BRANDIES USING GFAAS

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Introduction

"Rakija" (grape brandy) is a traditional alcoholic drink in the Republic of Macedonia and other Balkan countries which is produced by distillation of grape pomace or wine either traditionally (home-made) or industrially [1]. Although Macedonian regulations control several parameters associated to the quality of alcoholic beverages, such as methanol, aldehydes, esters, alcohols, total acidity, extract and furfurol and metals such as Cu, Fe, Zn, Pb and Sn, large quantities of brandies produced under domestic conditions are sold on the market without any quality control.

✓**Therefore, the aims of the work were: (1) to report a simple and fast method based on GFAAS technique for direct determination of trace elements (Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in brandies and (2) to study the effect of various technologies for grape brandy production on the metals content.**

Materials and Methods

Grape brandies

Three brandies (B1, B2, B3) home-made and stored in stainless steel tanks,

Five brandies produced by industrial distillation of which two (B4, B5) aged in French oak barrels and three (B6, B7, B8) aged with different oak chips toasted at 120 – 160°C, ~ 200°C and ~ 250°C [1].

Graphite Furnace Atomic Absorption Spectrometry (GFAAS)

Perkin Elmer model PinAAcle 900T was used for determination of Cd, Pb, Cr and Ni in brandy samples without dilution, while Cu, Fe, Mn and Zn were quantified after appropriate dilution. Sample aliquots of 20 mL were directly injected into the graphite tube and then a volume of 5 mL of chemical modifier was added.

Statistical Analysis

XLSTAT Software, Version 7.5.2, Addinsoft (Paris, France) was employed for statistical analyses, including one-way Analysis of Variance (ANOVA) and Principal Component Analysis (PCA).

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Results

Optimization and validation of the method

Table 1. Calibration parameters, matrix effects and detection limits in GFAAS using aqueous standards or standards prepared in ethanol

	Matrix[a]	Slope	Intercept	Correlation coefficient (r)	Matrix effect[b]	Residual s ($s_{y/x}$)[c]	LOD (µg l^{-1})[d]
Cd	water	0.0242	0.00099	0.9996	1.04	8.4 10^{-6}	0.12
	ethanol	0.0252	- 0.00113	0.9996		1.9 10^{-5}	0.27
Cu	water	0.00166	1.1 10^{-5}	0.9996	1.08	5.6 10^{-7}	0.60
	ethanol	0.00180	- 6.4 10^{-4}	0.9996		8.1 10^{-7}	1.00
Ni	water	0.0037	- 5.1 10^{-4}	0.9997	1.05	2.2 10^{-6}	0.67
	ethanol	0.0039	- 0.00137	0.9995		4.5 10^{-6}	1.00
Cr	water	0.01077	9,8 10^{-4}	0.9997	1.00	1.8 10^{-5}	0.43
	ethanol	0.01078	3.0 10^{-4}	0.9998		1.6 10^{-5}	0.43
Pb	water	0.00253	- 2.4 10^{-4}	0.9997	0.97	8.1 10^{-7}	0.57
	ethanol	0.00245	- 4.3 10^{-4}	0.9997		8.6 10^{-7}	0.68
Fe	water	0.01099	- 0.00327	0.9995	0.98	3.5 10^{-5}	1.00
	ethanol	0.01083	- 0.00353	0.9996		2.9 10^{-5}	1.00
Mn	water	0.00894	- 5.2 10^{-4}	0.9998	0.99	2.4 10^{-6}	0.29
	ethanol	0.00884	- 3.1 10^{-4}	0.9996		4.9 10^{-6}	0.37
Zn	water	0.03179	- 0.00142	0.9996	1.00	5.7 10^{-5}	0.36
	ethanol	0.03170	- 0.00254	0.9995		8.1 10^{-5}	0.46

[a] – 50% (v/v) ethanol; [b] – Ratio of ethanol/water calibration slopes; [c] – Calculated for n = 7 calibration standards; [d] – 3σ criterion; calculated from residual standard deviation and parameters of the calibration curve

Table 2. Results of Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn analysis for checking the accuracy and precision of the method by standard addition method

The content of standard addition in brandy B1 (6 repetitions)				
	STD-I 10 µg/L		STD-II 100 µg/L	
Elements	**Found concen.**	**Recovery %**	**Found concen.**	**Recovery %**
Mn	37.8±0.28	96.4±0.73	120±1.41	93.8±1.1
Fe	38.8±1.20	95.0±3.01	131±8.49	105±6.53
Cu	6127±4.24	99.9±0.07	6187±10.6	99.3±0.17
Zn	31.3±0.99	92.7±3.00	118±1.41	96.7±1.15
Cd	10.3±0.46	97.1±4.48	98±0.64	98.2±0.63
Pb	17.9±0.85	96.1±4.71	108±2.83	101±2.62
Cr	10.5±0.88	109±8.63	97.3±1.63	98.3±1.62
Ni	12.2±0.85	96.7±7.07	105±9.55	96.6±9.36

Metals Content in Brandies

Table 3. Concentration (µg L^{-1}) of elements in Macedonian brandies determined by GFAAS (mean±U for 95% confidence level; n=3)

Sample	Mn	Fe	Cu	Zn	Cd	Pb	Cr	Ni
B1	29 ± 3	30 ± 5a	6120 ± 156	23 ± 2a,b	< 0.3	8 ± 1a	< 0.4	2.0 ± 0.3
B2	< 0.4	841 ± 35	**71200 ± 1290**	**3160 ± 110**	< 0.3	9 ± 1a	2.0 ± 0.3	< 1
B3	49 ± 4	241 ± 25	**17300 ± 470**	175 ± 19	< 0.3	12 ± 2a	21 ± 2	7 ± 1
B4	38 ± 3a	62 ± 6	2010 ± 87a	33 ± 5	< 0.3	< 0.7	< 0.4	< 1
B5	36 ± 3a	74 ± 7	2250 ± 95a	27 ± 4a	< 0.3	< 0.7	< 0.4	< 1
B6	118 ± 10b	37 ± 5a	3450 ± 119	18 ± 2b	< 0.3	< 0.7	< 0.4	< 1
B7	87 ± 7	11 ± 2	4360 ± 134	< 0.5	< 0.3	< 0.7	< 0.4	< 1
B8	110 ± 11b	594 ± 35	5400 ± 114	48 ± 6	< 0.3	< 0.7	12 ± 2	5 ± 1
Max. limit	-	10000	10000	500	-	500	-	-

Conclusion

Concentration of Cu, Mn, Fe and Zn were suitable parameters to establish pattern recognition for home/industrial distillation process, aging method and type of oak chips. The distillation process influenced the mineral content of grape brandies. Brandies produced in domestic conditions presented high Cu and Zn contents, much over the maximum allowed levels. Brandies produced in industrial distillation units were found to be safe for consumption as the determined metals were below the maximum allowable concentrations. Manganese and Cu could be suitable markers for aging of industrial brandies with oak chips.

References

[1] Ivanova-Petropulos, *et al.* (2016). Rapid determination of trace elements in Macedonian grape brandies for their characterization and safety evaluation .*Food Analytical Methods*, accepted for publication.

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