was used to cover the dry sample/matrix spot. For the sandwich technique consecutively 0.5 μL matrix solution, 0.5 μL wine sample and again 0.5 μL matrix were applied on the target plate with careful drying of each sample layer before depositing the next. For the volume technique, the wine sample was vortexed for 2 min with matrix solution in a volume ratio 1:1 and 0.5 μL of this mixture was deposited onto the target plate. All sample preparations were left to dry at ambient conditions. To study the final crystal formation of the different sample/matrix preparations, images were taken using a light microscope with an attached DS-5M

Table 1
Wine samples used for MALDI linear TOF MS fingerprinting (*non-filtrated wine samples).

Wine cultivar	Vintage	Wine code	Statistical legend code
Istrian Malvazija	2012	IM_A_1	1
		IM_A_2	
		IM_A_3	
		IM_A_4	
		IM_A_5	
		IM_A_6*	2
		IM_A_7*	
	2013	IM_B_1	3
		IM_B_2	
		IM_B_3	
		IM_B_4	
		IM_B_5	
		IM_B_6	
		IM_B_7	
		IM_B_8	
Graševina	2013	GR_B_1	4
		GR_B_2	
		GR_B_3	
		GR_B_4	
		GR_B_5	
		GR_B_6	
		GR_B_7	
Žlahtina	2013	ŽL_B_1	5
		ZL_B_2	
		ZL_B_3	
		ZL_B_4	
		ZL_B_5	
Chardonnay	2013	CH_B_1	6
		CH_B_2	
		CH_B_3	
		CH_B_4	
Sauvignon Blanc	2013	SB_B_1	7
		SB_B_2	