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# Comparison of trace element and aroma compound contents of red wines

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**Abstract: Vörösborok nyomelem és aroma-anyag tartalmának összehasonlítása.** A bor minőségét különböző tényezők határozzák meg. A talaj, a klíma, a technológia és a szőlőfajta, mind jelentős hatással van a bor összetételére és belső értékére. Vizsgálatainkba ugyanarról a területről származó 5 féle vörösbort vontunk be: 2007-es évjáratú blauburgert, kékfrankost, cabernet-savignont, merlot-t és 2006-os bikavér cuvee-t. A nyomelemek koncentrációját mikrohullámú savas erjesztést követő plazma-tömegspektrometriával határoztuk meg, továbbá 16 aroma-vegyületet határoztunk meg a szilárd fazes kivonását követő GC-MS módszerrel. A nyomelem-tartalom gyakorlatilag nem függött a szőlőfajtától, az aroma-anyagok azonban – különösen a tetratetrakontán, az oktanoszán és az etil-oktanoát esetén – jelentős különbségeket mutattak.

## Introduction

Egri Bikavér (Bull's Blood of Eger) is a traditional red cuvee wine originated from the Northern Hungarian Wine-growing Region of Hungary [1, 2]. It is made from various blue grapes (Blauburger, Kékfrankos, Cabernet sauvignon, Cabernet franc, Merlot) under strict regulations of origin-protection. Bull's Blood of Eger is well known and consumed not only in Hungary but in various countries of Europe and the world. The quality assurance of wines needs well defined investigations e. g. determination of ethyl alcohol or sugar content, concentration of different organic acids and color compounds etc. [3]. However from toxicological point of view it is recommended to check the concentrations of toxic heavy metals originating from soil, fertilizers, pesticides or herbicides [4]. The trace element content of wines remains practically constant during storage, however aroma compounds change continuously. Concentrations of certain groups of primary aroma compounds coming from grapes and the fermentation

aroma compounds decrease during the maturation of wines. In the case of oxidative treatment mostly aldehydes and acetates are formed, while the application of reductive technology results in the formation of higher ester content. In this paper we studied the influence of the variety of grapes on the concentration of trace elements and aroma compounds in 6 red wines by applying Inductively Coupled Plasma Sector Field Mass Spectrometer (ICP-SF-MS) and Solid Phase Micro Extraction / Gas Chromatograph Mass Spectrometer (SPME/GC-MS) techniques, respectively. For determination of trace elements an Element2 ICP-SF-MS (Thermo Finnigan, Germany) was used. The operating conditions of this equipment are summarized in Table 1. Microwave-assisted digestion of wine samples was performed by using a Multiwave Paar Physica device (Paar, Austria). For this procedure six HQ50 quartz bombs (Paar, Austria) were used simultaneously.

*Table 1. Operating conditions of ICP_SF_MS system*

| | |
|---|---|
| Power (W) | 1200 |
| Ar gas carrier flow ($dm^3$/min) | 16.0 |
| Ar gas auxiliary flow ($dm^3$/min) | 0.8 |
| Ar nebuliser flow ($dm^3$/min) | 1.1 |
| Measurement mode | Medium resolution (R=4000) |
| Acquisition mode | E-scan |
| No. scans | 20 (5 runs, 4 passes) |
| Search window (%) | 80 |
| Integration window (%) | 60 |
| Calibration | External |
| Internal standard | 50pg/$cm^3$ In |
| Points per peak | 30 |
| Isotopes | $^{52}$Cr, $^{55}$Mn, $^{57}$Fe, $^{60}$Ni, $^{63}$Cu, $^{66}$Zn, $^{75}$As, $^{114}$Cd, $^{202}$Hg, $^{208}$Pb. |
| Nebuliser | Meinhard |
| Spray chamber | Scott |
| Sampler cone | Ni, ø 1.0mm orifice |
| Skimmer cone | Ni, ø 0.7mm orifice |

## Experimental

### Trace element analysis

*Reagents and standards*

Suprapure 65% $HNO_3$ (Merck, Germany) was used for the microwave-assisted digestion of wine samples. For tuning and mass calibration of ICP-SF-MS instrument an acidic (5% $HNO_3$) Merck Multi-element standard solution in concentration of 1ng/cm$^3$ for each element was employed. For internal standardization acidic indium (Merck) stock solutions (0.5 mol/dm$^3$ $HNO_3$) were prepared daily from their stock solutions by appropriate dilution with ion-exchanged water. The final $HNO_3$ concentration of the solutions was 5%.

*Analytical procedure*

For trace element analysis aliquots of 2cm$^3$ wine samples filtered through Millex PDVF filters of 0.2μm pore size were placed into quartz bombs. Aliquots of 2cm$^3$ $HNO_3$ were carefully added. The samples were subjected to microwave-assisted digestion for 40 min, at 1000W (nominal power value per six bombs) achieved with a ramp of 50W/min. Six bombs were used simultaneously for one digestion procedure. Between two digestions the bombs were cleaned with 5cm$^3$ $HNO_3$ (Suprapure) at 1000W, for 20 min. The purity of the resulting solutions was checked by ICP-SF-MS method. After digestion indium internal standard was added and the solutions were filled up to 40cm$^3$ with deionized water. These solutions were analyzed by ICP-SF-MS technique applying external calibration.

*Determination of aroma compounds*

Aroma compounds were adsorbed on a quartz fiber covered with poly-dimethylsiloxane (100μm PDMS, non-polar). The fiber was introduced into 5cm$^3$ vapor space above 100cm$^3$ wine sample, at room temperature (Fig. 1.).

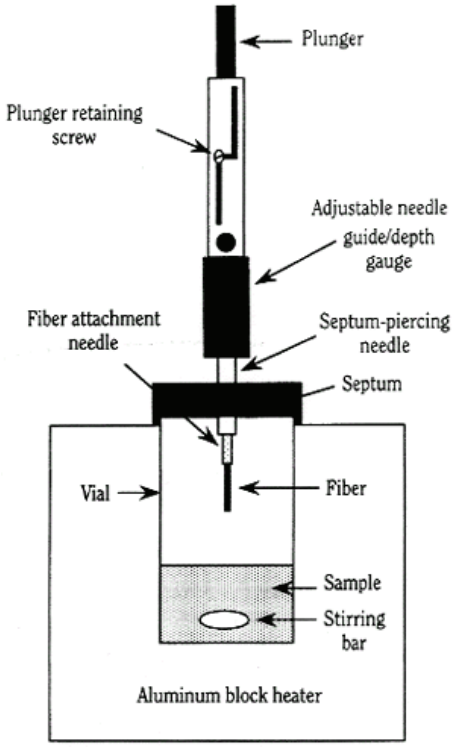
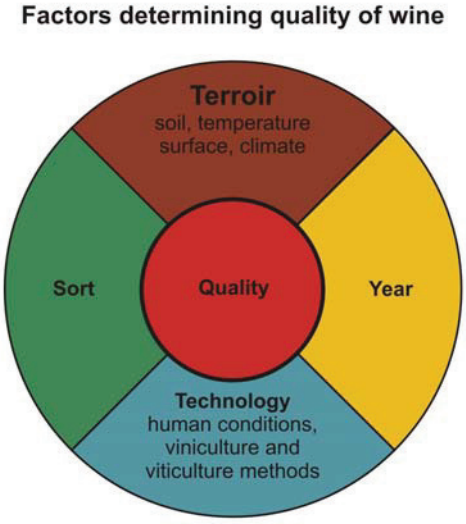



*Fig. 1. SPME set up for measurement of aroma compounds*

The contact time amounted to 15 min. In order to achieve the balance between the liquid and vapor phases, wine was stirred in closed vessel for 20 min, before the introduction of the fiber. After pre-concentration of aroma compounds the loaded fiber was put into a heated injector (220$^{o}$C) of the GC-MS system (Shimadzu QP 2010S) and analyzed after separation on HP-5MS (30m×0.25mm×0.25μm) column. The analytical signals of aroma compounds were related to the signal of ethyl alcohol.

**Results and discussion**

Five different wines of blue grape varieties (Blauburger, Kékfrankos, Cabernet sauvignon, Cabernet franc, Merlot) of the same year (2007) and of the same terroir and also a Bikavér wine of 2006 coming from the same terroir, made from the same varieties of red wines using the same technology, were involved in our examination.




The concentration of toxic trace elements (Cd, Hg, As, Pb) is negligible. The other elements have similar concentration, which means, that the variety of grapes has no significant influence on their uptake processes (Table 2.).

*Table 2. Concentrations (μg/cm$^3$) of trace elements in investigated red wines. Standard deviation data are calculated on the basis of the subsequent integrations within one run (n=20). Limits of quantification were calculated as 10 sigma. 1995/90$^{th}$ jur. 27§. 11$^{th}$ paragraph*

| | Cabernet franc 07 | Blauburger 07 | Merlot 07 | Cabernet Sauvignon 07 | Kékfrankos 07 | Bikavér 06 | Limit values * |
|---|---|---|---|---|---|---|---|
| **Cr** | 0.032±0.001 | 0.023±0.001 | 0.031±0.001 | 0.029±0.001 | 0.043±0.001 | 0.041±0.001 | - |
| **Mn** | 1.94±0.09 | 1.90±0.06 | 3.15±0.09 | 1.89±0.08 | 2.14±0.09 | 2.36±0.10 | - |
| **Fe** | 1.67±0.03 | 3.89±0.12 | 2.89±0.10 | 3.10±0.15 | 3.60±0.22 | 2.28±0.06 | 5 |
| **Ni** | 0.082±0.002 | 0.095±0.002 | 0.111±0.004 | 0.086±0.002 | 0.091±0.003 | 0.084±0.002 | - |
| **Cu** | 0.168±0.009 | 0.008±0.001 | 0.106±0.003 | 0.035±0.002 | 0.029±0.001 | 0.069±0.003 | 10 |
| **Zn** | 1.07±0.02 | 0.859±0.016 | 0.787±0.032 | 0.877±0.019 | 1.45±0.03 | 0.712±0.023 | 10 |
| **Pb** | 0.0075±0.0008 | 0.0037±0.0001 | 0.0043±0.0001 | 0.0037±0.0001 | 0.0070±0.0001 | 0.0032±0.0001 | 0.25 |
| **As** | <0.065 | <0.065 | <0.065 | <0.065 | <0.065 | <0.065 | 0.1 |
| **Cd** | <0.010 | <0.010 | <0.010 | <0.010 | <0.010 | <0.010 | 0.02 |
| **Hg** | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | <0.002 | 0.01 |

The analytical signals of 16 identified aroma compounds were related to the signal of ethyl alcohol (Table 3.).

*Table 3. Analytical signal of aroma compounds related to ethyl alcohol signals measured in vapor phase by GC-MS method.*

| Name | Bikavér 2006 | Blauburger 07 | Kékfrankos 07 | Cabernet sauvignon 07 | Cabernet franc 07 | Merlot 07 |
|---|---|---|---|---|---|---|
| **Ethanol** | 100 | 100 | 100 | 100 | 100 | 100 |
| **Ethyl Acetate** | 10,95 | 5,05 | 18,35 | 7,25 | 7,56 | 6,29 |
| **3-methylbutanol** | 15,98 | 22,09 | 14,9 | 16,8 | 16.68 | 21,86 |
| **Hexanol** | n.d. | n.d. | 0,33 | 0,68 | 0,37 | n.d. |
| **Isoamyl acetate** | n.d. | n.d. | 1,12 | 0,92 | n.d. | 3,19 |
| **Ethyl hexanoate** | 3,29 | 2,76 | 1,81 | 2,52 | 2,32 | 3,39 |
| **Phenylethyl alcohol** | 1,3 | 3,61 | 0,66 | 2,92 | 1,22 | 5,98 |
| **Diethyl butanedioate** | 1,21 | 0,83 | 0,17 | 0,91 | 1,11 | 2,13 |
| **Ethyl octanoate** | 9,17 | 8,09 | 3,07 | 6,67 | 4,18 | 18,82 |
| **Ethyl decanoate** | 3,4 | 9,1 | 5,82 | 2,54 | 2,05 | 8,5 |
| **Butylated hydroxytoluene** | 0,21 | n.d. | 0,5 | 0,3 | n.d. | n.d. |
| **Eicosane** | 4,64 | 14,94 | 8,1 | n.d. | n.d. | n.d. |
| **3-methylundecane** | n.d. | n.d. | n.d. | 0,73 | n.d. | 1,52 |
| **Octacosane** | 105,92 | 22,58 | 19,21 | 115,56 | n.d. | 101,61 |
| **Tetratetracontane** | 8,61 | n.d. | 87,47 | 5,25 | n.d. | n.d. |
| **Methyl decanoate** | n.d. | 2,7 | n.d. | n.d. | 1,356 | n.d. |

*n.d. not detectable*

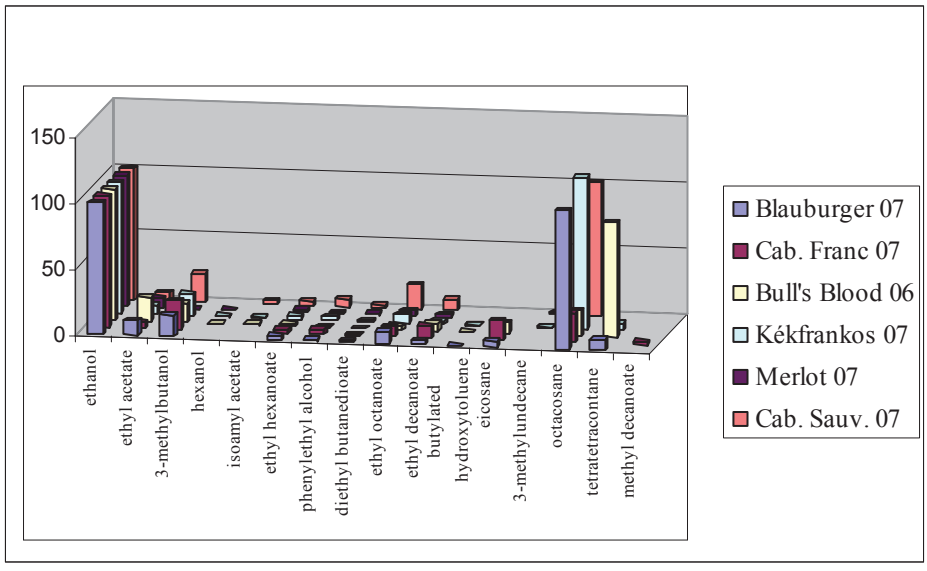



*Fig. 2. Analytical signals of aroma compounds related to ethyl alcohol signals measured in vapor phase after SPME by GC-MS*

These data demonstrate that the dominant aroma compounds are octacosane, tetratetracontane, isoamyl alcohol, ethyl octanoate and ethyl acetate. In the case of Bull's Blood, Blauburger, Cabernet Sauvignon and Merlot wines octacosane had the highest concentration, while in the case of Kékfrankos and Cabernet franc tetratetracontane and isoamyl alcohol are the dominant aroma compounds, respectively (Fig. 2.).

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