10th International Conference on Electroanalysis
European Society for ElectroAnalytical Chemistry
National University of Ireland, Galway
6-10 June 2004
BOOK OF ABSTRACTS

ESEAC2004 Sponsoring Agencies

Republic of Ireland sub-region of the Analytical Division, and the
Electroanalytical Group, of the Royal Society of Chemistry

Science Foundation Ireland, funded under the National
National University of Ireland, Galway
A study of heavy metal complexation in wines

I. Salinas, I. Esparza, C. Santamaría, J.M Fernández

Universidad de Navarra, Irunlarrea s/n, 31080 Pamplona, Navarra (Spain)
Department of Chemistry and Edafology
jmfdez@unav.es

This work is concerned with the loss of colour observed in some of the red wines of Navarra. Polyphenolic compounds are responsible for the structure and wine colour and can be found in the skin, seeds and pulp of the grapes. The colour and stability of these pigments depend on the pH and the presence of several metallic cations.

The present work deals with the identification and quantification of the metallic complexes responsible for the colour of wine and the study of their evolution with time throughout the fermentation of grapes. A method has been optimised to perform a chromatographic separation of the different polyphenolic fractions of wine, keeping constant chemical parameters like pH, alcoholic degree ... After separation, samples were digested under microwave and strong acidic media and their total metal concentration in Zn, Cu, Fe and Mn determined by atomic absorption spectroscopy.

The studied samples were must and wine, both fermented at different times ranging from 0 to 360 days, being 0 the time when grapes were introduced in the vessel where fermentation will take place. The evolution with time of the total metal content for each sample, shows a sharp decrease during the period 0-10 days, reaching the metal concentration a constant value from that day on. A parallel behaviour was observed between certain metals and the main anthocyanins present in wine, i.e., cyanidine-3-glucoside, petunidin-3-glucoside and malvidin-3-glucoside.

Differential pulse voltammetry was used to study complexation processes of Zn in must samples, at their natural pH. Titration curves allowed the calculation of ligand concentration and stability constants, following the suitable linearization methods.

Present work concerns the study, by differential pulse and square wave voltammetry, of the complexation behaviour of both Zn and Cu with model ligands resembling the main antocyanins present in must and wine samples.

Authors would like to acknowledge the "Viticulture and Enology Station of Navarre" (EVENA) for kind supply of grape, must and wine samples.
A study of heavy metal complexation in wines

I. Salinas, I. Esparza, S. Gómez, C. Santamaría, J.M. Fernández
Departamento de Química y Edafología, Universidad de Navarra, Irúnagarra s/n, 31080 Pamplona, Navarra
(Spain)

INTRODUCTION

The colour of red wines is one of the most valued organoleptic parameters in terms of wine quality, both for enologists and consumers. It is well known that phenolic compounds are responsible for the colour of wine and more specifically anthocyanins (a kind of polyphenolic compounds) are the red pigments located in the skin of grapes. The chemical structure of the anthocyanins identified in grapes and wine is shown below:

Malvidin and cyanidin are the most abundant anthocyanins and the Tempranillo variety presents the 3-glucoside substituent for both anthocyanins. From their chemical structure they can behave as chelating agents for metal cations such as Al, Fe, Cu, Zn, Mg, Mn ... which are also present in grapes and wine.

Electrochemical techniques have successfully been applied to the study of metal speciation in seawater, allowing the determination of several parameters like stability constant of the metallic metal concentrations and complexes stoichiometry.

The present work deals with the electrochemical study of must samples in order to find whether it is possible or not the direct speciation of must and wine samples by electrochemical techniques. Alternative routes are also explored.

EXPERIMENTAL

The studied samples were fresh must obtained squashing red grapes and filtering the juice to avoid the presence of any piece of skin or seeds. Must samples were diluted with just water. Electrochemical technique used was DPASV (differential pulse anodic stripping voltammetry).

(+)-Catechin was commercially available from Fluka. Zn and Cu were 1000ppm acidic solutions from Merck.

RESULTS AND DISCUSSION

DPASV was successfully used to study fresh must samples at different dilutions. These plots show the titration curves obtained after additions of aliquots of a Zn solution. Dilutions 1:5 and 1:25 behave as expected for a matrix containing non-saturated ligands able to chelate the increasing amounts of metal added: two slopes are recorded, the lowest one corresponding to complexed metal and the highest one to free Zn. The intersection of both straight lines gives the concentration of the ligands. The third sample, dilution 1:50, was too diluted and the two sloped calibration curve could not be registered.

However, when the mathematical algorithms usually applied to seawater analysis (Scatchard and Langmuir linearization methods) were used in our must samples (1:5 and 1:25), correlations did not follow the pattern described in literature. It was concluded that must samples were too difficult to be measured directly, possibly due to the high number of organic molecules able to participate as ligands for the studied metals.

From these results, a different strategy was utilised: model compounds resembling the structures of the main anthocyanins found in the fractions (with no 3-glucoside substituent) were studied electrochemically at the same pH of must and wine samples (pH = 4).

Figures D and E show the preliminary calibration curves obtained by DPASV when solutions of catechin (non-ionic model compound with R1=OH and R2=H, 3-flavonol) were spiked with Cu and Zn. A 1:1 molar correlation was found for both metals with catechin (for D a catechin concentration was 0.6µM and for E catechin was 1.4µM).

FUTURE WORK

Electrochemical studies will continue with different model compounds in order to optimise the conditions for quantification of Zn and Cu, but other metals like Fe and Mn will also be studied. Must and wine fractionated samples will be directly studied by DPASV. Theoretical studies, using Hyperchem software will be carried out in order to confirm the stoichiometry found electrochemically, for the same model compounds.

ACKNOWLEDGEMENTS

This work has been fully funded by the PIUNA Research Program of the University of Navarra.
Authors would like to thank EVENA (Estación de Viticultura y Enología de Navarra) for providing us the samples used in this project. I.E., I.S. and S.G. would like to thank the local Government of Navarra and the Friends of the University of Navarra, Incorporated, for funding support.

REFERENCES

2-Leighton F., Urquiaga I., Departamento de Biología Celular y Molecular Facultad de Ciencias Biológicas Pontificia Universidad Católica de Chile

E-mail:jmfdez@unav.es