THE CONTENTS OF Cu, Mn, Zn, Cd, Cr AND Pb AT DIFFERENT STAGES OF THE WINEMAKING PROCESS

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Abstract

In samples taken during different stages of winemaking process (from grapes, crushed grapes, pressed pomace, must deposit, deposit of lees, must before and after clarification and wine) the Cu, Mn and Zn contents were determined by flame atomic absorption spectrometry (FAAS) and the Cd, Pb and Cr contents were determined by electrothermal atomic absorption spectrometry (ETAAS). Grapes, crushed grapes, pressed pomace, must deposit and deposit of lees were microwave digested with nitric acid, hydrofluoric acid and hydrogen peroxide solution, while for must and wine no special treatments were necessary. The highest contents of Cu, Mn, Zn, Pb, Cd and Cr were determined in the pressed pomace, lees, and in white grape varieties also in must deposit. Mean values obtained of dry weight (pressed pomace, lees, must deposit) were 63 mg/kg, 300 mg/kg, 184 mg/kg for Cu, 11 mg/kg, 15 mg/kg, 134 mg/kg for Mn, 14 mg/kg, 35 mg/kg, 17 mg/kg for Zn, 0.3 mg/kg, 0.5 mg/kg, 0.6 mg/kg for Pb, 0.5 mg/kg, 1.0 mg/kg, 1.8 mg/kg for Cr, 15.4 μg/kg, 24.4 μg/kg, 13.0 μg/kg for Cd. The Cu content was decreasing from the grapes to the bottled wine, whereas the Mn, Zn, Cd, Cr and Pb contents in the bottled wine were higher than in musts in all investigated white and red grape varieties. In ten wine samples the following contents were determined: Cu; mean 0.12 mg/L (range: 0.06-0.30 mg/L), Mn; mean 1.04 mg/L (range: 0.60-1.78 mg/L), Zn; mean 0.50 mg/L (range: 0.13-1.03 mg/L), Cd; mean 0.34 μg/L (range: 0.08-1.04 μg/L), Cr; mean 17.0μg/L (range: 5.2-25.1 μg/L) and Pb; mean 25.3 μg/L (range: 16.4-37.8 μg/L).

Introduction

Different elements are required by plants. Copper, manganese and zinc are plant micronutrients. These elements are essential at low concentrations, but are toxic at higher levels. Lead, cadmium and chromium are not natural substances in plant nutrition. In the case of Cd and Pb, toxicity is induced by mimicking of lighter essential elements in uptake and biochemical behaviour.[1]

Total content of metals in wines depend on the impacts influencing the growth of grape berries and on the winemaking process. In order to protect the plants against diseases, weeds, and pests and to increase yield, different pesticides are used. The application of some pesticides can be reflected in higher contents of Cu, Mn and Zn in wine.[2-5] According to Lemperle,[6] the use of Cu fungicides for mildew control can

increase the Cu content in musts up to 15 mg/L. Bentonite used as the fining agent for the adsorption of wine proteins is a potential source of Cd. Increases of Cd in wine caused by bentonite are usually negligible, but in same cases, the Cd concentration in wines could increase from 0.07 to 0.4 μg/L by adding the bentonite.[7] The equipment in wine cellars made of brass (valve, faucets, pumps, pipes) contribute a large portion of the Pb in wine as has been reported by Kaufman,[8] while the Cr contamination can be primarily attributed to the stainless steel equipment.[9]

Our experiment was aimed at investigating the migration of Cu, Mn, Zn, Cd, Cr and Pb during the winemaking process of red and white grape varieties. For this purpose metals were determined at different stages of winemaking process, i.e. in grape, crushed grapes, pressed pomace, must deposit, deposit of lees, must and wine.

Experimental

Samples

From three different winegrowing regions in the North-Eastern Slovenia, where white grape vine varieties dominate, the grapes of cv. Sauvignon (at two different locations), cv. Pinot gris and cv. Gewürztraminer (at two different locations) were taken. The grapes of cv. Sauvignon were processed in Meranovo and Ivajnkovci cellars (micro locations, grape samples were taken from defined experimental plots: five rows, 20 vines/row), cv. Pinot gris in Jeruzalem-Ormož cellar and cv. Gewürztraminer in Vinag and Jeruzalem-Ormož cellars. Sampling of samples was done with grapes, pomace residue and must samples. The cv. Sauvignon must was clarified by natural settling of suspended solids whereas the other must samples were clarified by centrifugation. Sampling of must and must deposit was done after clarification. Sampling of lees and young wine was done when alcoholic fermentation was finished. At the end of winemaking process the bottled wines were analysed.

From winegrowing regions in the southern and western Slovenia, where the major part of the Slovenian red wines are produced, the grapes of cv. Cabernet Sauvignon, cv. Merlot, cv. Barbera and cv. Blaufränkisch (micro location) were obtained. The grapes of cv. Cabernet Sauvignon were processed in Vinakoper and Vipava cellars, cv. Merlot in

Vinakoper cellar, cv. Barbera in Vipava cellar and cv. Blaufränkisch in Martinčič cellar. After crushing, samples from the crushed grapes were taken. During the maceration sampling was performed on the sixth day. Sampling of lees and young wine was done after fermentation.

Reagents

For sample mineralization nitric acid (69-70%, J. T. Baker, Suprapure), hydrofluoric acid (40%, Merck, suprapure) and hydrogen peroxide solution (30%, Fluka) were used. All others reagents used were of analytical - reagent grade. Twice deionised water (Milli -Q Water System, Millipore) was employed throughout. The matrix solution of wine and must was prepared according to the literature.[10] Standard solutions of Zn, Mn, Cu, Pb, Cr and Cd were made from commercial stock standard solutions (Merck) at concentrations of 1000 mg/L.

Palladium matrix modifier solution (1 mg Pd^{2+}/L) was prepared by dilution $Pd(NO_3)_2$ (Merck) of a stock solution ($c(Pd^{2+})$=10.0±0.2 g/L) with deionised water in a 10 mL volumetric flask. A 10.0 g Mg^{2+}/L solution was prepared from magnesium nitrate hexahydrate (1.054 g $MgNO_3 \cdot 6H_2O$/10 mL). To avoid possible contamination 10 mL of HNO_3 (suprapure) was placed in PTFE vessels and digested in microwave oven 10 min at 650 W. Prior to analysis the glassware and polyethylene sample containers were soaked in 10% HNO_3 (suprapure) for 24 hours and than rinsed with twice deionised water.

Apparatus

Atomic absorption measurements were carried out with an Varian SpectrAA- 10 atomic absorption spectrometer equipped with a deuterium background corrector and single element hollow cathode lamp of Mn, Zn and Cu. Electrothermal atomic absorption measurements were carried out with an Varian GTA 100 graphite furnace, Zeeman background correction and autosampler.

Grapes and crushed grapes were homogenised in a household grinder (Moulinex). The possible contamination with the metals from the grinder was checked with the analysis of blank sample (whole berries of cv. Sauvignon and cv. Merlot). Samples dried

at 60 °C were ground in a Fritsch "pulverisete 14 " variable speed rotor mill. For sample digestion, a CEM (Model MDS 2000) microwave oven with maximum power of 650 W and 120 mL polytetrafluoroethylen (PTFE) vessels with the screw caps was used and for sample centrifugation the centrifuge Tehtnica CENTRIC 3000 R was applied.

Sample preparation

After homogenisation, approximately 6 g of grapes or crushed grapes were placed into PTFE vessels, treated with 5 ml HNO_3 (suprapure), 0.3 mL HF (suprapure) and 2 mL H_2O_2 and microwave digested as follows: 5 min at 225 W, 10 min at 0 W, 10 min at 325 W, 20 min at 540 W and 60 min at 650 W. The same procedure was used for the digestion of whole berries (blank sample). The average content of metals in blank samples (six parallel determinations of each sample) was in the same range as in grinded samples. The grinding of samples in laboratory could be excluded as a possible source of contamination. Pressed pomace samples were dried at 60 °C for 24 h and then they were ground. For separation of solid and liquid fractions, must deposit and deposit of lees after fermentation were centrifuged for 15 minutes at 1500 rpm. Solid fractions were dried (must deposit at 60 °C for 60 h, and less deposit at 60 °C for 36 h) and then they were ground. For microwave digestion 0.5000 ± 0.0001 g of the ground sample was weighted in PTFE vessel and treated with 5 ml HNO_3, 0.3 mL HF and 0.5 mL H_2O_2 and digested as follows: 10 min at 292 W, 10 min at 0 W, 15 min at 375 W and 60 min at 650 W. After microwave digestion, the solutions were cooled to room temperature and diluted to a total volume of 25 mL with deionised water. The entire procedure was also carried out for blanks, using the same protocol that was applied for real samples. For must samples after clarification and wine samples no special treatments were required.

Sample analysis

The determinations of Cu, Mn and Zn were performed by aspirating the digested solutions into a FAA spectrometer using the air-acetylene flame. For Zn determinations the deuterium background correction was required. For Cu, Mn, Zn, Cr, Cd and Pb determinations in digested solutions of grapes, crushed grapes, must deposit and deposit

of lees all working standards were prepared in 14% HNO_3 (suprapure) to match the acid concentration in digested solutions.

The influence of matrix interferences on the Cu, Mn and Zn determinations in must and wine was evaluated on the basis of the ratios b^B/b^C and b^B/b^A of the slopes of calibration graphs; b^A is the slope of calibration curve for matrix standard solutions, b^B is the slope of calibration curve obtained by the standard addition method, and b^C is the slope of calibration curve for water standard solutions. The results obtained are presented in Table 1. Working standards solutions for Cu, Mn and Zn determinations in wine and must were prepared in water solutions as well as in the matrix solution of wine or must.[10] By calibration with matrix adjusted standards solutions for wine and must the interferences caused by the main wine or must components that were present by calibration with water solutions were avoided and there was no need for the use of standard additions as shown in Table 1. When the calibration with matrix adjusted standards solutions was used, the must and wine samples could be analysed without treatment. This is in agreement with the Netzer previous work for Cu, Zn and Fe determination in wine and fruit juices.[10]

Table 1. Influence of wine and must matrix on Cu, Mn and Zn determinations.

	b^B/b^C (must)	b^B/b^A (must)	b^B/b^C (wine)	b^B/b^A (wine)
Cu	0.67	1.01	1.10	0.99
Zn	0.69	0.98	1.08	1.03
Mn	0.67	1.03	1.10	1.04

b^A-the slope of calibration curve for matrix standard solutions
b^B-the slope of calibration curve obtained by the standard addition method
b^C-the slope of calibration curve for water standard solutions

Since the certified standard references materials for Cu, Zn and Mn in analysed samples are not available, accuracy was checked with recovery assays by adding known amounts of analyte to four different grape, pressed pomace, must and lees deposit samples prior to the digestion step, to must and wine samples prior to the FAAS determinations and processing those samples in the same way as other experimental

samples. Mean recoveries of spikes were in the range from 97.5 to 103.6% for Cu determinations, from 95.3 to 103.2% for Mn and from 96.6 to 105.3% for Zn.

Analyses of Cr, Pb and Cd were carried out by ETAAS in the peak area mode. Argon of 99.99% purity at 3.0 L/min flow was used as the internal inert gas and the flow was stopped during the atomisation stage. Measurements were performed on pyrolytic graphite coated graphite tubes with a L′vov platform for Cd and Pb and without a platform for Cr. The platform was pre-heated to 60 °C for wine deposition, to 90 °C for must deposition and to 100 °C for samples after microwave digestion deposition (hot inject rate:10). A 5 μL volumne of chemical modifier was injected into the graphite tube. The optimisation of the temperature programme of the graphite furnace and the methods used for Cd, Pb and Cr determinations in different fractions of winemaking process is fully described in our previous paper.[11]

Results and discussion

The contents of metals examined at different stages of winemaking process are shown in Figures 1-5. The contents of grapes and crushed grapes are given in mg/kg or μg/kg of fresh weight. The contents of pressed pomace, must deposit and deposit of lees are given in mg/kg of dry weight. The results refer to the triplicate analysis of each sample.

In order to estimate if an increase or decrease in metal contents in the various sub-fractions occurred, the adjustment of the measured contents was considered in the discussion of results. Measured contents of metals in must samples were adjusted relatively to the original grape sample. The must extraction rate was about 70% for cv. Sauvignon, cv. Pinot gris, about 75% for cv. Cabernet-Sauvignon, cv. Merlot, cv. Barbera and cv. Blaufränkisch and 65% for cv. Gewürztraminer. In the next sub-fractions the measured contents of metals were adjusted relatively to the must sample taking into account 4% losses at must clarification stage, 1% at fermentation, 5% after fermentation and 2% at bottling.

Copper

The Cu content in grapes ranged from 1.6 to 8.1 mg/kg (average 4.7 mg/kg) for white and from 1.1 to 10.2 mg/kg (average 4.2 mg/kg) for red grape varieties (Table 2).

Table 2. Cu, Mn, Zn, Cr, Pb and Cd contents in white and red grape varieties.

	Cu (mg/kg)	Mn (mg/kg)	Zn (mg/kg)	Cr (μg/kg)	Pb (μg/kg)	Cd (μg/kg)
Sauvignon M	1.64±0.01	1.24±0.03	1.01±0.02	5.8±0.7	10±1	0.35±0.04
Sauvignon I	8.14±0.20	1.29±0.03	1.70±0.05	7.3±0.6	21±1	0.43±0.05
Gewürztramin. JO	3.32±0.03	1.19±0.02	1.00±0.02	11.0±0.9	6.1±0.4	0.22±0.02
Gewürztramin. V	2.27±0.06	0.71±0.02	1.11±0.03	6.3±0.7	11±1	0.28±0.03
Pinot gris	8.05±0.23	1.35±0.04	1.69±0.03	7.7±0.5	25±2	0.26±0.03
Blaufränkisch	4.01±0.11	1.05±0.03	1.51±0.04	8.3±0.7	18±1	0.34±0.03
Merlot	10.2±0.1	1.58±0.02	1.22±0.04	10±0.9	18±2	0.22±0.03
Cabernet-Sauv. K	4.62±0.08	1.89±0.03	1.32±0.04	23±2	18±1	0.37±0.04
Cabernet-Sauv. V	1.14±0.03	3.28±0.10	1.38±0.05	8.2±0.6	12±1	0.31±0.03
Barbera	1.13±0.02	8.9±0.1	1.10±0.03	10.5±1.1	10±1	0.20±0.02

Mean value of three replicate analyses of each sample ± standard deviation at 95% confidence level. Sample labels: Sauvignon M- Sauvignon Meranovo, Sauvignon I– Sauvignon Ivajnkovci, Gewürztramin. JO- Gewürztraminer Jeruzalem-Ormož, Gewürztramin. V- Gewürztraminer Vinag, Cabernet-Sauv. K - Cabernet-Sauvignon VinaKoper, Cabernet-Sauv. V- Cabernet-Sauvignon Vipava.

The Cu contents were higher in musts obtained from pressing the grape varieties of higher Cu content. They ranged from 1.3 to 8.0 mg/L. The Cu contents in all analysed young wines after fermentation were lower than in musts after clarification (Figure 1). The decrease of copper concentration after the fermentation could be attributed to the yeast *Saccharomyces cerevisiae* which is well known to be an effective bioaccumulator of metals ions including copper (II).[12] Another possible explanation for the Cu reduction is also the formation of CuS and Cu_2S complexes that were deposited and removed from the medium.[13] Hydrogen sulphide, required for the formation of CuS and Cu_2S complexes, was produced by yeast during fermentation due to the presence of elemental sulphur on the grape skins.[14-15] The Cu contents ranged from 80 to 252 mg/kg in must deposit and from 194 to 855 mg/kg in lees. The overall average was 184 mg/kg of must deposit and 300 mg/kg of lees. Whereas among grape and must samples significant differences in Cu content were observed, after fermentation the values were more uniform in white young wines, with Cu levels ranging from 0.10 to 0.14 mg/L with an

average 0.11 mg/L. The contents of Cu in red young wines samples were much more scattered and ranged from 0.1 to 1.0 mg/L (average 0.37 mg/L).

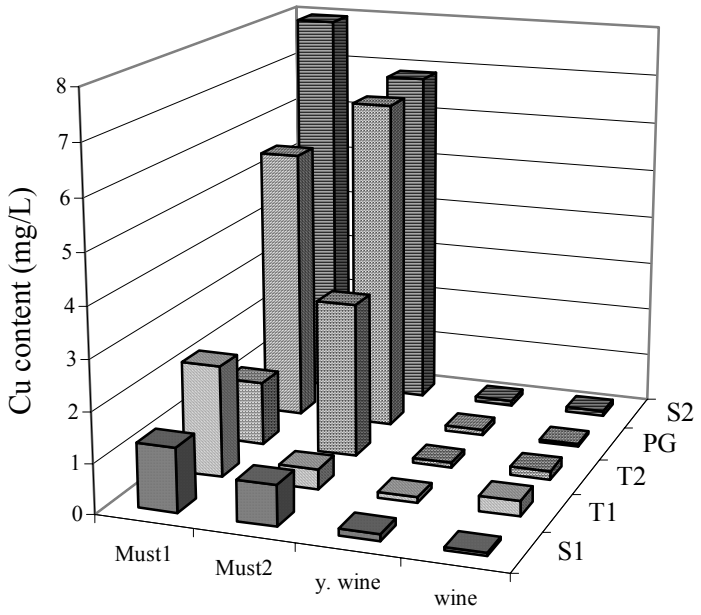

Figure 1. Cu content in white grape varieties during winemaking process. Sample labels: Must1: must before clarification, Must2: must after clarification, y. wine: young wine, wine: bottled wine, S1, S2: Sauvignon, PG: Pinot gris, T1, T2: Gewürztraminer.

Manganese

In white grape varieties the Mn content was in the range from 0.7 to 1.4 mg/kg with an average 1.1 mg/kg (Table 2). In comparison to the white grape varieties, the Mn content in red grape varieties was higher and ranged from 1.1 to 8.9 mg/kg with an average 3.4 mg/kg. During the winemaking process the Mn was removed in pressed pomace (6.9 to 20.2 mg/kg), lees deposit (9.8 to 25.3 mg/kg) and in white grape varieties also in must deposit (4.1 to 19.5 mg/kg). The overall average was 11.3 mg/kg of pressed pomace, 15.4 mg/kg of lees deposit and 12.9 mg/kg of must deposit. In white grape varieties the Mn content remained unchanged between the must clarification stage and alcoholic fermentation stage. Mn content in young white wines ranged from 0.4 to 0.7 mg/L with an average 0.5 mg/L, but increased in bottled wines to the values between 0.6 to 1.0 mg/L with an average 0.8 mg/L (Figure 2). The Mn concentrations in red wines were higher than in white wines and ranged from 0.8 to 1.8 mg/L with an average

1.1 mg/L. The concentrations of Mn in white and red wines are comparable with those reported in the literature.[16-17]

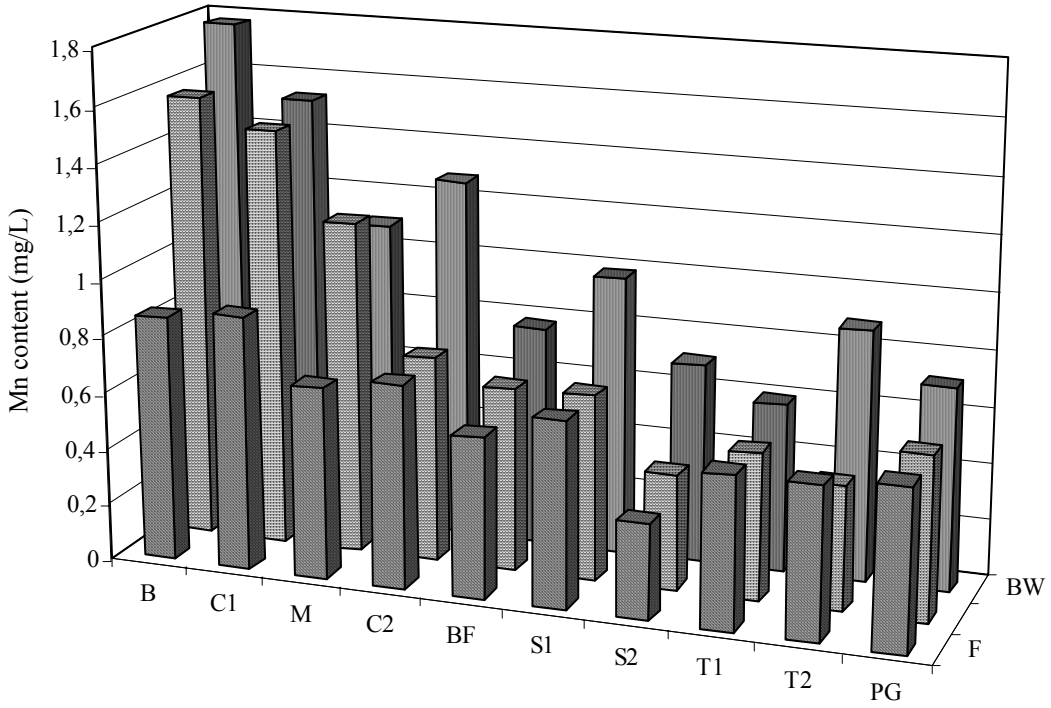

Figure 2. Mn content in white and red grape varieties during winemaking process. Sample labels; F: for white grape varieties must after clarification and for red grape varieties the liquid fraction taken at the sixth day of maceration, YW: young wine, BW: bottled wine, B: Barbera, C1, C2: Cabernet Sauvignon, M: Merlot, BF: Blaufränkisch, S1, S2: Sauvignon, PG: Pinot gris, T1,T2: Gewürztraminer.

Zinc

No differences between red and white grape varieties were found in Zn contents (Table 2). They ranged from 1.0 to 1.7 mg/kg for white and from 1.1 to 1.5 mg/kg for red grapes samples with an overall average of 1.3 mg/kg. The average Zn content was 13.6 mg/kg in pressed pomace, 16.8 mg/kg in must deposit and 30.5 mg/kg in lees deposit. In white wines Zn concentrations ranged from 0.4 to 1.0 mg/L (average 0.6 mg/L) and in red wines from 0.1 to 0.6 mg/L (average 0.4 mg/L). The Zn concentrations were lower in young wines (ranged from 0.11 to 0.56 mg/L) than in musts, but they were higher in bottled wines (average 0.5 mg/L). The concentrations of Zn in wines are comparable to those reported in literature.[17] The migration of Zn during wine production is shown in Figure 3.

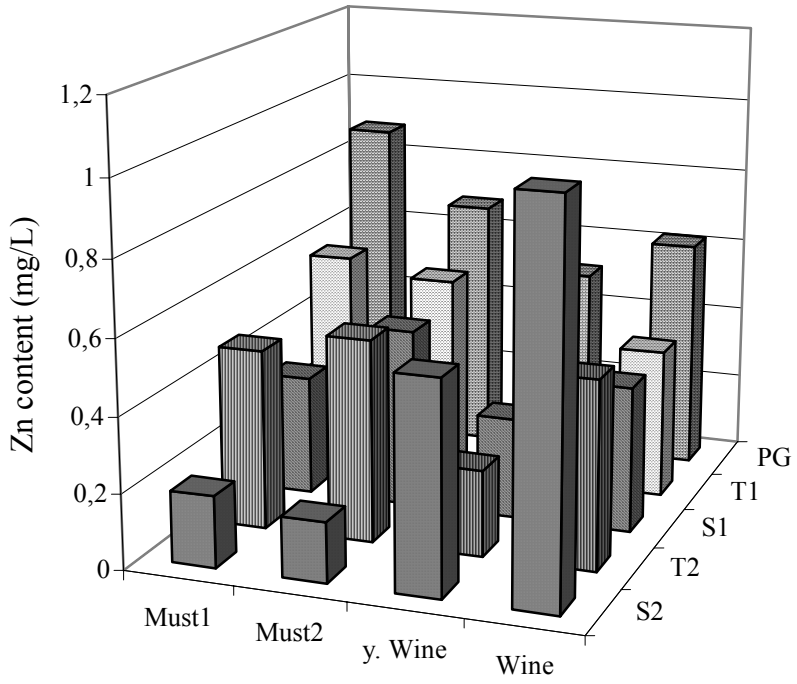

Figure 3. The Zn migration during white wine production. Sample labels: Must1: must before clarification, Must2: must after clarification, y. Wine: young wine, Wine: bottled wine, S1, S2: Sauvignon, PG: Pinot gris, T1,T2: Gewürztraminer.

Cadmium

The average Cd content in white and in red grapes samples was 0.3 μg/kg (Table 2). The Cd was retained in pressed pomace, lees deposit and in white grape varieties also in must deposit with an overall average 10 μg/kg of pressed pomace, 24 μg/kg of lees deposit and 13 μg/kg of must deposit. Its concentration in bottled wines was higher than in young wines. The reason is probably secondary metal pickup from bentonite that was added to wines before bottling for the adsorption of proteinaceuos materials from wines.[7] The average Cd contents of white table wines were from 0.2 to 1.0 μg/L and from 0.1 to 0.3 μg/L for red wines.

Chromium

The contents of Cr in musts were lower than in grape samples (Figure 4) because Cr has been retained in skins and seeds in pressed pomace (0.2 to 1.3 mg/kg).

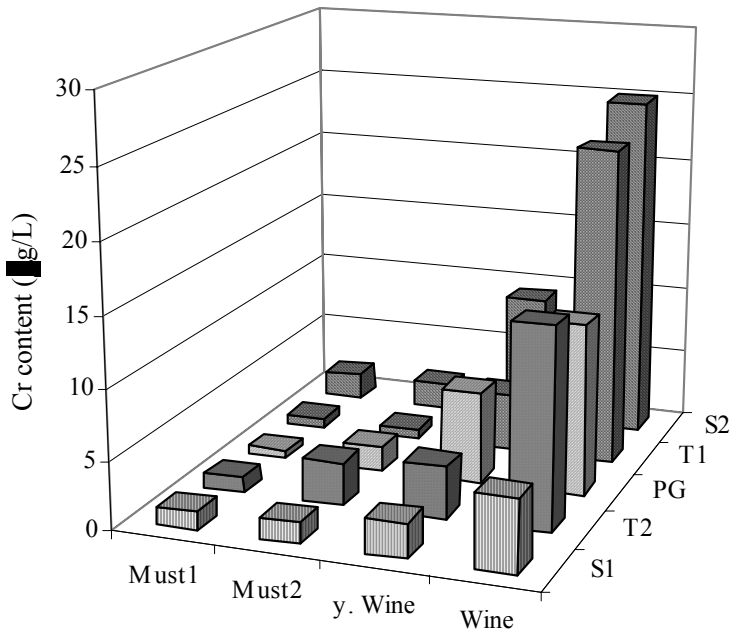

Figure 4. Cr content in white grape varieties during winemaking process. Sample labels: Must1: must before clarification, Must2: must after clarification, y. Wine: young wine, Wine: bottled wine, S1, S2: Sauvignon, PG: Pinot gris, T1,T2: Gewürztraminer.

The cv. Sauvignon must was clarified by natural settling of suspended solids, whereas cv. Pinot gris and cv. Gewürztraminer musts were clarified by centrifugation. The data obtained show that the Cr content was the same in cv. Sauvignon (Ivajnkovci) must before and after clarification, whereas the Cr content was higher in musts after clarification of cv. Pinot griss and cv. Gewürztraminer in comparison to the values in musts before clarification. In bottled wines Cr levels ranged from 5.2 to 25.1 μg/L. These concentrations are comparable with those reported in the literature.[18] They were from two to three times higher than in young wines. The Cr concentrations in wines were determined immediately after bottling; therefore the contamination connected with the nature of metal oxides,[19] used for bottle pigmentation could be excluded. An increase of Cr concentration was observed with all white and red grape varieties processed in seven different cellars. Cr levels were somewhat higher in red (average 18 μg/L) than in white wines (average 16 μg/L).

Lead

Teissedre reports the highest lead contents in seeds, lower in skins and the lowest in pulp.[20] The contents of Pb in musts (1.3 to 5.4 μg/L with an average 3.5 μg/L) after pressing were lower than in grape samples (6 to 25 μg/kg with an average 15 μg/kg). This agrees with recent work by Stockley who reported that the concentration of lead in must is approximately 10 times less than that of grapes.[21] The Pb contents in pressed pomace ranged from 0.25 to 0.32 mg/kg for white grape varieties with an average 0.29 mg/kg. Peleerin reported that in wine most of lead is complexed with a pectic polysaccharide rhamnogalacturonan (II) that is not degraded during vinification.[22] Lead not complexed with rhamnogalacturonan (II) was probably removed as precipitates of PbS in lees deposit. The formation of insoluble complexes with wine proteins was also a possible cause for the Pb removal.[23] The average Pb content in lees deposit was 0.50 mg kg^{-1}. In white table wines an average Pb level was 27.6 μg/L and in red wines it was 22.9 μg/L. These concentrations are comparable with those reported in the literature.[24] The changes in Pb content during winemaking process are shown on Figure 5.

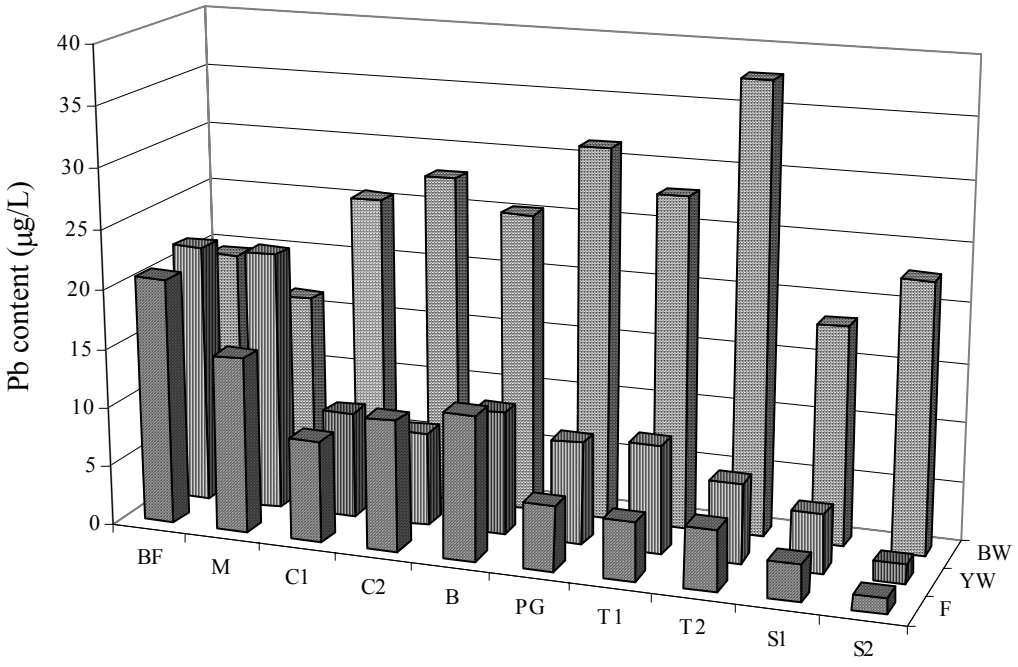

Figure 5. Pb content in some stages of winemaking process. Sample labels: F; for white grape varieties must after clarification and for red grape varieties the liquid fraction taken at the sixth day of maceration, YW: young wine, BW: bottled wine, BF: Blaufränkisch, M: Merlot, C1, C2: Cabernet Sauvignon, B: Barbera, PG: Pinot gris, T1,T2: Gewürztraminer, S1, S2: Sauvignon.

Conclusions

The migration of Zn, Cu, Mn, Cd, Pb and Cd during the different stages of winemaking process was investigated. The metals were retained in pressed pomace, must and lees deposit. The contents of investigated metals in musts were lower than in grapes. Cu was the only metal whose concentration decreased from the young wine stage to the bottled wines stage. The contents of other investigated metals in wine were higher than that in musts, but on average, they were considerably lower in comparison to the maximum values allowed by Office International de la Vigne et du Vin (OIV 1999).[25]

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Povzetek

V vzorcih odvzetih v različnih stopnjah predelave grozdja (v grozdju, drozgi, tropinah, usedlini po razsluzu mošta, v drožeh, v moštu pred in po razsluzu in v vinu) smo določili vsebnost Cu, Mn in Zn s plamensko atomsko absorpcijsko spektrometrijo (FAAS) in vsebnost Cd, Pb in Cr z elektrotermično atomsko absorpcijsko spektrometrijo (ETAAS). Vzorce grozdja, drozge, tropin, usedline po razsluzu mošta in droži smo razkrojili v mikrovalovni peči z dušikovo (V) kislino, fluorovodikovo kislino in vodikovim peroksidom. Za mošt in vino predhodna priprava vzorcev ni bila potrebna. Najvišje vsebnosti Cu, Mn, Zn, Pb, Cd in Cr smo določili v tropinah, drožeh in pri belih sortah grozdja tudi v usedlini po razsluzu mošta. Srednje vrednosti preračunane na suho snov (tropin, droži, usedline po razsluzu mošta) so bile 63 mg/kg, 300 mg/kg, 184 mg/kg za Cu, 11 mg/kg, 15 mg/kg, 134 mg/kg za Mn, 14 mg/kg, 35 mg/kg, 17 mg/kg za Zn, 0.3 mg/kg, 0.5 mg/kg, 0.6 mg/kg za Pb, 0.5 mg/kg, 1.0 mg/kg, 1.8 mg/kg za Cr, 15.4 μg/kg, 24.4 μg/kg, 13.0 μg/kg za Cd. Vsebnost Cu je padala od grozdja do stekleničenega vina. Pri vseh analiziranih belih in rdečih sortah so bile vsebnosti Mn, Zn, Cd, Cr in Pb v stekleničenih vinih višje kot v moštih. V desetih vzorcih vina smo določili naslednje vredosti: Cu; srednja vrednost 0.12 mg/L (območje: 0.06-0.30 mg/L), Mn; srednja 1.04 mg/L (območje: 0.06-1.78 mg/L), Zn; srednja 0.50 mg/L (območje: 0.13-1.03 mg/L), Cd; srednja 0.34 μg/L (območje: 0.08-1.04 μg/L), Cr; srednja 17.0 μg/L (območje: 5.2-25.1 μg/L), Pb; 25.3μg/L (območje: 16.4-37.8 μg/L).