Identification of toxic and other matters in wines by the method of Atomic Absorption Spectrophotometry (AAS)

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1. Objective:

Quality wines are produced in our country. The main objective of this paper was identification of toxic matter, heavy metals and minerals in wines as final produce, with a view of improving nutritional quality of our wines, produced in 2008-2009.

Another important fact for this research was the determination of the presence of remnants from protective solutions containing toxic elements (Cu and Pb)[1][2].

2. Duration of the research exercise:

The research took a nine-month period, starting from April 1, 2009 and until December 15, 2009.

2.1. Sampling:

The samples for analysis were taken in cellars of private producers in Rahovec, Krusha Vogel and Gjakova, in the presence of sanitary inspectors of Prizren and Peja, and the officials of the Wine Institute in Rahovec, which is part of the Ministry of Agriculture**.**

2.2. Marking samples

Five (5) types of white wine and eight (8) types of red wines were taken, a total of thirteen (13), for analysis, as provided below[2]:

White wines: Chardonnay 2009, Rigne Riesling 2009, Italian Riesling 2009, Cabernet Sauvignon 2009, Smederevka 2009

[1] Evgjini Papazisi Tonin Rjolli Dr. Abdul Sinani "Food Technology and Environmental Protection (Teknologji ushqimore dhe mbrojtje mjedisi1)".

[2] PKB" Kosovo Vino" DOO Mala Kruša "Elaborat" 1993.

Red wines: Merlot 2009, Cabernet 2009, Pinot noir 2009, Vranac 2009, Prokupka 2009, Game 2009, Red wine 2009, Red wine 2006 as a comparative sample.

Samples were marked by sorting numbers, as per type.

3. Testing methods

Researchers have used the methodology as per International Standard of Wines[38] "Compendium of International Methods of Analysis – OIV 2009" and internal procedures of the analytical laboratory of the KAI, as provided below MA-E-AS 322-02 K, MA-E-AS 322-03 Na , MA-E-AS 322-04 Ca, MA-E-AS 325-Fe, MA-E-AS 322-06 Cu,
MA-E-AS 322-07 Mg, MA-E-AS 322-08 Zn, MA-E-AS 322-10 Cd,

Sample preparation procedure for testing, internal method Nr 01.22.0012

Pb identification procedure, AAS method, internal method Nr 01.22.0021

Cd, Cr identification procedure, AAS, internal method Nr 01.22.0022

Na, K, Ca, Mg, Zn identification procedure, AAS, internal method Nr 01.22.0024

Cu, Mn, Fe identification procedure, AAS, internal method Nr 01.22.0025

3.1 Short description of testing methods[4]

3.1.1 Working tools and apparatus:

Combustion oven 1200^0C

Drying oven 250^0C

Platinum container

Exicator Eksikator

Normal container 100 cm^3

Pipette 50 cm^3

Pipette 10 cm^3

AAS

3.1.2 Reagents[5]: Chlorine Acid (HCl) 1:3

Standards for Na, K, Ca, Mg, Zn, Fe, Cu, Mg, Pb, Cd, Cr 1000ppm, manufactured by Merck

Distilled water < 1uS

[3] Compendium of International Methodes of Analysis –OIV 2009

[4] *Inž.Salko Muštovič*"Vinarstvosa enohemijom i mikrobiologijom".

[5] J.Trajkoviq M. Miriq J. Baras S.šiler " Analize Životnih namirnica".

3.1.3 Tab 1 Conditions for determination of elements by AAS

Element	Na	K	Ca	Mg	Zn	Cu	Fe	Mn	Pb	Cd	Cr
Wave-length nn	589.0	766.5	422.7	285.2	285.2	324.8	248.3	279.5	283.3	228.9	357.9
Size nm	0.2	0.7	0.7	0.7	0.2	0.7	0.2	0.7	0.7	0.7	0.7
Flame	Ac/air	Ac/air	Ac/air	Ac/air	Ac/air	Ac/air	Ac/air	Ac/air	Ac/air	Ac/air	Ac/air

3.1.4 Tab 2 amounts taken and emaciation

Element		Na	K	Ca	Mg	Zn	Cu	Fe	Mn	Pb	Cd	Cr
Amount of sample for mineralization	ml	50	50	50	50	50	50	50	50	50	50	50
First emaciation 1:1	ml	100	100	100	100	100	100	100	100	100	100	100
Second emaciation		1:10	1:10	1:10	1:10				1:10			
Working standards	C_1 ppm	2	2	5	0.5	0.5	2.5	2	1			
	C_2 ppm	4	5	10	1	1	5	4	2			
	C_3 ppm	6	10	20	2	2	10	8	4			

Description of method: The method is based on blazing the sample on 550^0C, dipping on chlorine acid 1:3, watering (emaciation), and final determination by AAS.

3.2.1 Working method: A sample of 50 cm^3 is taken in a platinum container and is entered into a drying oven. Samples are dried and then placed in a incinerating oven at 550^0C for 4 hours. Platinum containers with incinerated samples are inserted into the exicator. After cooling, samples are dipped into 20 ml of HCl 1:3, and put into a normal container of 100 cm^3 and emaciated up to the mark (emaciation 1). Emaciated samples are tested with AAS, as per conditions given in the table. For a blind test, the solution 1 % HCl was used

3.2.2 Calculation: For identification of matters, elements' standards at three concentrations were used (C_1 , C_2 and C_3) tab

Calculation of absorption factor

$F=(C_1 + C_2 + C_3) / (E_1 + E_2 + E_3)$

$M(Pb,Cd,CR)\ (ppm) = F \times E_{sample}$

Sample content calculation

$M(Pb,Cd,Cr)\ mg/lit =(F \times E_{sample} \times V_h)/ V_p$

Where: f-absorption factor

C_1 ,C_2, C_3 - standard concentrations

E_1 ,E_2 ,E_3 – standard absorption

E_m – sample absorption

V_h - emaciation (100cm^3)

V_p – sampling (50 cm^3)
Or M(Pb, Cd, Cr) mg/lit = (F x E_{sample} x 100)/ 50 = F x E_{sample} x 2

4 Presentation of result: Results of analysis for heavy metals and minerals in white and red wines are given in a tabular form: Tab 3-6 .

4.1 Tab. 3 Results of analysis for heavy metals in white and red wines of 2009

Ord. no	Producer	Type of wine	Na	K	Ca	Mg	Zn	Cu	Fe	Mn	Pb	Cd	Cr
			mg/lit										
1	SHPK Haxhijaha	Italian Riesling	2,99	287,2	67,8	26,56	0,72	0,36	3,19	0,55	0,16	0,00018	0,018
2	SHPK Haxhijaha	Ranje Riesling	3,28	320,8	57,63	35,15	0,99	0,43	2,39	1,38			
3	SHPK Haxhijaha	Smederevka	4,5	365,2	67,8	28,44	1,11	0,43	4,78	0,8			
4	SHPK Haxhijaha	Smederevka	2,62	333,2	67,8	28,87	1,03	0,51	3,98	0,75	0,13	0,0012	0,0198
5	SHPK Haxhijaha	Chardonnay	1,97	298,8	56,5	31,12	1,06	0,55	2,39	0,8	0,10	0,00024	0,0144
6	SHPK Haxhijaha	Pinot noir	2,65	524,3	53,85	44,54	0,99	0,25	5,1	2,25			
7	SHPK Haxhijaha	Merlot	2,81	467,8	55,5	40,78	0,77	0,42	6,5	1,25	0,11	0,0006	0,0251
8	SHPK Haxhijaha	Pinot noir	3,28	431,6	54,24	39,39	1,04	0,43	4,78	1,95			
9	SHPK Haxhijaha	Game noir	2,79	464,8	56,5	43,47	0,92	0,4	4,18	2,53			
10	SHPK Haxhijaha	Prokupka	2,58	498,7	53,11	41,86	0,96	0,42	5,78	2,21			
11	SHPK Haxhijaha	Cabernet	1,66	531,6	62,15	33,7	1,03	0,25	3,78	1,52			
12	SHPK Haxhijaha	Vranac	2,7	564,1	50,85	41,86	0,98	0,25	4,78	1,68	0,15	0,0006	0,018

4.2 Tab 4 Results of analysis for heavy metals in degustation white and red wines of 2009

Ord no.	Producer	Type of wine	Na	K	Ca	Mg	Zn	Cu	Fe	Mn	Pb	Cd	Cr
			mg/lit										
1	Stone castle Rahovec	Italian Riesling	3,38	298,8	68,93	33,81	1,61	0,6	3,77	0,83	0,13	0,0006	0,018
2	Stone castle Rahovec	Ranje Riesling	3,58	355,4	71,19	37,19	1,34	0,51	4,18	1,1			
3	Stone castle Rahovec	Chardonnay	3,38	398,4	68,9	35,95	1,03	0,34	2,26	1,2			
4	Stone castle Rahovec	Cabernet Sauvignon	4,78	431,6	54,24	39,39	1,04	0,43	3,28	1,95			
5	Stone castle Rahovec	Vranac	5,58	498,4	58,76	34,34	1,03	0,25	2,41	1,94			
6	Stone castle Rahovec	Game	2,39	465,2	56,5	38,48	1,12	0,24	2,26	1,3			
7	Stone castle Rahovec	Red Wine	5,18	498,6	55,37	35,15	0,94	0,34	2,85	1.25			
8	Stone castle Rahovec	Pinot noir	4,97	498,5	56,5	37,19	0,8	0,32	3,2	1,25	0,15	0,0012	0,0144

4.3 Tab. nr.5 Results of analysis for heavy metals in degustation white and red wines of 2009

Ord no.	Producer	Type of wine	Na	K	Ca	Mg	Zn	Cu	Fe	Mn	Pb	Cd	Cr
			mg/lit										
1	SHPK DEA Gjakova	Rizling	5,18	335.2	66,67	31,39	0,61	0.34	3,28	1,1			
2	SHPK DEA Gjakova	Vranac	5,98	431.6	44,07	40,56	1.16	0.32	3,62	1,05	0,11	0,0024	0,0198
3	SHPK DEA Gjakova	Pino noir	8,17	597.6	65,5	37,83	0,1	0.21	3,44	0,89			
4	SHPK DEA Gjakova	Game	7,37	531.2	54,24	35,26	0,75	0.34	2,95	1,57			

4.4 Tab.nr 6 Results of analysis for heavy metals in degustation white and red wines of 2009

Ord no.	Producer	Type of wine	Na	K	Ca	Mg	Zn	Cu	Fe	Mn
			mg/lit							
1	NP " Kosovavera"Krushe e vogël	Red wine	5.98	431.6	65.5	40.56	1.20	0.34	3.44	0.79

Tab. Nr 7 Heavy metals (Pb, Cd and Cr) limits allowed as per EU Directive 466/2001, Regulations NN 16/05 and 29/05, Regulation 5/92 of FZ, and mineral values taken from the website File://F/kemijski sastav-Vinopedija.htm

Metal	Regulation No. 5/92 of FZ - Serbia	Regulations No. 16/05 and 29/05 NN – Croatia	EU Directive 466/2001	Website File ://F/kemijski sastav-Vinopedija.htm ppm
Pb	< 0.3	< 0.2	0.2	0.3
Cd	< 0.1	-	-	0.01
Cr	<0.1	-	-	0.1
K				200-2200
Na				20-150
Mn				0.5-10
Fe				4-35
Ca				40-200
Mg				15-200
Cu				< 2
Zn				0.5-5

5 Conclusions

1. Results presented in tables 3-6 show that samples of white and red wines have not exceeded the values (limits) of heavy metal content (Pb, Cd and Cr), and therefore, samples tested have given undetected levels in the method applied.
2. In relation to the presence of elements Na, K, Ca, Mg, Zn, Cu, Fe and Mn (tables 3-6), tested samples also show normal values.
3. There are no distinct differences between results of samples from different producers or cellars
4. As for the sample of "Red Wine" 2006 taken in the "KosovaVera" cellar in Krusha Vogel, as a comparative sample, there is not much difference from samples taken from other cellars with wines of 2009, both types show allowed values.
5. From the results obtained, one may conclude that tested products have been produced in conditions of no contamination with heavy metals in soil, air, water or any other contamination source, and their consumption does not pose any hazardous presence of heavy metals.

Literature:

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