

# UHPLC-HRMS analysis for the evaluation of formation and degradation of polysulfides in wine

The contribution of sulfur compounds to wine aroma has been studied for several years, as their role can be either positive, contributing to the fruitiness and typicality of some white wines like Sauvignon blanc, or negative when related to off-flavours caused by H<sub>2</sub>S. Recently, H<sub>2</sub>S formation from degradation of polysulfides has gained interest in the wine sector as it could potentially lead to wine defects or quality reduction (1). It has been proposed that polysulfides can be formed upon oxidation of thiol compounds (for example glutathione and cysteine) with Cu<sup>2+</sup> or elemental sulfur and could form a reservoir for H<sub>2</sub>S release post-bottling (2,3,4). Polysulfide formation has been demonstrated in several matrices including real wines (5,6,7), but the exact reaction mechanisms have not been proven yet. It has been suggested that both chemical and biochemical activities can play a role (8), which is a topic that is still under investigation. In the present work we investigated the possible technological factors that could influence the formation of polysulfides. Furthermore, we proposed a new method using both liquid chromatography with mass spectrometry and parallel ion chromatography in order to study the degradation of single polysulfides and the formation of H<sub>2</sub>S, respectively.

## METHODS

For the study we used ultra-high-performance liquid chromatography (UHPLC) coupled to hybrid quadrupole/high-resolution mass spectrometry (HRMS, Q-Orbitrap) for the detection, characterisation and accumulation of polysulfides. For the study of polysulfide degradation UHPLC was used with an on-line fraction collector (UHPLC-FC) in order to isolate the single compounds. After collection the sampled compound was kept at 30°C to promote degradation and injections were performed until complete degradation. For the detection of H<sub>2</sub>S Ion Chromatography (IC) was used. For the technological studies, wines fortified with varietal thiols were treated with Cu<sup>2+</sup> or Ag<sup>+</sup> and subjected to accelerated aging and different musts were fermented with different oenological yeasts in single vinifications.

## RESULTS

Using UHPLC-FC and subsequent UHPLC-HRMS it was possible to follow single polysulfide degradation in time. The technological studies revealed treatment effects of post-fermentation treatments with Cu<sup>2+</sup> and Ag<sup>+</sup> and significant differences were found in polysulfide profiles of wines fermented with different oenological yeasts. These studies gave new insights in the formation and degradation mechanisms of polysulfides, which is considered relevant with regard to potential alterations of wine quality.

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