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PROTON TRANSFER REACTION TIME OF FLIGHT MASS SPECTROMETRY TO DETERMINE CHANGES IN FLAVOR COMPOUNDS DURING LAGREIN RED WINE MATURATION IN WOODEN AND STAINLESS STEEL VESSELS

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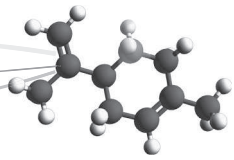
Proton Transfer Reaction-Mass Spectrometry allows the rapid, non-invasive on-line monitoring of volatile organic compounds released form complex matrices such as foodstuffs or from dynamic processes such as manufacturing processes and food consumption. The recently developed PTRToF-MS is characterized by high sensitivity, dynamic on-line capability, rapid response time, and remarkably improved mass resolution that provides in many cases the unambiguous discrimination of chemical formula and detection of the VOCs. PTR-MS has been successfully implemented for the discrimination of red and white Italian wines and the temporal flavour release during wine swallowing (1, 2).
Lagrein wine is a typical PDO Italian red wine produced in the Trentino-Alto Adige area hosted in the northern part of Italy. Along with Marzemino, it is a descendant of Teroldego, and related to Syrah, Pinot Noir and Dureza wines (3).
The flavour of wine can be attributed to the grape variety, oenological, vinification and maturation processes and in addition the wine barrel blending ratios. The vinification process gives rise to principal flavour components under the influence of grape variety and oenological processes resulting in formation of esters, carboxylic acids, alcohols, ketones, aldehydes, terpenes, lactones and phenolics (4). The use of wooden barriques or oak chips is among the well-established methods for wine maturation. The maturation process contributes to the flavour of wine by elimination of undesirable compounds, extraction of desirable compounds from the barrel, maintenance of desirable varietal compounds and increasing complexity of compounds present (5). These reactions when successfully conducted enable a characteristic flavour bouquet and superior quality traits.
In the present study we apply, for the first time, PTR-ToF-MS to wine samples to investigate the effects of oak (three French brands, one American brand), acacia and stainless steel vessels on the volatile compound profile of Lagrein wine during maturation. Wine from the same vinification process was transferred to the six vessels and wine sub-samples removed after 6 and 11 months, diluted (wine;water 1:40 w/w) and headspace gas was measured using a PTR-ToF-MS instrument (Ionicon Analytik GmbH, Innsbruck, Austria).
Two-way ANOVA demonstrated that major flavour compounds and their fragments significantly ($p<0.001$) differentiated samples on the basis of maturation time. In particular, methanol, acetaldehyde, ethyl acetate, hexanoic acid/hexanoates and fragment at m/z 41.038 (related to alcohols) exhibited a significant increase during ageing. In contrast, peaks related to 2-ketones, alpha-diketones, hexen-1-ol, terpineol, and most of the higher esters/carboxylic



acids decreased. From the mass peaks related to phenolic compounds such as furfural, hydroxymethylfurfural (HMF), guaiacol, ethylphenol, benzaldehyde, and whiskey-lactone showed a significant increase ($p<0.05$). Principal components analysis of the entire spectral data set acquired for wine samples analysed at 6 and 11 months maturation, discriminated wine maturated in stainless steel tank from those aged in oak and acacia. These results show that PTR-ToFMS can be used to understand process- and storage-induced volatile compound changes and due to the high throughput capability can play a valuable role in elucidating maturation mechanisms in wine.

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