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REGULAR ARTICLE

CADMIUM, COPPER, LEAD AND ZINC CONCENTRATIONS IN LOW QUALITY WINES AND ALCOHOL CONTAINING DRINKS FROM ITALY, BULGARIA AND POLAND

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ABSTRACT

We studied Cu, Cd, Pb and Zn concentrations in low quality wines produced in Bulgaria and Italy and in alcohol containing multi-fruit drinks produced in Poland. All the metals were present in tested products. Cadmium was not detected in Italian and Polish products. In one of the Bulgarian wines cadmium was detected in concentration of 0.004 $mg \cdot l^{-1}$. Italian wines were not contaminated with Pb. Its concentration was the highest in Polish drinks (0.88±0.52 $mg \cdot l^{-1}$). The largest and statistically significant differences occurred between Cu and Zn contents. Both metals had the highest concetrations in Italian wines (Cu - 0.13±0.05 $mg \cdot l^{-1}$; Zn - 0.83±0.56 $mg \cdot l^{-1}$), and the lowest in Polish products (Cu - 0.04±0.001 $mg \cdot l^{-1}$; Zn -0.18±0.16 $mg \cdot l^{-1}$).

Keywords: metals, wines, multi-fruit alcoholic drinks, Italian, Bulgarian, Polish

INTRODUCTION

Heavy metals are widely dispersed in the environment. They enter the food chain and occur in different concentrations in human food **(Roychowdhury et al., 2003)**. The contamination of food with heavy metals is a serious problem. Heavy metals are taken up from the digestive tract and exhibit harmful influence on all kinds of tissues. The uptake of heavy metals in human digestive tract usually does not exceed 5 to 10 percent of their concentration in food **(Beckett et al., 2007)**. On the other hand some metals exhibit toxic properties in relatively low doses, and moreover they concentration in tissues gradually increases due to accumulation process **(Beckett et al., 2007)**. Metals disturb ionic balance and mineral regulations, induce oxidative damage to cell structures, produce injuries to DNA and induce cancer transformations **(Waalkes, 2003)**. Thus many countries established the highest permissible concentrations of some heavy metals in different kind of food. In European Union heavy metals are ruled by European commission regulation from 19 December 2006 **(EC/1881/2006)**. This regulation focus on cadmium, lead, mercury and tin. The general limits for other metals have not been established so far. Depending on kind of food limits set for lead are 0.02-1.5 $mg.kg^{-1}$ of fresh weight. Lead limits in fruits and wine are 0.1-0.2 $mg.kg^{-1}$ of fresh weight. General limits for cadmium are in the range of 0.05-0.5 $mg.kg^{-1}$ of fresh weight. The cadmium content limits in wine are not estblished, although in fruits its concentration should not exceed 0.05 $mg.kg^{-1}$ of fresh weight **(EC/1881/2006)**.

In our studies we focused to concentration of lead, cadmium, copper and zinc in low quality and low prize wine from Italy and Bulgaria and in multi-fruit alcohol containing drinks produced in Poland. We assume that this kind of wine is made of low quality fruits, and control of contaminants level in such wine may be also of low quality.

MATERIAL AND METHODS

We studied copper, cadmium, lead and zinc concentrations in commercially available wines produced in Italy (Montepulciano region, Cabernet sauvignon), Bulgaria (Melnik, Cabernet sauvignon) and Poland (Świętokrzyskie district). Bulgarian and Italian wines were made of grapes. Polish wines were multi-fruit alcoholic products. Metals were estimated in three different bottles of wine from each country. Samples taken in triplicate from each bottle were treated with HNO_3 in 1:1 ratio. After the complete mineralisation metals were estimated with BUCK 200A spectrophotomter using flame atomic absorbtion technique. Each metal was estimated 3 times in each sample of wine. Lead concenration was addtitionally measured with anodic stripping voltammetry technique with working CGMDE mercury electrode. As variables were not normally distributed we used non-parametric Kruskal-Wallis ANOVA followed by post hoc analysis. Statistical significance was defined at $p<0.05$.

RESULTS AND DISCUSSION

Cadmium was estimated exclusively in one of the Bulgarian wines at very low concentration. Other wines did not contain cadmium. Zinc ($p=0.0032$) and copper ($p=0.0003$) level varied between tested wines in a statistically significant manner. The highest level of copper was estimated in Italian wines, the lowest in Polish products. This differences were statistically significant ($p=0.0005$). Similarly the highest level of zinc contained Italian wines, whereas Polish products contained significantly lower level of zinc ($p=0.002$). On the oher hand Polish drinks had the highest concentration of lead. Lead was also found in one of the studied Bulgarian wines. The differences in lead concentration between Polish and Bularian products were not significant ($p=0.33$). Testet Italian wines were not contaminated with Pb. The results are presented in table 1.

Table 1 Mean cadmium, copper, lead and zinc concentrations ($mg \cdot L^{-1}$) in low quality wines produced in Italy, Bulgaria and Poland.

	Bulgarian wines		Italian wines		Polish products	
	mean	min-max.	mean	min-max	mean	min-max
Cd	0.004	0-0.04	—	—	—	—
Cu	0.08±0.02	0.07-0.09	0.13±0.05*	0.09-0.21	0.04±0.001*	0.03-0.04
Pb	0.67±0.70	0-1.22	—	—	0.88±0.52	0.20-1.22
Zn	0.36±0.06	0.29-0.44	0.66±0.28*	0.24-1.05	0.18±0.16*	0.02-0.36

* statistically significant differences between compared wines at $p<0.05$.

Heavy metals in wine may have different sources. Zinc and copper are naturaly present in grapes and other fruits. On the oher hand they may be introduced to vineyards with pesticides and fertilisers. Additionally wine may be contaminated during various technological processes **(Dugo et al., 2005)**. An excess of both metals may result in serious health problem **(Mezzetti et al., 1998)**. In our studies we found singnificant differences in zinc and copper level between tested wines. Zinc level in Italian wines was over 2 and 4 times higher than in Bulgarin and Polish products. Other results of our studies indicate that fruits grown in central part of Poland contain about 1-2 mg of zinc per 1 kilogram. Soups contained 1-10 mg of zinc per litter and soft drinks such as juices, tea and coffee from 0.6 to 5 mg of zinc per litter. Copper concentrations in the above mentioned products was in the range of 0.05 to 0.75 ppm **(Dziadkiewicz et al., in print)**. Thus the tested wines represented only negligible source of essential metals in comparison to other food products.

Other tested metals i.e. cadmium and lead are typical xenobiotics. They do not play any biological role in living organisms. Their presence in wine may be related to the uptake from contaminated soil. Such contamination may also occur during technological processes **(Dugo et al., 2005)**. There are no proposed limits for cadmium in wine. The estimated concentration in Bulgarian wine was below the highest permissible limits in fruits and other food stuff established by European Committee **(EC/1881/2006)**. Thus considering cadmium, tested wines were clean. High level of lead in some of the products from Bulgaria and Poland was surprising. Although it should be noted that some of the samples of Bularian wines were not contaminated with lead, and some of the Polish products had lead level within the permissible level. Nonetheless mean concentration of Pb in Polish and Bulgarian wines was higher than allowable level of lead in wine (0.2 ppm) established by European Committee **(EC/1881/2006)**. High concentration of lead in some wines indicates that the control of contamination was of low quality.

Our studies indicate that large differences in copper and zinc content may occur between different wines. The high level of lead in some low quality and low price wines suggest that such products need more precise control of chemical contamination.

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