

PTR-MS AS A NEW TOOL FOR FRUIT METABOLOMICS

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Proton Transfer Reaction-Mass Spectrometry (PTR-MS), has been evaluated as a possible tool for rapid non-destructive investigation of the volatile compounds present in the flavour profile of fruit. We show that PTR-MS coupled with multivariate and data mining methods may be successfully employed to address cutting edge problems in fruit metabolomics, by providing accurate varietal and clonal physical fingerprinting.

As a first application, we addressed the classification of several raspberry cultivars having different levels of gray mold susceptibility (*Botrytis cinerea*) and compared results for two headspace analysis methods, namely solid-phase microextraction/gas chromatography-mass spectrometry (SPME/GC-MS) and proton transfer reaction-mass spectrometry (PTR-MS). Given the high number of classes, advanced data mining methods, for instance machine learning ones, are preferred to standard methods such as principal component analysis (PCA), which furthermore does not provide a quantification of class separation. Random forest-recursive feature elimination (RF-RFE) was used to perform feature selection. In particular, the most important GC-MS and PTR-MS variables related to the degree of gray mold susceptibility between the selected raspberry cultivars have been investigated. We point out that moving from GC-MS profiling to PTR-MS fingerprinting leads to a cultivar characterization which is still related to the corresponding *Botrytis* susceptibility level and therefore marker identification is still possible.

As a second application, we characterized apple clones by PTR-MS coupled with a time-of-flight mass spectrometer (PTR-ToF-MS), aiming at unveiling real properties which differentiate the mutated individuals. This is a cutting-edge problem in technical management and royalty application. We studied the VOCs emission profile of five different clones belonging to three well known apple cultivars, such as Fuji, Golden Delicious and Gala. In all three cases we set classification models able to distinguish all cultivars and some of the clones considered in this study. Furthermore, in the case of Gala we also identified a set of compounds contributing to such clone differentiation. Beside its applicative relevance, no data on the volatile profiling of apple clones are available so far. Our studies indicate the viability of a metabolomic approach for fruit volatile compounds based on rapid PTR-MS fingerprinting.