Electrochemical and colorimetric assessment on the influence of target metals on wine color

Departamento de Química y Edafología, Universidad de Navarra, 31080 Pamplona
*jmfdez@unav.es

Three year old samples of Vitis vinifera origin-controlled red wine samples were spiked with adequate amounts of metals and subsequent colorimetric parameters evolution and complexing capacity behaviour were checked. The used approach consisted in the study of the complexing capacity of natural occurring ligands on wine with respect to Zn and Cu by means of stripping voltammetry in acetate pH 4 buffered 1:5 diluted samples onto which increasing amounts of standard metals were added. The resulting titration curves allowed the ligand concentration to be estimated, and the Scatchard and/or Langmuir algorithm transformation permitted the elucidation of the predominant stoichiometries of existing complexes. This technique has proved very sensitive to detect changes in the composition of samples along fermentation time as a function of major ligand populations [1]. Samples treated in exactly the same way were subjected to spectrometric analysis at selected wavelengths. Stability of polyphenol-metal complexes and its possible redistribution on increasing metal concentration can be followed-up by both classical and Cielab space colorimetric parameters. We have already observed that Fe addition modified certain colorimetric parameters reflecting a change in the polyphenol-metal complexes nature [2].

INTRODUCTION

Fermentation of wines is a process which involves many different chemical transformations affecting the concentration of most of the components of this complex matrix. Previous studies have shown a dramatic evolution in polyphenol and metal concentrations during the first three or four days, remaining almost constant after that time.

Metal concentrations are generally determined both by Atomic Absorption Spectroscopy (AAS) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), but electrochemical techniques have also been applied to calculate the total and soluble metal concentrations depending on the chemical treatment of the sample (dissolution, digestion, acidification, dilution with water and no pH control). Dilation of a wine under no pH control conditions induces important changes in the natural equilibria of the matrix, as has been reported elsewhere.

In the present work, an electrochemical technique (DPSAV) will be used to follow up the evolution of ligand-metal complexes during the first sixty days of a wine fermentation under dilution at pH control conditions. The concentration of ligand and conditional complexing constants were calculated by Scatchard and Langmuir algorithms. Molecular modelling studies of the main polyphenols present in wine were undertaken with Hyperchem®. These studies were done in the presence of Cu and Zn in order to confirm the stoichiometry of the most energetically favourable ligand-metal complexes, since the application of Scatchard and Langmuir algorithms implies the formation of 1:1 metal – ligand complexes.

EXPERIMENTAL

The studied samples were must and wine (V. vinifera Tempranillo variety grown in Navarra), fermented at different times ranging from 0 to 60 days, being 0 the time when grapes were introduced in the vessel where fermentation will take place. Commercial wines selected for this study were also Tempranillo variety from grapes grown in different parts of Navarra and La Rioja (Fortius 2002, Alex, 2004, Ochoa, 2002, Piedemonte, 2004, Campo Viejo, 2002). All must and wine samples were diluted 10 times with a pH 4 acetic – acetate buffer. Zn and Cu were the metals studied and titration curves for both metals were registered after spiking the diluted wine samples with 50µL of the standard solutions of Zn (2.5 ppm) or Cu (2.0 ppm).

Total concentrations of Cu and Zn were obtained from AAS measurements of the corresponding digested samples.

RESULTS

Current – potential curves registered for must and wine samples at different fermentation times and for commercial wines after the addition of increasing amounts of the corresponding metal. Oxidation of the curve with increasing amounts of copper both peaks increase in intensity with copper concentration. The I-E curve for day 1 must will be the last 20 additions. Peak 1 keeps increasing with copper concentration but peak 2 stops increasing. Titration curve for peak 1: Typical shape for ligand species in solution. B Titration curve for peak 2: unusual shape, ligand species adsorbed on the electrode surface. Both titration curves (C and D) show the presence of three different slopes which match with the same copper complexation range. The first slope in plot C corresponds to Cu(sal)2(CuCl)2 reaction. The second slope in the same plot corresponds mainly to Cu(sal)2CuCl reaction. The third slope in plot C is the Cu²⁺/Cu zero metal in solution. Titration curve B corresponds to Cu₂Cl₂/CuCl₂ reaction. The three consecutive slopes decrease continuously with added copper concentration indicating the progressive saturation of the complexing capacity of the adsorbed ligand. Similar results for natural waters have been published elsewhere.

I-E curves drawn below correspond to different fermentation times and display a similar pattern to the one explained above, although the position of both peaks are not exactly the same. They evolve with the titration time and for long times and high concentrations of added copper, they behave similarly to commercial wines, e.g. Ochoa. Peak 2 decreases in intensity from day 1 (plot B) to day 58 (last additions) and tends to disappear for commercial wines, as can be seen in the plot corresponding to Ochoa. Following this behavior. Titration curves corresponding to peak 1 of commercial wines display three consecutive slopes that decrease continuously with added copper concentration. The second and third peaks in commercial wines were not observed at all in the case of Palacio de Azcona, for which peak 1 titration curve shows just two sections instead of the three sections displayed above because the corresponding ligand is not present in solution anymore.

REFERENCES


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