

Monitoring of selected Elements in Wine and geochemical Characterization of Soil from Vineyards Regions in Slovakia

MILAN SUHAJ – MÁRIA KOREŇOVSKÁ – ĽUBOMÍR DAŠKO

Food Research Institute, Priemyselná 4, 824 75 Bratislava

Abstract. The results of monitoring of selected elements As, Cd, Cr, Hg, Ni and Pb in soils from 6 basic vineyards in Slovakia were compared to the data of selected monitored elements in Slovak wines with the aim of wines geographical authentication. Correlation analysis proofed that relation between contents of selected elements in wine is closely related with their content in soils almost all regions. The highest correlation level between composition of soil and wine exceeding 90 % were in Low Carpathians and Tokaj vineyard region. From the point of view of applicability of selected group of elements for vineyard regions and wine authenticity determination Principal Components Analysis as a statistical tool was used. Based on PCA method very high level of differentiation was achieved in the case of vineyards soils. Applying PCA method to distinguish geographic origin of wine from different vineyards regions the level of geographic authenticity was not so good. Proper selection of specific elements which could be useful for wine geographical traceability will be used in the next research of wine geographical authentication.

Key words: wine, soil, vineyards, authentication, elements

1. Introduction

There is evident increasing interest in food authenticity in relations to growing requirements on quality, food origin recognition, traceability and food safety. To meet all these requirements it is critical to improve knowledge of characteristic criteria of authenticity and specific quality markers. In accordance with these requirements EU adopted food legislation EC No. 178/2002, which defines duties to develop scientific methods relating to food risk assessment and food traceability procedures. There are many papers available related to wine origin traceability based on trace elements profile. Elements can be considered as good indicators of wine origin since they are not metabolized or modified during the vinification process (Arvanitozannis, 1999). Multi-element analysis using 35 elements determination by inductively coupled plasma mass spectrometry (ICP-MS) was used to classification of Spanish and English wines (Baxter, 1997). Eleven elements, K, Na, Ca, Mg, Fe, Cu, Zn, Mn, Li and Rb, were determined in dry and sweet wines bearing the denominations of origin of Canary Islands, Spain (Frías, 2002). Distribution of heavy metals (Pb, u, Zn and Cd) in the system soil – grapevine – grape was investigated by Angelova, 1999. The authenticity and geographical origin of wines produced in Slovenia were investigated by a combination of IRMS and SNIF-NMR methods and the stable isotope data were evaluated using principal component analysis (PCA) and linear discriminant analysis (LDA), (Ogrinc 2001). The usefulness of lanthanides or rare earth elements has also been clearly demonstrated since La, Ce, Pr, Nd, Eu, Gd, Tb, Ho, Er,

Tm, Yb, Lu are some of the lanthanides successfully employed for distinction between regions (McCurdy, 1992).

There is food basket monitoring (FBM) in Slovakia since 1993 dedicated to monitor selected food additives and contaminants in the foodstuff with the aim to assess human loading with selected substances. In the monitoring database which is in the Food Research Institute (FRI) there are concentrations levels data of selected trace elements in Slovak wines from six vineyards (Low Carpathian, Nitra, South Slovakia, Central Slovakia, East Slovakia and Tokaj) which are defined by Decree of Ministry of Agriculture No. 153/1998 C L. on vineyards and viticulture. Vineyards in Slovakia cover in total 20 000 ha. Almost 80 % of vineyards are in the region of western Slovakia, 13 % in the central Slovakia and almost 7 % in eastern Slovakia. The soils in Low Carpathian region are skeletal, light, only slightly trapping water and well adsorbing energy from the sun. From the geology point of view, there are deep magnetites pararuls, but also biotic granites and granodiorites. South Slovakian vineyard region has the highest temperature with dry climate and mild winters. The soils are mostly light sandy up to middle hard unskeletal with deeper profile. Nitra vineyard region is heterogeneous from the geographical point of view. North regions are mostly skeletal soils with profile based on limestone, dolomites, quartzite and sandstones of Mesozoic. South and west parts dominate neogenic sediments with origin from south region. Geological base of soils from central Slovakian region is composed of neogenic sediments, shale and sandstones without skeleton. There are highly nutritive middle hard and hard soils.

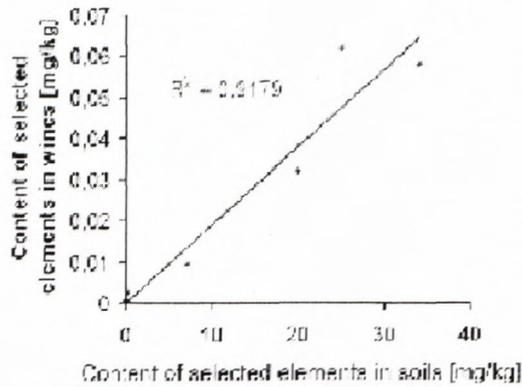


Fig. 1 Correlation of the content of selected elements in wines and soils from Low Carpathian Region

East Slovakian vineyard region is heterogeneous from the geological point of view. Under Vihorlat dominate hard, clay – mudstone soils, created on neogenic alluvial – pyroxenes and andesine. Vineyards located in limestone and caves region have rendezite skeletal soils with ripple slope relief. In Streda nad Bodrogom there are light sandy soils. The smallest region from the area point of view Tokaj has rocky, gravel, sandy-clay soils with higher content of skeleton. They were created on alluvial base from younger Paleozoic, on rezolits, andesine and their tuffites. Typical is higher acidity and high content of minerals (Hronský, 2001).

In this paper are evaluated analytical results of selected elements in wine from the monitoring databank. They are compared with geochemical characteristics of soils from vineyards regions. The aim is to find correlation with geographical origin of wine.

2. Materials and methods

The attempt to trace wine origin based on trace elements profile applying statistical identification of different vineyards regions of Slovakia is related to the results of food basket monitoring. We applied the data for wine and soil from vineyards regions from the Center for evaluation of presence of food additives and contaminants in Food Research Institute Bratislava and data on geochemical composition of soils from vineyards regions of Slovakia (Čurlík, 1999). We have taken into account only the wine regional origin no year of production, sort or other wine evaluation criteria. Statistical comparison and differentiation of 6 vineyards of Slovakia was based on results of content of selected elements As, Cr, Cd, Ni, Pb and Hg. I was studied correlation between content of trace elements in wine with relations to their content in soils from vineyards regions in Slovakia. We applied for basic statistical evaluation software Microsoft Excel 2002 and Unistat 4.53 for multivariate analysis (PCA). By PCA parallel projection of components by angles $\alpha = 126^\circ$ and $\beta = 24^\circ$ was applied.

3. Results and discussions

The results of monitoring of selected elements in soils from 6 basic vineyards in Slovakia are in the Tables 1 and 2. Comparing the data of selected monitored elements in soil and wine remarkable correlation is evident. Correlation analysis proved that relation between contents of

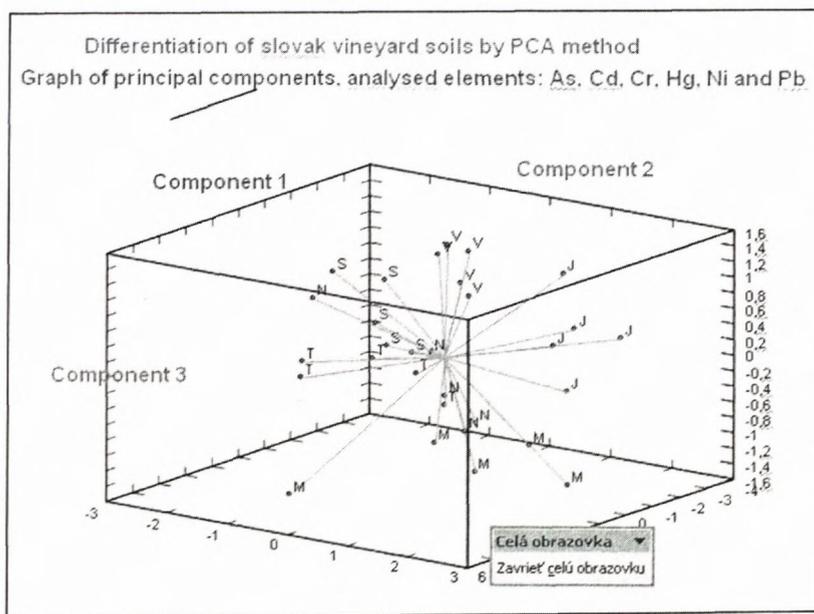


Fig. 2 Differentiation of Slovak vineyard soils by PCA methods

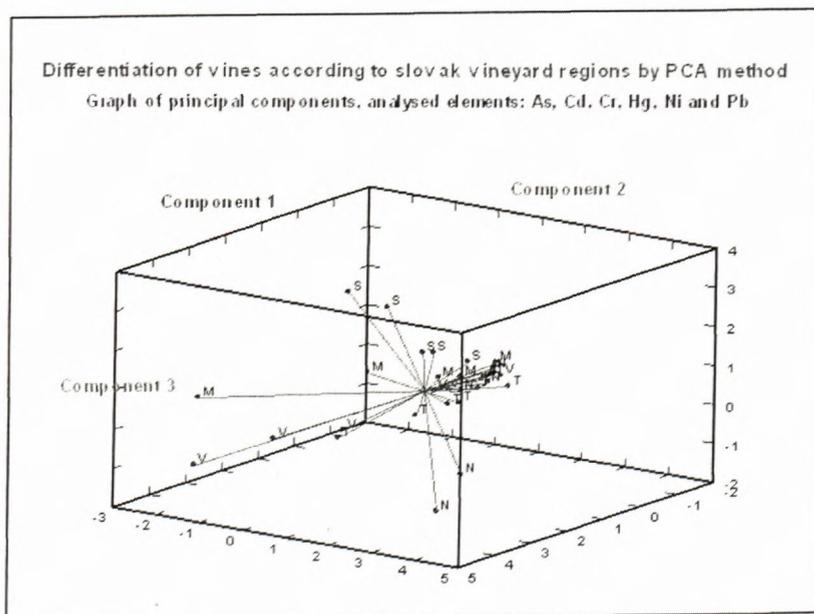


Fig. 3 Differentiation of some slovak vines by PCA method.

Table 1 Distribution of selected elements in soils from wine yards (WY) regions in Slovakia

Element	Elements distribution [mg/kg] in soils ¹⁾ in WY ²⁾ Slovakia					
	J	M	N	S	V	T
Pb	3 – 13	20 – 69	13 – 30	16 – 30	13 – 20	16 – 30
As	4 – 7.2	7.2 – 16.2	7.2 – 9.9	5.3 – 7.2	3.3 – 5.3	5.3 – 9.9
Hg	0.02 – 0.05	0.05 – 0.14	0.03 – 0.08	0.05 – 0.14	0.03 – 0.08	0.05 – 0.14
Cr	46 – 85	34 – 101	67 – 125	85 – 101	85 – 101	67 – 101
Ni	25 – 44	25 – 44	16 – 33	16 – 33	25 – 33	16 – 25
Cd	0.1 – 0.4	0.3 – 0.4	0 – 0.2	0 – 0.2	0 – 0.3	0 – 0.2

¹⁾ Čurlík, J. – Šefčík, P. (1999): Geochemical atlas of Slovakia. Part V: Soils. MŽP SR, VÚPaOP, Bratislava, 1999, 99 s.

²⁾ WY: Wine yards regions in Slovakia: J – South Slovakia, M – Low Carpathian, N – Nitra, S – Central Slovakia, V – East Slovakia, T – Tokaj

Table 2 Distribution of selected elements in wines from wine yards regions of Slovakia.

Element	Elements distribution [mg/kg] in wines from WY ¹⁾ regions in Slovakia Xmin – Xmax/Xaverage ²⁾					
	J	M	N	S	V	T
Pb	0.02–0.05 0.0386	0.002–0.08 0.0321	0.001–0.06 0.0261	0.09–0.2 0.1613	0.01–0.3 0.05	0.003–0.259 0.05
As	0.001–0.007 0.005	0.005–0.045 0.0095	0.002–0.026 0.0083	0.007–0.067 0.0025	0.002–0.01 0.005	0.001–0.005 0.003
Hg	ND	ND – 0.004 0.0007	ND – 0.002 0.0005	ND – 0.002 0.0003	ND – 0.003 0.0006	ND – 0.001 0.0004
Cr	ND	0.002–0.29 0.0584	0.002–0.18 0.065	ND – 0.06 0.0324	0.041–0.07 0.055	0.09
Ni	ND	0.03–0.14 0.0620	0.002–0.564 0.0961	ND–0.127 0.18	0.028–0.1 0.064	0.05
Cd	0.001–0.005 0.0023	0.001–0.025 0.0066	0.001–0.008 0.0023	0.001	0.001–1.642 0.0391	0.001–0.02 0.0084

¹⁾ as in Table 1

²⁾ amount of samples n = 1 up to 100

Table 3 Correlation of content of As, Cd, Cr, Hg, Ni a Pb in wines and soils of vineyards regions of Slovakia

Wine yard region, correlation coefficient					
South Slovakia	Low Carpathian	Nitra	Central Slovakia	East Slovakia	Tokaj
0.8585	0.9581	0.7348	0.0801	0.8413	0.9122

selected elements in wine is closely related with their content in almost all regions. An example of this correlation is on the Figure No. 1 for Low Carpathian region, the survey of defined correlation coefficients is in the Table No. 3. The highest correlation level between composition of soil and wine exceeding 90 % were in Low Carpathians region and Tokaj region. Central Slovakian region was the region with very low level of correlation less than 8 %. It could be consequence of relatively small amount of results from this region available for vineyards and wines.

From the point of view of applicability of selected group of elements for determination of authenticity of vineyard regions and wine interesting tool is statistical evaluation. The aim of statistical evaluation applying the method of principal components (Principal Components Analysis – PCA) was the proper differentiation of vineyards and wines based on the regions. Based on PCA method very high level of differentiation was achieved in the case of vineyards soils, Figure 2. Its evident that based on statistical evaluation selected elements provide suitable data sources for reliable distinguish of vineyards ex-

cept of Nitra region. When such reliable level of discrimination was achieved in soil data analysis, for wine data deducing from correlation patterns the results should be similar. But it is not the case. Applying PCA method to distinguish geographic origin of wine from different vineyards regions the level of geographic authenticity was not so good Figure 3. It is interesting, that most efficient segregation was achieved for wine from central Slovakia region which as only one was separated but in correlation analysis for wine from this region there was found the lowest level of correlation with the region soil matrix. It is evident that for identification of wine from different regions selected contaminated elements were not suitable choice.

Conclusions

It is evident that selected elements from Monitoring of food additives and contaminants As, Cd, Cr, Hg, Ni and Pb in soils from wine yards regions are suitable tool for geographical authenticity, which is interesting for soils

traceability but not interesting for requirements of wine geographical origin authenticity. We are now focused for proper selection of specific elements which could be useful for wine geographical traceability.

Literature

- Angelova, V. R., Ivanov, A. S. & Brajkov, D. M. (1999): Heavy metals (Pb, Cu, Zn and Cd) in the system soil – grapevine – grape. *Journal of the Science of Food and Agriculture*, 79: pp. 713–721.
- Arvanitoyannis, I. S., Katsota, M. N., Psarra, E. P., Soufleros, E. H. & Kallithraka, S. (1999): Application of quality control methods for assessing wine authenticity: Use of multivariate analysis (chemometrics). *Trends in Food science & Technology*, 10: pp. 321–336.
- Baxter, M. J., Crews, M. H., Dennis, M. J., Goodall, I. & Anderson, D. (1997): The determination of the authenticity of wine from its trace element composition. *Food Chemistry*, 60: pp. 443–450.
- Čurlík, J. & Šefčík, P. (1999): Geochemical atlas of SR. Part V: Soils. MŽP SR, VÚPaOP, Bratislava, 99 p.
- Frías, S., Conde, J. E., Rodríguez, M. A., Dohnal, V. and Trujillo, J. P. (2002): Metallic content of wines from the Canary Islands (Spain). Application of artificial neural networks to the data analysis. *Nahrung/Food*, 46: pp. 370–375.
- Hronský, V. (2001): Slovak wines, BELIMEX, Bratislava, 118 p.
- McCurdy, E. , Potter, D. & Medina, M. (1992): Trace elements in wines. *Laboratory News*, No. 9, pp. 10–11.
- Ogrinc, N., Košir, I. J., Kocjančič, M., & Kidrič, J. (2001): Determination of authenticity, regional origin, and vintage of Slovenian wines using a combination of IRMS and SNIF-NMR Analyses. *J. Agric. Food Chem.* 49: pp. 1432–1440.