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EVALUATION OF INFLUENCE OF THE LOCALITY, THE VINTAGE YEAR, WINE VARIETY AND FERMENTATION PROCESS ON VOLUME OF COOPER AND LEAD IN WINE

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ABSTRACT

We have focused on the influence evaluation of the locality, the vintage year and fermentation process on the volume of copper and lead into grape must and wine. First of all copper and lead volume was assessed into fresh grape musts. Subsequently the musts were fermented. During the wines analyses we found great decrease of copper by the fermentation process. Assessed Cu^{2+} values vary from 0.07 to 0.2 $mg.L^{-1}$ and represent a decrease of the original copper volume from 90 to 97%. On the copper content into grape has probably the significant influence also the precipitation amount, which falling in the second part of the vegetation half a year. Total rainfall in the period before the grape harvesting (the months of August - September**)** was for the first year 153 mm and for second year 137,5 mm. During both observed vintage years it was concerning to the above average values. Copper is not possible to eliminate totally in the protection of the vine against fungal diseases, because against it does not come into existence resistance into a pathogen. For resolution of this problem it is suitable to combine the copper and organic products. Fermentation affect as a biological filter and influence also lead volume. Into analysed wines we found the decrease of the lead volume from 25 to 94%. Maximal assessed Pb^{2+} value into wine was 0.09 $mg.L^{-1}$. The linear relationship between lead and copper into grape must in relationship to the lead and copper into wine was not statistically demonstrated. We found the statistically significant relationship in lead content into grape must by the influence of the vintage year, which as we supposed, it was connected with the atmospheric precipitation quantity and distribution during the vegetation. On the base of the assessed results of the lead and copper volume into wine, we state that by using of the faultless material and appropriate technological equipment during the wine production, it is possible to eliminate almost completely the problems with these heavy metals content into our wines and it is from the view of technological as well as hygienic.

Keywords: Viticulture; grape must; wine; heavy metals; copper; lead

INTRODUCTION

Intensive soil cultivation is oriented mainly on the economic effect achievement. This can cause to insufficient ecology consideration and subsequently to the environment damage with the toxic elements from the fertilizers, composts and pesticides. In the past we observed such behaviour with the agricultural soil handling. In the present time a view on the ecology and healthy environment is totally different. The grapevine is cultivated mainly by the integrated and environmental friendly way. However the agricultural soil can contain contaminates residues from the past. These contaminants enter after the crop plants intake into the food chain. It belongs here copper and lead.

Mineral substances content into grape must is very unstable value, which is not influenced only by the original amount coming from the vineyard and external environment, but also by the application of the additive matters and residues from the technological machines equipment (Table 1).

Table 1 The highest allowed amounts of the lead and copper into fruit musts, grape musts and wines within the meaning of the valid legislative (*Codex Alimentarius*).

Element	Fruit musts ($mg.L^{-1}$)	Wine ($mg.L^{-1}$)
Lead	0.05 (1)	0.2 (2)
Copper	5.0 (1)	1.0 (3)

(1) Regulation of Ministry of the Agriculture and Rural Development of the Slovak Republic and Ministry of Health of the Slovak Republic from 11 September 2006 No. 18558/2006-SL, by which it is issuing the Chapter of Codex Alimentarius of the Slovak Republic, regulating food contaminants as amended by.

(2) Commission Regulation (EC) No. 1881/2006 from 19 December 2006, by which are setting maximum levels for certain contaminants in foodstuffs.

(3) Commission Regulation (EC) No. 606/2009 from 10 July 2009, from which are laying down certain detailed rules for implementing Council Regulation (EC) No. 479/2008 as regards the categories of grapevine products, oenological practices and the applicable restrictions.

MATERIAL AND METHODOLOGY

After sampling of the biological matter, we processed the grape by the uniform way. Unclarified must (Samotok - juice extract from grapes gained by using only its own weight) was not in touch with any contaminant during whole working process and it could not be enriched with some of observed elements. Into obtained must we measured (1) the sugar content in $kg.hl^{-1}$ on the Slovak Normalized Must-Weight Scale (Slovak: Normalizovaný muštomer), which indicates how many kilograms of sugar are contained in one hundred liters of grape juice, according to Slovak Technical Standard (STN) 25 7621 with modification of the measured values according to the temperature correction, (2) the total acid content by titration (STN 56 0216) and (3) pH potentiometrically.

The observed chemical elements content into must we assessed, after wet way burning according to STN 2676/1990 (Nitric acid, Perchloric acid, Sulphuric acid) by atomic spectrophotometer according to the EU certified method (2676/1990). We worked with analyser SP-9 (PYE-UNICAM). From the reason of the errors elimination by possible heavy metals contamination from the chemical reagents, we made a blank test.

Into fermented must we observed the biodegradation of lead and copper by fermentation process. We performed the analyses after complete musts fermentation, in both observed vintage years 60 days after the grapes pressing. The state of the musts fermentation we measured by assessing of the alcohol content *ebullioscopically.*

The obtained results we evaluated statistically by the analysis of variance and they are listed into enclosed Tables and Graphs. Each measurement we performed four times and we evaluated them by the analysis of variance method.

Experimental sites characteristic

Established

The experimental site is situated at an altitude of from 150 to 250 m.a.s.l. in the central part of the river Nitra. The average annual air temperature is 7.4 °C, during the vegetation period is 13.6 °C. The average total annual rainfall is 593 mm, during the vegetation period is 338 mm. The average annual sunshine duration is 2 200 – 2 400 hours, during the vegetation period is 1 500 – 1 600 hours.

Soil type: typical rendzina, brown rendzina. They are medium-heavy soils and heavy soil, medium textured soils (skeleton content 25 – 50%), medium deep, with slope 12 – 17°.

Spacing: 3x0.9 m. Keeping of grapes: the simple drape grapes. Rootstock**:** Kober 5 BB.

Dolné Krškany locality

The interested area is situated at 150 – 200 m.a.s.l. on the moderately undulating plain to upland. Average annual temperature is 9.7 °C, during the vegetation period 16.6 °C. The average total annual rainfall is 595 mm and during the vegetation period is 333 mm. The average annual sunshine duration is 2 300 – 2 600 hours, during the vegetation period is 1 600 – 1 700 hours.

Soils type includes carbonate chernozem. From the soil granularity view it is concerning to clay – loam soil, moderately deep, with slope 15 – 20°.

Spacing: 3x1.1 m. Keeping of grapes: the simple drape grapes. Rootstock: 5 BB.

Experimental varieties characteristics

Rulandské b i e l e (Pinot blanc)

It is concerning to the variety of French origin, which is cultivating in Alsace from 14 century. It belongs to the Burgundy (Slovak: Burgundské) family and according to the French resources; it was created as burgeon variation from Burgundské sivé (Rulandské šedé). Geo-ecological variety groups: Vitis vinifera L., subspecies sativa D.C., proles occidentalis Negr.

Bunch of grapes is small to middle size (100 – 120 mm long), cylindrical, the stem creates one main spindle, with one to two simple short ailerons near the base. Berries are densely deployed. It belongs to the moderate early variety. The beginning of the blossom accounted for 4th – 16th of June, the beginning of the berries ripening for 6th – 22nd of August and grapes harvesting for 25th September – 10th of October.

Rulandské biele belongs to the groups of variety using for production of the high quality white wines. For achievement of the full wines with a varietal bouquet, which is reflected more in the taste than in the scent, it is demanding relatively high sugar content of the grape must. Its quality acquires fine bouquet by ageing **(Pospíšilová, 2005)**.

S v ä t o v a v r i n e c k é (St. Laurent)

The origin of this variety is not accurately known. Originally it was reproduced as a table variety in Germany. Geo-ecological variety groups: Vitis vinifera L., subspecies sativa D.C., proles occidentalis Negr. Bunch of grapes is moderately large (120 - 150 mm long). Spindle creates aileron near the base. It is cylindrical or cylindrical-conical. The beginning of blossom accounted for 9th – 26th of June., the beginning of the berries ripening for 11th – 28th of August grapes harvesting before 10th of October. With a view to the early ripening it not required top-class positions **(Pospíšilová, 2005)**. However in cooler positions it increases the acid content into berries, what into red wine is not accepted by consumers.

RESULTS AND DISCUSSION

Copper

Copper intake by vitis is estimated for 50 – 100 $g.he^{-1}$ per year. The optimal content into leaves ranges from 10 – 20 ppm. Fertilising is not necessary, while is used 1 – 2 copper fungicide sprayings, what is sufficient to the normal vitis demand **(Vanek, 1996)**. In the past, the Cu^{2+} compounds played a very important task, because they were the most often used for vitis protection, mainly Bordeaux mixture ($CuSO_4$ + $Ca(OH)_2$) against downy mildews (Plasmopara viticola). Traditional vineyard soils, generally contain higher copper resources then soils with the other cultivated plants **(Pfeiffer and Rupp, 1993)**. Therefore it is important that the interval between the copper feeds application and the grapes harvesting is the longest as it is possible. Although it is possible to decrease copper content into wine by the appropriate technological measures, **Dersch (1993)** recommends spraying by the copper feeds to restrain. If the vineyards are spraying by the fungicides before grapes ripening, it is possible to import the unknown tone and double copper content into wines.

At high copper concentrations in foodstuffs as consumed there may cause the serious changes in the homeostatis body balance. Important is also relationship between copper to iron metabolism and zinc **(Bencko et al., 1984)**. In several samples of unfermented musts from the year 1994 **Bujdoš (1996)** found more than 5 $mg.L^{-1}$ of copper.

Into musts from Oponice and Nitra localities, we determined values Cu^{2+} in the range from 1.06 to 1.74 $mg.L^{-1}$, in both observed vintage years. Up to double copper amount (3.34 $mg.L^{-1}$) we determined in one case of Burgundy white wine in Krškany locality. Neither in this case was not exceed the highest allowed amount (5 $mg.kg^{-1}$), what means the copper content assessed by the Codex Alimentarius (Table 1). By this means highly demonstrated increase was probably caused by the vineyard spraying with sulphate product during bunch closuring. The highest allowed Cu^{2+} amount for the copper content into fruit juice, which is assessed by the Codex Alimentarius, is valid also for the table grapes must, which is consumed in the fresh state. **Ailer (1997)** find out into fresh musts of the variety Chrupka biela, Irsay Oliver and Julski biser Cu^{2+} values in the range from 1.06 to 1.35 $mg.L^{-1}$.

Application of the copper oxide pesticides significantly influence the copper content into must. **Michlovský and Hanák (1990)** compared the copper content into must of the interspecified vine varieties with limited chemical protection with noble varieties of Vitis vinifera. For a variety of Bianca, the above mentioned authors found out 0.28 $mg.L^{-1}$ Cu^{2+}, what is in comparison with our results lower value and in the noble variety of Rizling vlašský with full chemical protection up to 6.55 $mg.L^{-1}$ Cu^{2+}. **Ailer (1999)** observed the influence of the complementary extra-root nutrition on Cu^{2+} content into must. He used two different leaf fertilizers. Results of his three-year research were ranging in the interval from 0.53 to 1.69 $mg.L^{-1}$. **Henze and Bauer (2004)** indicate into red Swiss wine the values of Cu^{2+} 0.0528 $mg.L^{-1}$ and into white Spanish wine values of Cu^{2+} 0.0555 $mg.L^{-1}$.

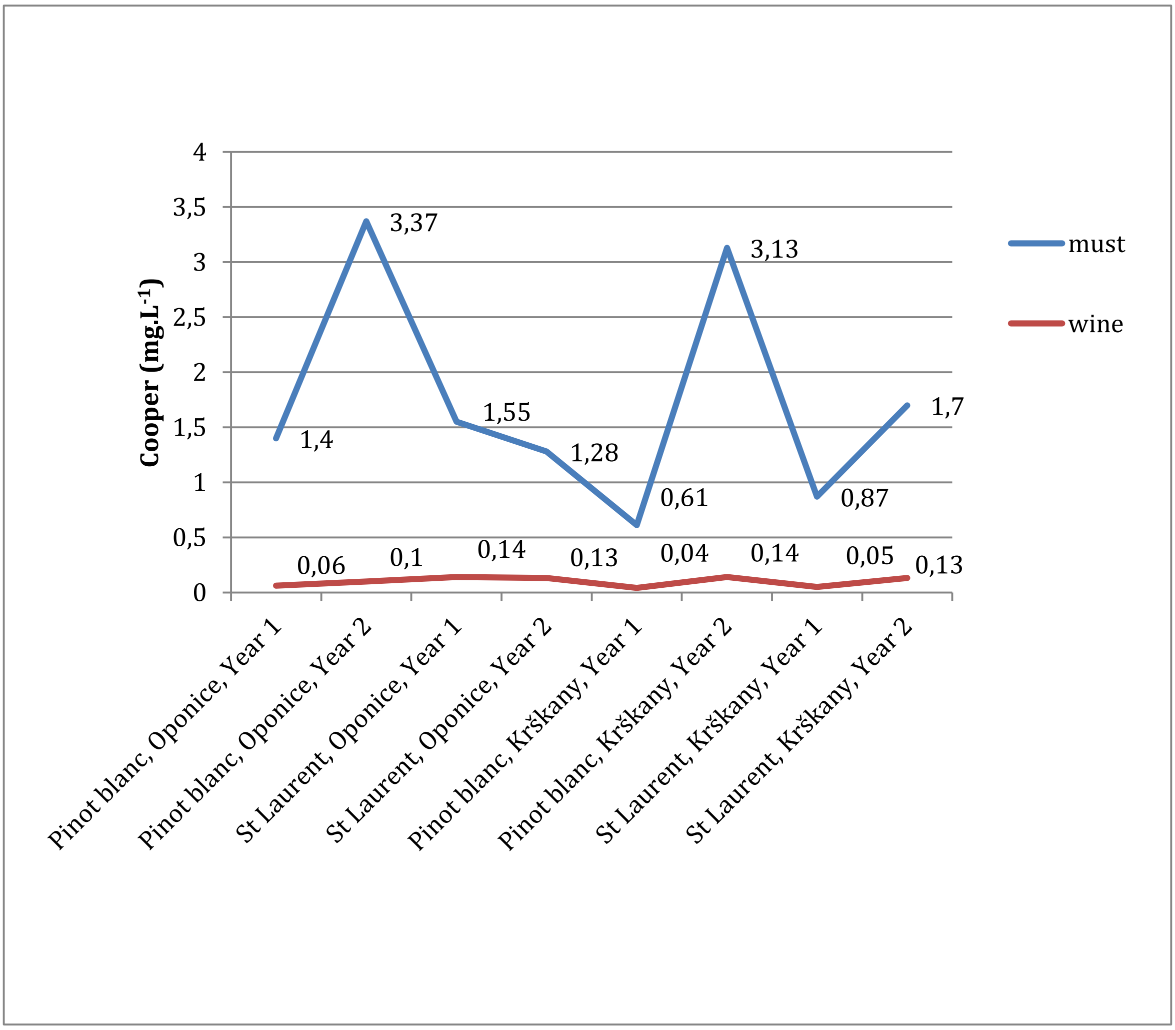

Figure 1 Content of copper in different variants – must and wine ($mg.L^{-1}$).

Table 2 Results of lead assessment individual variants.

Locality	variety	period	Content of lead (mg.L^{-1})	
			must	wine
Oponice	Pinot blanc	Year 1	0.071	0.004
		Year 2	0.006***	0.003
	St. Laurent	Year 1	0.14	0.04
		Year 2	0.015***	0.002
Krškany	Pinot blanc	Year 1	0.07	0.09
		Year 2	0.021***	0.01
	St. Laurent	Year 1	0.02	0.01
		Year 2	0.016*	0.012

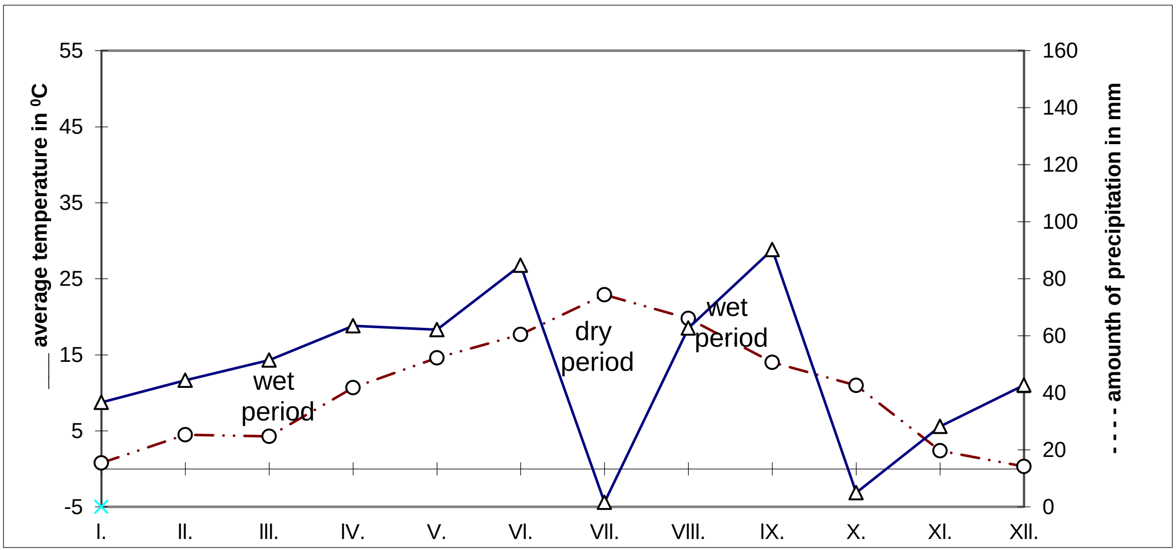

Figure 2 Climatogram of average monthly temperatures and precipitation in the subject area - Year 1.

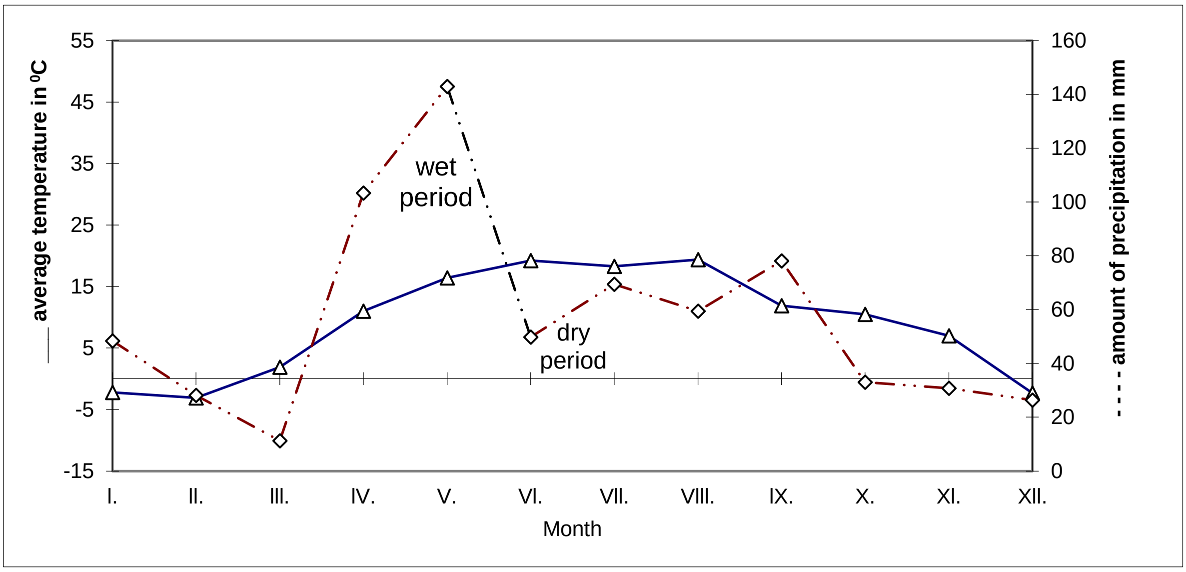

Figure 3 Climatogram of average monthly temperatures and precipitation in the subject area - Year 2.

On the copper content into grape has probably the significant influence also the precipitation amount, which falling in the second part of the vegetation half a year. Total rainfall in the period before the grape harvesting (the months of August - September**)** was for the first year 153 mm and for second year 137.5 mm. During both observed vintage years it was concerning to the above average values. Copper is not possible to eliminate totally in the protection of the vine against fungal diseases, because against it does not come into existence resistance into a pathogen. For resolution of this problem it is suitable to combine the copper and organic products. Into Austrian must from the vintage year 1992, the copper content ranges from 0.4 to 0.7 mg.L^{-1}. By the tripe application of Kupfer - Fusilan copper fungicide during the time span 11 – 5 weeks before the grape harvesting, the copper content increased on 2.9 to 5.1 mg.L^{-1} **(Dersch, 1993)**. Therefore this chemical element is not totally trouble-free, mainly in the vintage years with strong infectious pressure of the fungiform diseases, those are demanding an intensive chemical protection by the fungicides. We recommend, mainly during the vintage years with dry autumn, to observe the copper content into grape from vineyards, those were treated by the appliances with Cu^{2+} content. It is important that the interval between applications of the copper oxide appliances is the longest as it is possible. For the integrated cultivation of the vine, it is copper content used for the vineyard protection against fungiform diseases defined by the value 3 kg.he^{-1} per year (Figure 1).

Lead

Lead is an important compound of the energetic, but as also the transportation air pollutants. Lead intake by plants from soil depends on the organic matter in soil, pH value, on the quantity of phosphorus, carbonates, calcium and magnesium. In living organisms, the haematopoietic system, the central nervous system, but as well as the digestive tract are especially sensitive to lead. It causes breakdown of red blood cells and inhibits the iron synthesis with porphyrins. It damages the synthesis of acid delta – aminolevulinic, which is one of the basic haem components. It influences negatively on the variety of enzymes, which is associated with blocking SH groups **(Tölgyessy et al., 1989)**. Lead distribution into grape berries observed **Teissedre (1994)**, while atmospheric lead created only 16,3% from the total amount into berry. The other portion of lead (in average 0.058 mg.kg^{-1}) came from soil. Lead content into individual berry parts decreased in the order to grape seed – peel – pulp. **Ailer (1997)** found out into fresh musts of the table grapes varieties Chrupka biela, Irsay Oliver and Julski biser, the average lead value 0.035 mg.L^{-1} during the three-year monitoring.

Lead is a classic example that its tolerated limit was changing with advancing knowledge about its toxicity and with its accurate content assessment into grape cultivating in the unspoilt nature. In the year 1953 the International Organisation of Vine and Wine (O.I.V.) assessed the tolerated threshold limit 0.6 mg.L^{-1}. In the year 1975 the threshold limit was decreased on 0.5 mg.L^{-1} and in the year 1987 the limit was set on 0.3 mg.L^{-1} **(Bujdoš and Magdina, 1994)**. At the present time the maximal allowed lead amount into wines is allowed on 0.2 mg.L^{-1} and enologists demand that in the following years is projected a possibility of its further content decrease, as far as the technological advances allow it, because it is undesirable component into wine.

Lead content into undrained musts was ranging from 0.006 to 0.124 mg.L^{-1} and several values exceeded the hygienic limits assessed for fruit juices (0.05 mg.L^{-1}) enshrined in the Codex Alimentarius. However it was concerning to the wine grapes, those were dedicated for the further wine processing. Into fermented musts, we mostly found a considerable lead decrease by the fermentation process. Assessed limits, those were ranging from 0.001 to 0.115 mg.L^{-1}, do not achieved the threshold hygienic limit for lead content into wine (0.2 mg.L^{-1}). From our assessments arise that into wines and musts, those were obtained using appropriate technologies, without possibilities of their secondary contamination, it is a content of this risk element into quantities that do not constitute a danger to the consumer health. Influence of the foliar nutrition on Pb^{2+} content into must of the wine grapes varieties observed **Ailer (1999)**. He set the values in the interval from 0.007 to 0.014 mg.L^{-1}. **Eschnauer and Ostapczuk (1992)** set the lead values into the young German wines. Assessed value that average was 0.041 mg.kg^{-1}, have been very low and authors do not consider the riskiness of this element. **Henze and Bauer (2004)** identified into red Swiss wine Pb^{2+} values 0.0326 mg.L^{-1} and into white Spanish wine specified Pb^{2+} values 0.089 mg.L^{-1}.

In South Africa was the average Pb^{2+} content 0.046 mg.L^{-1} into wines of during the years 1995 – 1996. In Argentina it was found into musts in average 0.138 mg.L^{-1} of this heavy metal, while the lead content into soil and its plant absorption are statistically **(Doboš, 1997)** (Table 2).

Copper and lead biodegradation during the alcoholic fermentation

The mineral substances content decrease into wine is explaining by the yeast utilization during must fermentation, by the solubility decrease of some components into alcoholic solution as well as by the wine stabilization process.

Must contains in average from 3 to 5 g.L^{-1} of the mineral substances, but their content into wine is considerable lower (from 1.5 to 3 g.L^{-1}). During the analysis of fermented musts we found considerable high copper content decrease by the fermentation process. Assessed values from 0.07 to 0.2 mg.L^{-1} represent a decrease of the original copper content about 90 to 97%, while between its original quantity amount into must and its final content into wine is not a direct correlation. Whereas the subject of our analysis were fermented, undrained musts in the laboratory conditions, it can be assumed, that by the wine lees extraction the copper content decrease even considerably. In the consequence of this positive fact, it can be almost completely eliminated the possibility of the maximal permissible Cu^{2+} content values exceedance into wines.

It is positive that the fermentation acts as a biological filter also on the lead content. In the analysed fermented wines we found the decrease of the lead content about 25 to 94%, while in most cases it was more than 50%. A large part of these metals is eliminated during the fermentation in the insoluble sulphides form, because of what it is not the limit value exceeded into wines.

CONCLUSION

For intensive agro-technology it is not possible to eliminate completely the negative interventions in the biological environment equilibrium. The individual agro-technological interventions it is therefore possible to realize in the appropriate agro-technologic periods and restrict them on the minimal, however sufficient amount for healthy grapes production without cultivation risks. By using of the faultless material and appropriate technological equipment during the wine production, it is possible to eliminate almost completely problems with copper and lead content into our wines and it is from the view of technologic and hygienic. The analysed wines did not exceed the highest permissible amounts of copper and lead assessed by the valid legislation.

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