APPLICATION OF LIQUID CHROMATOGRAPHY COMBINED WITH LOW-FIELD DRIFT TUBE ION MOBILITY TIME-OF-FLIGHT MASS SPECTROMETRY (HPLC×IM-TOFMS) FOR RED WINE FINGERPRINTING

Tim J. Causon*[1], Violeta Ivanova-Petropulos[2], Dragana Petrusheva[2], Elena Bogeva[2], Stephan Hann[1]

[1]Division of Analytical Chemistry, Department of Chemistry, University of Natural Resources and Life Sciences (BOKU), Muthgasse 18, Vienna, 1190, Austria

[2] Faculty of Agriculture, University "Goce Delčev", Krste Miriskov, 10-A, 2000 Štip, Republic of Macedonia

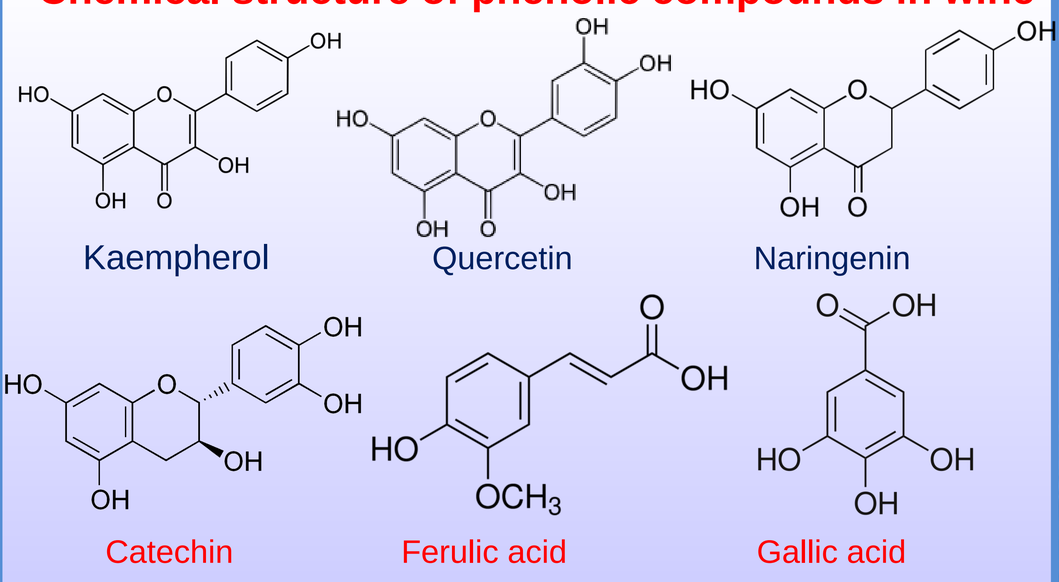
e-mail: tim.causon@boku.ac.at

INTRODUCTION

The analytical characterization of wine *via* targeted and non-targeted metabolomics strategies has proven to be valuable for improving understanding of wine chemistry and establishment of reliable varietal and geographic fingerprints. The combination of high performance liquid chromatography with low-field drift tube ion mobility time-of-flight mass spectrometry (HPLC×IMS-TOFMS) offers potential for the confident characterization and fingerprinting of wine using a metabolomics-type workflow.

The aim of the work was to provide a meaningful fingerprint of red wines from Macedonia, applying HPLC×IMS-TOF-MS technique, using full dataset containing retention, accurate mass and $^{DT}CCS_{N2}$ values.

Chemical structure of phenolic compounds in wine



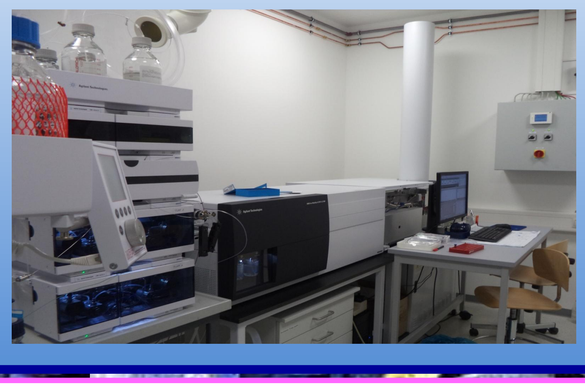
MATERIALS AND METHODS

Red Wine samples: Cabernet Sauvignon, Frankovka, Merlot, Pettit Verdo, Plavan Mali, Pinot Noir, Syrah, Tempranilo and Vranec. Traditional winemaking was applied.

Sample preparation: Filtration and dilution 1:10 with 10 mM ammonium formate (pH 3.75).

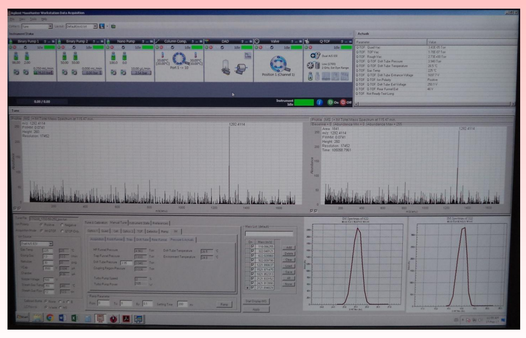
HPLC×IMS-TOF/MS *instrumentation*

- Agilent 1290 Infinity II LC system coupled to an Agilent 6560 IMS-QTOF mass spectrometer and Agilent G1607A dual Jetstream ESI source



HPLC×IMS-TOF/MS *conditions*

- Zorbax Eclipse Plus C18 Rapid Resolution column (2.1 × 50 mm, 1.8 µm d_p)
- Eluent A: 0.1% v/v formic acid in water, Eluent B was methanol



RESULTS AND DISCUSSION

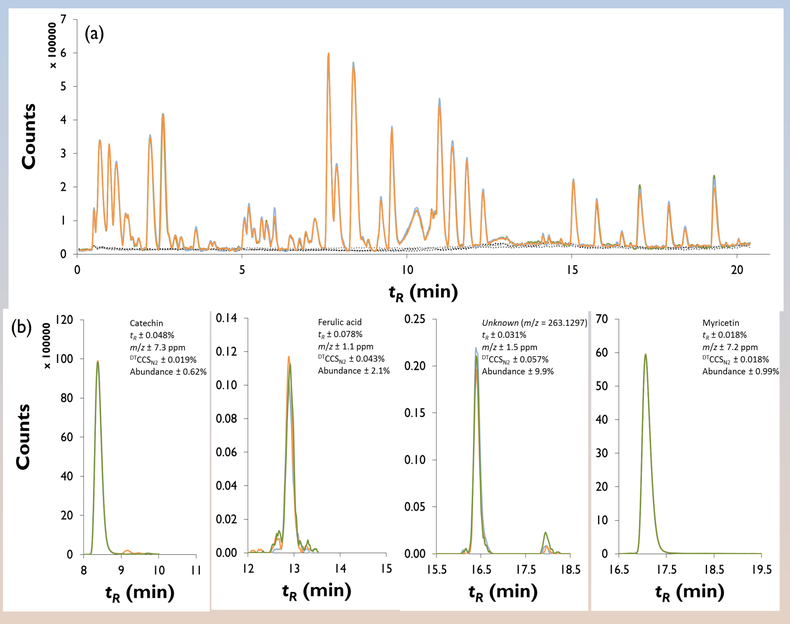


Figure 1. (a) Base peak chromatograms recorded for pooled QC (n=3, solid lines) and blank QC (n=4, dashed lines) samples spread out across the measurement sequence. (b) EICs of standard compounds spiked into wine recorded during the measurement sequence (n=3, injected at evenly spaced intervals across the 22 hour sequence).

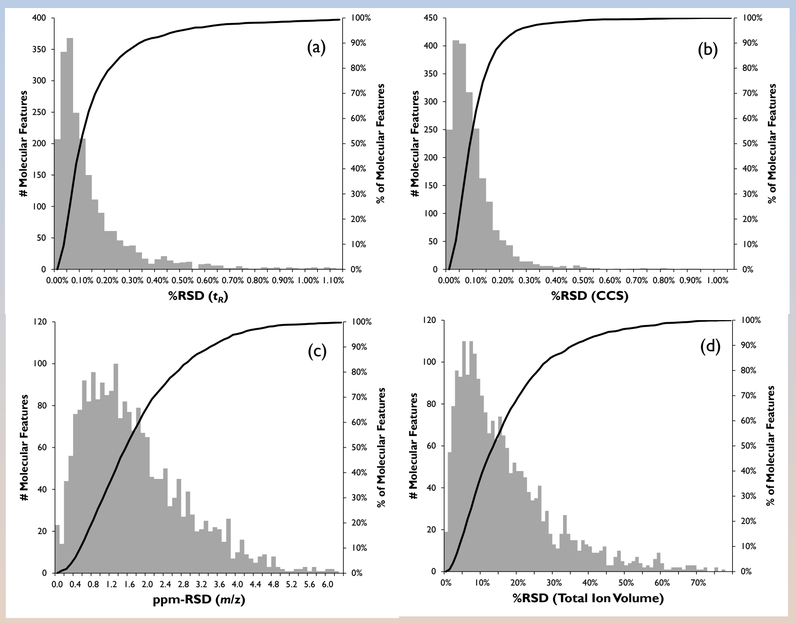


Figure 2. Summary of 2183 molecular features aligned across 3 pooled QC replicates from MassProfiler workflow. Retention time ±0.2 min, mass alignment of 10 ppm ±2 mDa, and frequency in 3/3 replicates required. Molecular feature searching was restricted to ≥2 min (retention time) using the common organic molecules isotope model with maximum charge state of 2 and minimum ion intensity of 50. Molecular features were further filtered using a Q-Score of 70 and a total ion abundance of ≥10 000.

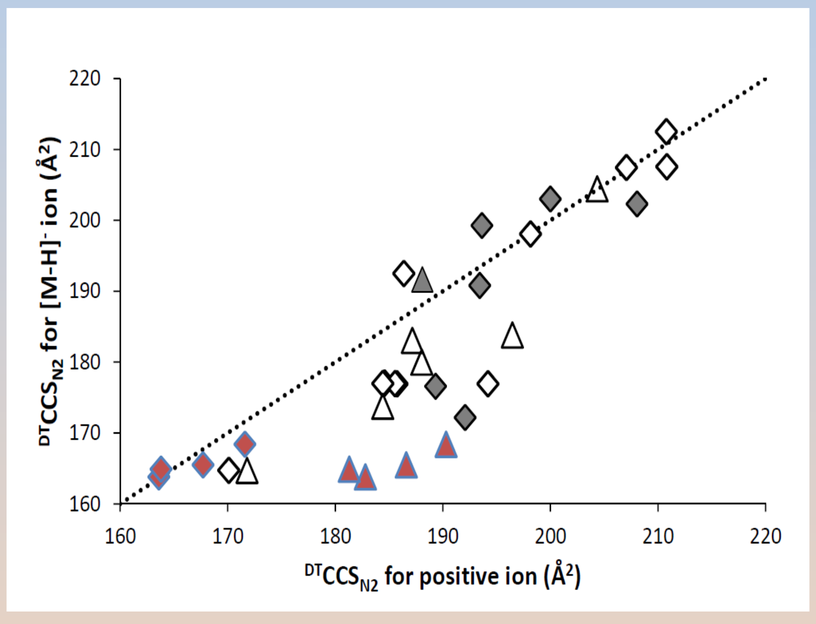


Figure 3. Correlation of $^{DT}CCS_{N2}$ values determined for aligned positive and negative mode molecular features for Vranec (white) and Pinot Noir (grey) with comparison to data from analytical standards (blue). For positive ions, protonated (diamonds) and sodiated (triangles) species are shown separately.

CONCLUSION

- Assessment of a range of traditionally produced wines originating from the Republic of Macedonia allowed detailed fingerprints for individual varieties to be established applying LC×IM-TOFMS techique.
- Each putative compound of interest for a given wine type by statistical assessment is annotated with retention (LC), accurate mass and standardized CCS information.

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