

New Achievements Regarding Trace Elements in Wine

by Zoltán Murányi

I. Introduction and Objectives

Wine is one of the most significant agricultural products in Hungary. Its production and consumption standards have both improved in the country during the past few years. Wines produced in the Hungarian historical wine-growing regions are regarded as 'Hungaricum' in the world's markets and with the growing value of these wines, Hungarian wine producers receive more and more international recognition.

For the above reasons, the analytical examination of wine bears both scientific and economic importance: it promotes improving the quality of wine producing technologies, determining the optimal storage conditions and satisfying the demands of the foreign markets. It may also contribute to changing certain subjective wine qualification aspects into objective. In addition, these examinations will broaden our knowledge about processes that take place in the course of wine production and also in the 'life' of wine regarding its physiological effects.

As a number of metals found in wine also have such physiological effects and technological importance, their analysis is an essential part of the above research. On the other hand, the total

quantity of the different metals and the ratio of their physical and chemical forms are influenced by several factors.

The main objective of this study is to analyze some factors that influence the metal content in wines produced in the two most significant wine-growing regions of Hungary (Eger and Tokaj) searching the answer to the following questions:

1. Which are the most appropriate measuring and sample preparation methods for determining the total metal content?
2. To what extent is it possible to reproduce the method developed earlier for determining the content of primary metals (i.e. metals originating from grapes) in wine?
3. How much is the primary metal content of wine influenced by the wine-growing area and the type of grapes?
4. How much is the total metal content of wine influenced by the wine producing technology? The concentration of which secondary metals (i.e. metals acquired during wine production) is significant?
5. How is the total metal content and the physical forms (enological speciation) influenced by the storage method and the quality of the storage dish?
6. What is the quickest, most inexpensive but secure way of determining the Fe(II)/Fe(III) ratio that is extremely important for the stability of wine?
7. How is the above ratio influenced by the production, treatment and storage technologies of wine?

8. What could be the added value of these results and their statistical analyses to the species and origin protection of wine?

II. Methods and Equipment

Each sample was taken from the storage dish 10 cm below the surface. For determining the primary metal content, the wine had been fermented in a special fermentation and sampling instrument previously developed.

For determining the total metal content, from each wine three samples of 25 cm³ were atmospherically digested by a compound of nitric acid and hydrogen-peroxide, and the remaining substance was then dissolved in a nitric acid solution of 0.1 mol to make 25 cm³. To examine the enological speciation, the fractions were separated with filter-paper (MN 640 d) and cellulose-nitrate membrane filter of 0.2 µm pore size. The metal content of the previously prepared samples was determined with a Spectro brand Spectroflame type instrument in mono/polychromator mode, and an ARL 3410 type ICP-AES instrument in sequence mode. Both instruments had been calibrated by matrix adjustment.

The unstable Fe(II) content was determined with a 2,2'-dipyridin reagent directly from wine, and with a Jasco V-530 type UV/VIS photometer.

The results were statistically processed by using the „factor analysis” module of the SPSS for Windows 7.0 software.

III. New Scientific Achievements

1. A special fermentation and sampling dish has been developed that is suitable for modeling wine production free of technological contamination, thus making it possible to determine the primary metal concentration of six different types of wine. This achievement can serve as a basis for measuring the metal content increasing effect of wine production technologies.
2. By examining the total metal content of one type of wine (Zweigelt) produced in several subsequent years from grapes grown in different wine-growing areas it has been concluded that the primary metal content values determined by the method described at point 1 may be reproduced, which means that the metal concentrations of a given wine in a given wine-growing area show minor deviation.
3. It has been proven that the metal content of wines (Zweigelt in our case) produced from the same type of grapes by using different (small/large scale or experimental) technologies may differ to a significant extent possibly resulting from the technology itself. For the majority of trace elements (Fe, Al, Zn, Cu, Pb, Cd) in wine from both regions (Eger and Tokaj) the greater part of their total content is acquired as secondary concentration. The quality of the storage dish has also proved to have influence on the metal content of wine: wines stored in stainless steel contain greater quantities of the constituent

metals (Fe, Cr), the metal content of wines stored in wooden barrels made in different locations may also differ to a certain extent, and some major metal contamination in the wood may be revealed in the wine as well.

4. It can also be regarded as new achievement that the dissolution, precipitation and deposition processes of wine production can be described by examining the enological speciation and by monitoring the changes. Some of the metals that are present in finished wines as micro-elements were found to be bound to colloid particles like Pb, Cu, Zn, while others like Cd were found to be present as real solution (no reference to these metals has yet been found in any enological literature).
5. A quick and inexpensive method has been developed for determining the unstable Fe(II) content of wine. This showed that the unstable Fe(II) content has close relationship with the conditions of wine production and storage. The change of the Fe(II)/Fe(III) ratio during airing has been examined as modeled under laboratory conditions, and the change in the percentage of the Fe(II) content during wine production has also been monitored with special regard to the effect of treatments.
6. The multivariable statistical analysis of the total metal content of wines has shown that – similarly to the secondary metal content – the quantity of certain metals (Ca, Sr, Na, Mn) is in close relation with the wine-growing area, while others (Fe, Pb, Zn, Al) are mostly influenced by the enological technology. Based on the multivariable statistical analysis of the individual

metals, wines produced in different wine-growing areas can be divided into distinct groups.

IV. Practical Application of the Achievements

The method developed is suitable for determining the primary content that is typical of wines produced in a given wine-growing area by a certain method, and it may serve as a basis for qualifying and possibly improving the enological technology applied (regarding the acquired metal content).

By understanding the enological speciation (after making the necessary refinements) better knowledge can be gained regarding the expected physiological and technological effects of certain metals in wine, and the optimal method for removing them can be better determined.

The examination of the unstable Fe(II) content of wine is essential for maintaining its stability. This examination can be conducted in a quick and inexpensive way by the above method in any laboratory.

The content of the appropriately selected metals may well identify the wine-growing area of the wine. This achievement may lead towards objective origin protection. The appropriate indicator metals need to be selected by the statistical analysis of a certain number of examination results.

V. Related Publications by the Author

1. Murányi Z., Papp L.: **Untersuchung der Migration von Makro- und Mikroelementen in einem Egerer (Ungarn) Trauben-Most-Wein-System.** (Die Migration von Na, K, Ca, Mg, P, Fe, Mn und Zn in Trauben-Most-Wein-Systemen von Blaufränkisch, Zweigelt, Riesling und Királyleányka.) *Die Weinwissenschaft, Vitic. Enol. Sci.* 1996, **51** (1), 25-28.
2. Murányi Z., Papp L.: **Effects of Viticultural Technology on the Concentration of Inorganic Components.** *Microchemical Journal.* 1997, **55**, 81-87.
3. Murányi Z., Papp L.: **ICP-AES metal content analysis of wines made with different technologies.** *ACH Models in Chemistry.* 1997, **134** (4), 529–537.
4. Murányi Z., Papp L.: **„Enological” Metal Speciation Analysis.** *Microchemical Journal.* 1998, **60**, 134–142.
5. Murányi Z., Kovács Zs.: **Statistical evaluation of aroma and metal contents of Tokay wines.** *Microchemical Journal.* 2000, **67**, 91-96.

VI. Related Lectures by the Author

1. Murányi Z., Papp L.: **Szőlő, must, bor elemforgalmának vizsgálata ICP-OES módszerrel I.** XXXVI. Magyar Színképelemző Vándorgyűlés, 1993, Lillafüred, Előadásösszefoglaló, 199-203.
2. Murányi Z., Papp L.: **Szőlő, must, bor elemforgalmának vizsgálata ICP-OES módszerrel II.** XXXVII. Magyar Színképelemző Vándorgyűlés, 1994, Kaposvár, Előadásösszefoglalók, 167-170.
3. Murányi Z., Papp L.: **Effects of Viticultural Technology on the Concentration of Inorganic Components.** VII. Italian-Hungarian Symposium on Spectrochemistry, Innovative Methodologies for Health and Environmental Protection. 1995, Róma, Abstract book, 98.

4. Murányi Z., Dinya Z.: **Különböző technológiával készült borok aroma komponenseinek vizsgálata GC-MS módszerrel.** Vegyészkonferencia, 1996, Eger, Előadásösszefoglalók
5. Murányi Z., Papp L.: **Különböző technológiával készített borok fémtartalmának vizsgálata ICP-AES technikával.** 39. Magyar Spektrokémiai Vándorgyűlés, 1996, Mosonmagyaróvár, Előadásösszefoglalók, 36-39.
6. Murányi Z., Papp L.: **Determination of the iron (II) content in wines.** 40. Magyar spektrokémiai vándorgyűlés. 1997, Debrecen, Book of abstracts, A49.
7. Murányi Z., Papp L.: **„Enological” metal speciation analysis.** VIII Hungarian-Italian Symposium on Spectrochemistry. 1997, Debrecen, Book of abstracts, HI46.
8. Murányi Z., Papp L.: **Borokban lévő vas(II)tartalom és változásának vizsgálata.** 41. Színképelemző Vándorgyűlés. 1998, Budapest, Előadásösszefoglalók, 121-123.
9. Murányi Z., Kovács Zs., Dinya Z., Papp L.: **Statistical evaluation of aroma and metal contents of Tokay wines.** IX. Italian Hungarian Symposium on Spectrochemistry, 1999, Siena, Abstract book, 62.
10. Murányi Z., Papp L.: **Fémek fizikai formájának változása a bor keletkezése során.** 42. Magyar Spektrokémiai Vándorgyűlés, 1999, Veszprém, Előadásösszefoglalók, 57-60.
11. Murányi Z.–Papp L.: **A borok vastartalmáról.** XIII. Élelmiszertudományi Konferencia, 2000, Budapest, Előadásösszefoglalók, 23.
12. Murányi Z., Papp L.: **Investigation of the iron(II) content and its change in wines.** 1st International IUPAC Symposium Trace Elements in Food, 2000, Warsaw, Abstract book, 108-109.
13. Z. Murányi–Zs. Kovács: **Statistical evaluation of aroma and metal contents in wines made in traditional wine growing areas of Hungary.** X. Hungarian-Italian Symposium on Spectrochemistry, Eger (2001), Abstract book, 41.
14. Murányi Z.–Papp L.: **Examination of metal content of Tokay wines made by traditional technologies.** MicroCAD 2002 International Scientific Conference, Miskolc (2002) 107-113.