DART-HRMS FOR WINE EVALUATION
feasibility study

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INTRODUCTION

Polyphenols in wine are compounds with beneficial health effects: among them the flavolons, flavanols, stilbenes show a high antioxidant power, in addiction to give wine different colour, astringency and flavor. Volatile organic compounds are associated with wine flavor: they are mostly formed from yeast during fermentation and their quantity is related to the vinification process adopted. The most important volatile compounds are higher aliphatic alcohols, ethyl esters, acetates and phenols; among them there are also heavier sulfur compounds, as thiols and thioesters, which have a detrimental effect on the wine aroma.

The following preliminary study aims to test the effectiveness of an analytical method of screening non-targeted for a general overview of the products based on a holistic assessment of results. The detection of certain molecules such as organoleptic markers can be a great tool to learn more about wine chemical profile without using chromatographic techniques, and to provide details about vinification steps; in this way the producers will be able to know in advance and in shorter time the characteristics of their wines and make changes to improve their products

MATERIALS AND METHODS

ANALYTICAL METHOD FOR SAMPLE PREPARATION

A set of 6 white wines and 12 types of red wines are tested, each coming from different origin and quality.

1 ml wine
Add 10 ml Ethyl acetate
Vortex for 30 sec
Trasfer 5 µl to a dip-it surface
DARTHRMS analysis
Targeted evaluation mMass | NonTargeted evaluat. Metaboanalyst

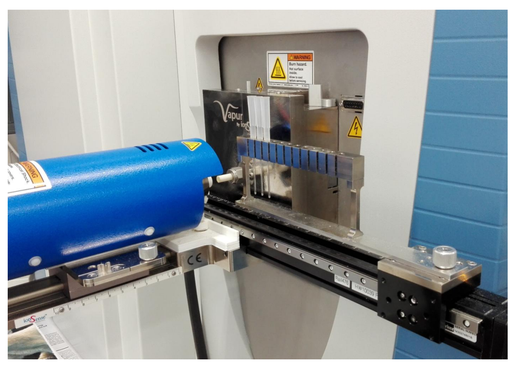

Fig.1 DART ion source with ORBITRAP inlet

INSTRUMENTAL CONDITIONS

The analysis are made with an high resolution mass spectrometer with a DART (Direct Analysis in Real Time) ion source and an Orbitrap mass analyzer (Thermo exactive plus). The instrumental condition are showed in the tables 1-2.

DART	
Temperature	350 C
Grid Voltage	250V
Gas	Helium
Polarity	Positive/Negative
Speed	0.5 mm/s
Dopant	Ammonium 25%

Tab.1 Instrumental conditions used for DART ion source analysis

ORBITRAP	
Polarity	Positive/Negative
Mass Range	From 75 to 1125 m/z
Time analysis	0.33 min
Resolution	70000 FWHM
AGC	3e6
Capillary Temperature	250 C
Slens-RF	55
CID	0 eV

Tab.2 Instrumental conditions used for ORBITRAP mass analyzer

CHEMIOMETRIC EVALUATION

To extract the most significant informations all experimental data were processed with MetaboAnalyst, a web application which provides many treatment and normalization procedures, to perform a classification of wines and the identification of discriminating signals.
The main results are showed in the figures

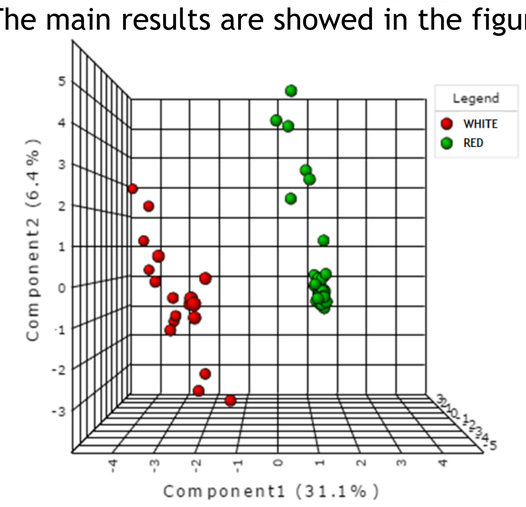

Fig. 4 Comparison of fingerprinting and profile of red and white wines using partial least square discriminant analysis (PLS-DA).

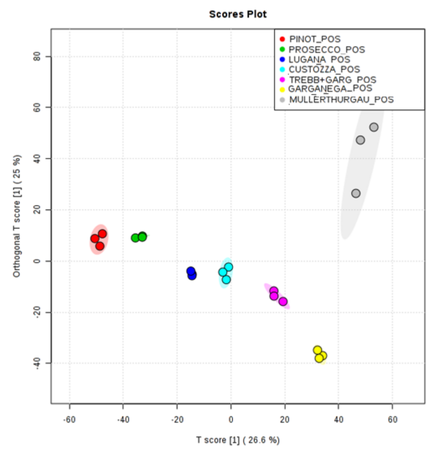

Fig. 5 White wines statistical models using orthogonal partial least squares discriminant analysis (OPLS-DA): Pinot, Prosecco, Lugana, Custozza, Trebbianella, Garganega, Mullerthurgau

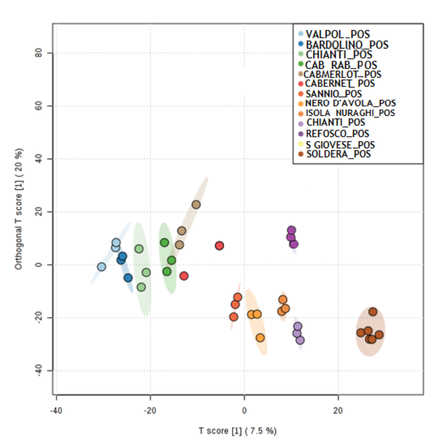

Fig. 6 OPLS-DA scores plot for red wines: Valpollicella, Bardolino, Chianti, Cabernet-Raboso, Cabernet-Merlot, Cabernet, Sannio, Nero d'Avola, Isola dei Nuraghi, Refosco, S. Giovese, Soldera.

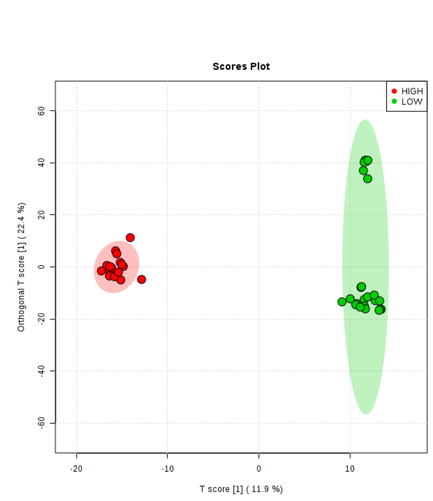

Fig. 7 OPLS-DA scores plot for comparison of high and low quality red wines.

RESULTS

The spectra obtained in both positive and negative ionization mode, are showed in the figures 2-3.

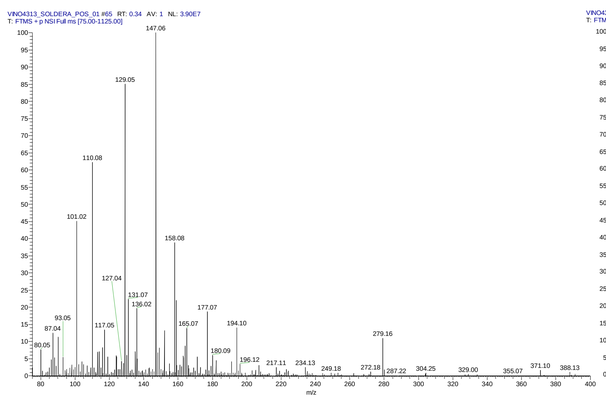

Fig.2 DART-HRMS spectra of a Soldera sample, a red wine, acquired using positive ionization

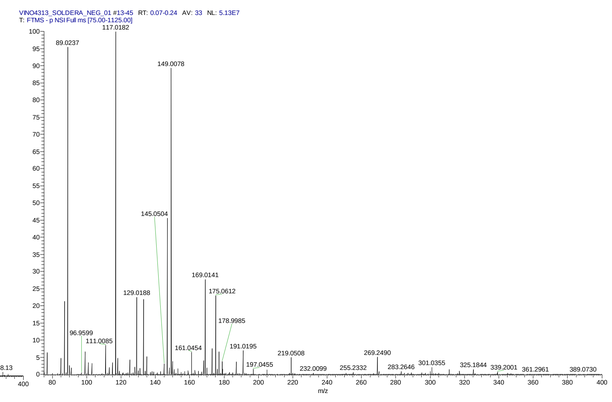

Fig.3 DART-HRMS spectra of a Soldera sample, a red wine, acquired using negative ionization

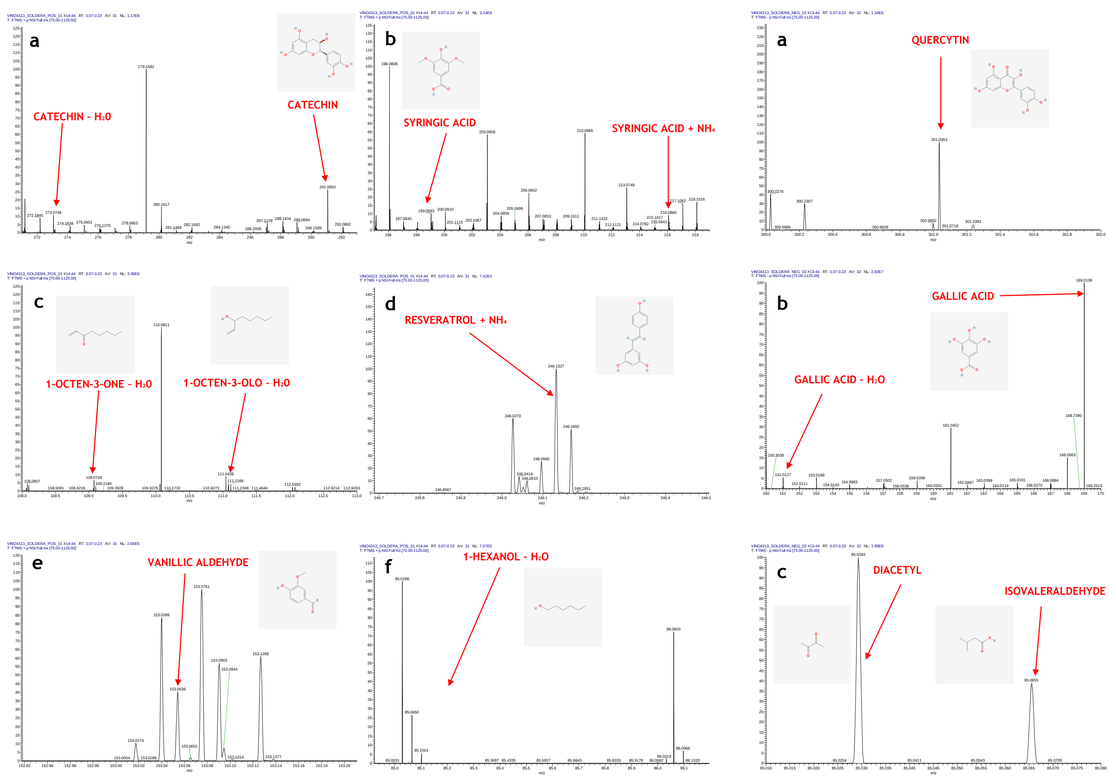

Fig.2a-f Different m/z ranges in DART-HRMS of wine samples acquired using positive ionization. **a)** (m/z 272-292) Catechin; **b)** (m/z 196-218) Siryngic acid; **c)** (m/z 108-113) 1-Octen-3-one and 1-Octen-3-olo; **d)** (m/z 245-246) Resveratrol ; **e)** (m/z 152-153) Vanillic aldehyde; **f)** (m/z 85-86) 1-Hexanol.

Fig.3a-c Different m/z ranges in DART-HRMS of wine samples acquired using negative ionization. **a)** (m/z 330-332) Quercytin; **b)** (m/z 150-170) Gallic acid; **c)** (m/z 85) Diacetyl and Isovaleraldehyde.

CONCLUSIONS..

Concerning the feasibility of the proposed analytical approach, it can be concluded that:
(1) DART-ORBITRAP allows analyses directly on the sample in shorter time and with a minimum sample preparation;
(2) The spectra contains complete informations about the analyzed sample, representing a great tool to know about nutritional factors and organolephical wine properties.
(3) Chemiometric evaluation shows the possibility to perform wines classification and discrimination.

References

1. R. Flamini, P. Traldi, Mass Spectrometry in Grape and Wine Chemistry, Wiley, January 2010, ISBN: 978-0-470-39247-8
2. J.Rubert, O. Lacina, C. Fauhl-Hassek, J.Hajslova, Metabolic fingerprintinc based on high-resolution tandem mass sprectrometry: a reliable tool for wine authentication?, Analytical and Bioanalytical Chemistry, Springer, May 2014