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Analytical Methods

Correlation and distribution of elemental markers of origin in the production of Bryndza sheep cheese

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Abstract

The successful classification of Bryndza, a typical Slovak national sheep cheese, from nine different Slovak producing regions, was based on canonical discriminant analysis. Elemental markers of origin (Ba, Cr, Cu, Hg, Mg, Mn, Ni and V) were determined by graphite furnace (GF) and flame atomic absorption spectrometry (AAS). High correlations of elemental markers were found between pasture soil, grass, and Bryndza cheese originated from different regions. The concentration of these markers in pasture soils, grasses, as well as in all the milk and Bryndza cheese-making process was monitored. Their content in sheep milk, lumpy cheese, whey, boiled sheep whey and final Bryndza cheese was significantly correlated with the soil elemental markers. The final product was only slightly contaminated by the individual elements during the Bryndza production, without any significant influence on the Bryndza origin classification and/or traceability.

Keywords: Bryndza cheese; Elemental markers; Correlation; AAS

1. Introduction

Cheeses are considered to be a good source of several minerals and there is no doubt that their presence and abundance in different cheese types are strongly dependent on the country or region of milk origin and last but not least, on the manufacturing procedures, processing and post-processing of cheese products. From the last two mentioned, the addition of salts and other optional ingredients together with the method of coagulation, thermal treatment of the curd, and the resulting acidity significantly influences both the characteristic properties of cheese, its taste and flavour as well as the mineral content.

The calcium content in cheese is essentially influenced by the acidity of milk at the coagulation stage and on the degree of expulsion of whey from the curd. In ripened whole milk cheeses, where coagulation is performed using enzymes, the calcium and phosphorus mostly remain in the curd. Calcium chloride can be added to cheese milk in order to compensate for the losses of calcium during pasteurization and to improve the curdling process. Cheese manufacturing procedures affect the content of several minerals as well. If, for instance, a high acidity is developed during cheese production, calcium and magnesium salts become more soluble and are thus easily removed with the whey during washing. Likewise, frequent washings tend to lower the content of other minerals in the curd. The sodium content of cheese is strongly influenced by the addition of sodium chloride (salt) as an optional cheese ingredient during its processing. Separation of the curd from the whey in cheese-making causes a significant partition of nutrients and a considerable change in the nutrient. Finally, the content of nutrients and other component in final cheese in comparison to their abundance in milk is strongly influenced by the separation of curd from whey (Dairy Foods Association, 1998; Kosikowski & Mistry, 1997).

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Thirty varieties of commercial goat milk cheeses collected from 13 manufacturers in 11 states of the USA were evaluated by Kosikowski and Park (1990) for their concentration profiles of basic nutrients, major and trace minerals, their mutual correlations, as well as to the presence of mineral and their ratios. Wide variations in the concentrations of P, K, Ca, Na, Cl, Fe, Al, and Zn were found among the investigated varieties. Moreover, high variance in Fe and Al content were found between cheeses, indicating the possible uptake of these elements into the products during farmstead manufacturing processes. Percentage of ash was positively and significantly correlated with the concentrations of macrominerals but negatively and less appreciably correlated with concentrations of Fe, Al, Mn, and Cu. The Na:K ratio was found to be the highest of the five mutual mineral ratios. Meaningful values of Ca:P and Ca:Mg ratios were also proved among six of 13 goat cheese evaluated in this study.

Effects of processing on the concentration of lead in Manchego-type cheese was studied by Cosano, Rojas, and Lopez (1994). The concentrations of the minerals, i.e. Na, K, Ca and Mg, as well as the trace elements, i.e. Fe, Cu, Zn and Se, were determined in 400 samples of goats' dairy products (100 raw milk, 100 whey, 100 fresh and 100 semi-hard cheeses) produced in the island of Tenerife were recently investigated by García et al. (2006). As they found, both the minerals and trace elements revealed significant differences in the concentration between the dairy products analysed. The season of production had a greater influence on the mineral and trace element concentration than the region of production and the amount of fibre in the goats' diet.

Coni et al. (1996) performed a comparative study of selected trace elements such as Al, Ba, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Pt, Sr and Zn in sheep and goat milk as well as in a typical cheese products made from them. Their continuous salting and ripening were also monitored after 1, 4 and 8 weeks of the post-production storage. Results obtained revealed considerable differences in trace elements content between sheep and goat milk and the respective cheese products. As they also concluded, the concentration ranges of metallic compounds in milk and cheeses are strongly dependent on the animal species, feeding, season of milk production as well as on environmental conditions, and manufacturing processes.

Coni, Bocca, and Caroli (1999) measured the concentrations of selected trace elements, i.e. Al, Ba, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Pt, Sr and Zn in raw ewes' milk and in typical ewes' milk cheeses. Samples of milk, curd, whey, cheese after moulding, cheese after salting, commercial cheese (Pecorino), Ricotta, Scotta and Brine were also analysed during seven complete cycles of cheese production for their content of the above mentioned trace elements, in order to monitor the distribution of each element in the main product, by-products and waste products during the cheese-making process. They discovered considerable differences among the trace element contents in raw ewes' milk and related products, indicating that manufacturing processes play a key role in their distribution.

De La Fuente, Olano, and Juárez (1997) examined the distribution of main elements (calcium, magnesium and phosphorus) and microelements (zinc, iron, manganese and copper) between the soluble and colloidal phases of ewes' and goats' milk. The percentages of calcium, magnesium and phosphorus were higher in the soluble phase of goats' milk (32.8%, 66.4% and 38.6%, respectively) than that of ewes' milk (20.8%, 56% and 34.8%, respectively). The distribution of iron and copper differed conspicuously. The content of iron in the soluble phases of ewes' and goats' milk was 28.5% and 44.3%, respectively. In addition, the content of soluble copper ions is also higher in ewes' milk (33.3%) when compared to goat's milk (18.1%).

Slovak Bryndza is a national typical sheep cheese, produced in Slovakia but also in other Central European countries. In 2007 a study focussed on the problem of its geographical authentication was published by Koreňovská and Suhaj (2007). The main aim of this study is to replenish the results published in our previous study. Now the main focus is the analysis of the relationship between the presence of selected elemental markers (trace elements) and region of cheese production. Additionally, markers concentration and changes during the Bryndza cheese-making process was also monitored. Samples of sheep cheeses were obtained from nine different Slovak producers. The mutual correlation and distribution of marker elements was monitored "in line" in all steps of Bryndza productions, starting from sheep pasture soils and grass components analysis to sheep milk, lumpy cheese, whey, boiled sheep whey, and final Bryndza cheese.

2. Materials and methods

2.1. Samples

Twenty-seven samples of soils, 27 grass and 58 Bryndza cheeses from nine different Slovak regions and producers (ČK – Červený Kameň, LM – Liptovský Mikuláš, RU – Ružomberok, TU – Turčianske Teplice, TI – Tisovec, HS – Horná Súča, VF – Vel'ká Franková, JA – Jaklovce, and ZS – Zvolenská Slatina) were analysed to the content of following elemental markers Ba, Cr, Cu, Hg, Mg, Mn, Ni, and V. The correlations between soils from pastures, grasses and final Bryndza cheeses products were estimated. Distribution of these elements from soils to grasses → sheep milk → sheep cheese → whey → boiled sheep whey, and finally, to Bryndza cheese was monitored in two Bryndza cheeses manufactured by (LM) and (ČK) producers. Each numerical value was obtained as the average of triplicate measurements. All the analysed samples of Bryndza cheeses were of summer type and were obtained directly from producers.

2.2. Digestion of cheese matrix and grass

Samples of a grass, sheep milk, sheep cheese, whey, boiled sheep's whey, and Bryndza cheese were digested in a microwave digestion system MLS 1200 MEGA (Milestone, Sorisole, Italy). The individual sample of grass (1 g); sheep cheese, Bryndza cheese (0.5 g each), as well as of sheep milk, whey and boiled sheep whey (2.0 g each) were introduced into a teflon microwave digestion vessels. HNO_3 (65% w/v, 2–4 ml) and H_2O_2 (30% w/v, 0.5 ml) were added. The microwave digestion program was applied as follows: 250 W (1 min), 0 W (1 min), 250 W (5 min), 400 W (5 min), and 650 W (5 min). The respective digested samples were adjusted to the volume of 10 ml with ultra pure water and used for further analyses.

2.3. Analytical techniques

A Perkin–Elmer 4100 atomic absorption spectrometer (Norwalk, Connecticut, USA) equipped with a deuterium lamp background-correction system and HGA 700 graphite tube atomizer with pyrolytically coated graphite tubes and flame was used for metal determination. The presence and concentration of Mg and Mn metals were determined from atomic spectrometry measurements, using an air/acetylene flame. Ba, Cr, Cu, Ni, and V were detected on a graphite tube atomizer.

The instrumental conditions for above mentioned metals determination are shown in Table 1. Analytical characteristics of AAS and X-RFS (X-ray fluorescence spectrometry) methods (technique, limit of quantification (LOQ), combined uncertainty (u_C)) used for their determination are summarized in Table 2. All results were expressed as the average of triplicate measurements. The limit of quantification was calculated according to EURACHEM recommendation, (Fleming, Albus, Neidhart, & Wegscheider, 1997). The combined standard uncertainty was calculated as $(u_A^2 + u_B^2)^{1/2}$ (Eurachem, 2000). The accuracy of the results was verified by standard addition method, as the certified reference materials for determination of these elements in cheese were not available. Analytical method recovery in matrix was assessed by analysis of samples fortified with elements to the level 0.005 mg l^{-1} and 0.010 (0.025) mg l^{-1}. The fortification of samples was performed before their microwave digestion. The mean recoveries of elements varied from 84% to 120% (Table 3). The accuracy of the method was tested by the determination of Ba, Cr, Cu, Ni, Mg, Mn, and V using DC 73351 Tea, NCS ZC 73008 Rice – reference materials and NCS DC 73319 soil, all obtained from China National Analysis Center, Beijing, China.

2.4. Analysis of soil

Twenty-seven samples of soils from nine regions analysed under our study represent an average from a mix sub-samples of pasture soil and were taken from area of 100 m^2 from the depth soil horizon of 0–20 cm, 2 kg each. The samples were first dried to a constant weight. For the determination of total content of chemical elements, the fraction with granularity $\leqslant$0.125 mm was used. Mg and Mn ions were determined by AAS – flame after microwave digestion using the decomposition mixture of concentrated acids $HF + HNO_3 + HCl$ (Merck, Darmstadt, Germany). Elements Ba, Cr, Cu, Ni, and V were determined by X-ray fluorescence spectrometry (X-RFS, SPECTRO LAB 2000, Kleve, Germany) from pressed tablets of soil samples.

2.5. Chemicals

All chemicals used in experiment were of analytical grade. Stock solutions of each element (Ba, Cr, Cu, Hg, Ni, Mg, Mn and V, concentration 1.00 g l^{-1}, each) were

Table 1
Instrumental conditions for determination of some elements, atomic absorption spectrometry (AAS), graphite furnace (GF), flame AAS (F), atomic absorption (AA), background-correction (BG)

Element	Wavelength (nm)	Lamp current (mA)	Technique by AAS	Gas	Signal type	Suppressor modifier
Ba	553.6	25	GF	Argon	AA	No
Cu	324.8	15	GF	Argon	AA-BG	No
Cr	357.9	25	GF	Argon	AA-BG	No
Mg	285.2	15	F	C_2H_2–air	AA-BG	0.1% $LaCl_3$
Mn	279.5	20	F	C_2H_2–air	AA	No
Ni	232.0	25	GF	Argon	AA-BG	No
V	318.4	25	GF	Argon	AA-BG	No

Table 2
Analytical characteristics for the determination of elements in cheese matrix and soil, limit of quantification (LOQ) and combined uncertainty (u_C)

Element	Technique	LOQ (mg kg^{-1})	u_C (%)	Technique	LOQ (mg kg^{-1})	u_C (%)
Ba	GF-AAS	0.005	13.3	X-RFS	10	1
Cu	GF-AAS	0.010	6.9	X-RFS	2	5
Cr	GF-AAS	0.004	5.3	X-RFS	5	2.5
Ni	GF-AAS	0.010	14	X-RFS	2	6
Mg	Flame	0.090	3.5	Flame	1	2.5
Mn	Flame	0.060	6.6	Flame	1	1.5
V	GF-AAS	0.006	6.3	X-RFS	20	2

Table 3
Recovery for determination of selected elements by AAS methods in Bryndza cheese

Element	Element determined ($mg\,l^{-1}$)	Element added 1 ($mg\,l^{-1}$)	Element found ($mg\,l^{-1}$)	Recovery (%)	Element added 2 ($mg\,l^{-1}$)	Element found ($mg\,l^{-1}$)	Recovery (%)
Ba	0.0604	0.0125	0.0124	99	0.025	0.0296	118
Cr	0.0084	0.005	0.0052	104	0.010	0.010	100
Cu	0.0312	0.005	0.006	120	0.010	0.0098	98
Mg	1.222	0.250	0.211	84	–	–	–
Mn	0.0347	0.005	0.0055	110	0.010	0.010	100
Ni	0.0108	0.005	0.0052	104	0.010	0.0102	102
V	0.0052	0.005	0.0058	116	0.010	0.0098	98

from Merck (Darmstadt, Germany); working standard solutions were prepared by their appropriate dilution. Ionic suppressor, Lanthanum chloride (5% w/v) was delivered from Slovak Metrology Institute, Bratislava, Slovakia. Ultra pure water from Milli-Q equipment (Analyst HP, Wolf, UK) with conductivity of 18 MΩ cm was used.

2.6. Determination of Hg

For the determination of mercury in cheeses, an AMA 254 AAS (Altech, Prague, Czech Republic) was used. It is a single-purpose mercury analyser, in which mercury vapours are generated after thermal oxidation treatment of the sample in a stream of oxygen. These vapours are subsequently collected in a gold amalgamator. The collected mercury is then thermally released from the amalgamator, expelled and carried by oxygen stream into the measuring cuvettes located in a thermally controlled environment. Absorbance of Hg is measured using AAS method at 254 nm. The accuracy of the method was tested by the simultaneous determination of mercury concentration in BCR-150 skim milk power reference material (Brussels, Belgium).

2.7. Statistics

For the visualization and classification of Bryndza cheeses from different Bryndza producing regions, canonical discriminant analysis was applied, using l Unistat® v. 5.6 (Unistat Ltd., 4 Shirland Mews, London W9 3DY, England) statistical software. Correlation coefficients were calculated using Microsoft® Excel 2002.

3. Results and discussion

The selection of the traceability markers used in this study for Bryndza cheese products classification and mutual differentiation followed from the information collected in the Slovakian geochemical atlas of soils (Čurlík & Šefčík, 1999), which summarizes the distribution of about 36 different soil elements in Slovakia. We chose Ba, Cu, Cr, Hg, Mg, Mn, Ni, and V concentration variability for the differentiation. In Table 4, the correlation coefficients and mean values of authenticity markers, determined in samples of soils, grasses and Bryndza cheeses from nine main producing areas of different producers are summarized. Results show relatively high variability of elemental content, especially in soils with the higher content of Cr, Ni, and Hg (e.g., in samples from Jaklovce region localised closely to the former non-ferrous metals mine Krompachy (North-East Slovakia)). As follows from the values of correlation coefficients between the individual element content in pasture soils and grasses on one side and in soils and Bryndza on the other, respectively (Table 4), the correlations are significant for all investigated commodities obtained from all Slovak Bryndza cheese producing regions.

The correlation coefficients as a measure of mutual relationships of elemental markers determined in pasture soil, grass, sheep milk, boiled sheep whey, Bryndza, whey, and lumpy sheep cheese obtained from Červený Kameň and Liptovský Mikuláš regions, are summarized in Table 5. As follows from the data, substantial correlations between the concentration of monitored markers in pasture soil and their content in grass, sheep milk, Bryndza cheese products and by-products were determined. The correlations between the sets of markers strongly support the approach used in this work, to use just the selected elements for tracing the Bryndza cheese producers under the conditions of Slovakia cheese production.

For better visualization, the mutual correlations of elemental markers determined in soil, grass and Bryndza cheese obtained from all investigated Slovak regions is presented in the form of a correlation matrix (Table 6). As follows from the data, several interesting highly correlated dependencies were found between some elements. This fact can be plausibly explained by the partial geochemical similarities of the Slovak Bryndza cheese producing regions, as they lay relatively close one to each other. On the other hand, several low values of correlation coefficients indicate, especially in the case of magnesium, which in fact, was the only element without any interdependence to other elements, the traceability of cheese product based on this marker will not lead to acceptable and reliable results.

The effect of conditions during the Bryndza cheese production on the composition and distribution of elemental markers in milk, Bryndza, whey, boiled sheep whey and lumpy cheese originated from two Slovak regions (Červený Kameň and Liptovský Mikuláš) was also investigated. As

Table 4
Correlation between element content (mean ± SD; *n* – number of samples) in pasture soils and grasses, resp. soils and Bryndza cheese for producing regions

Region	Matrix	*n*	Element contents (mg kg^{-1})								Correlation coefficient
			Ba	Cu	Cr	Hg	Mg	Mn	Ni	V	
ČK	Soil	3	427 ± 27	55.6 ± 10.1	112 ± 4	0.095 ± 0.010	9833 ± 1200	5912 ± 4392	87.7 ± 12.7	155 ± 28	–
	Grass	3	10.8 ± 2.7	7.56 ± 1.19	1.88 ± 1.24	0.0046 ± 0.0009	1267 ± 320	63.2 ± 8.6	1.82 ± 0.93	2.95 ± 0.99	0.9565
	Bryndza	6	3.08 ± 0.14	1.53 ± 0.09	0.230 ± 0.032	0.0003 ± 0.0001	351 ± 14	0.238 ± 0.024	0.399 ± 0.012	0.251 ± 0.021	0.9414
LM	Soil	3	403 ± 41	43.6 ± 20.9	57.7 ± 6.1	0.073 ± 0.015	19233 ± 6306	553 ± 50	23.1 ± 2.6	50.3 ± 9.9	–
	Grass	3	30.9 ± 13.5	7.50 ± 1.26	1.18 ± 1.01	0.0076 ± 0.0006	1825 ± 87	36.3 ± 20.1	1.59 ± 1.42	0.609 ± 0.601	0.9999
	Bryndza	8	2.78 ± 0.50	0.881 ± 0.210	0.232 ± 0.043	0.0001 ± 0.0001	284 ± 13	0.233 ± 0.027	0.460 ± 0.296	0.181 ± 0.080	0.9996
RU	Soil	3	471 ± 169	13.3 ± 4.0	49.0 ± 15.0	0.143 ± 0.032	31683 ± 26212	695 ± 285	17.3 ± 6.4	74.7 ± 32.7	–
	Grass	3	80.3 ± 41.8	8.69 ± 0.11	2.17 ± 0.65	0.0168 ± 0.0046	2131 ± 539	66.5 ± 11.9	2.97 ± 1.18	2.09 ± 0.97	0.9997
	Bryndza	4	3.47 ± 0.24	0.753 ± 0.302	0.321 ± 0.119	0.0002 ± 0.0001	350 ± 13	0.229 ± 0.040	0.497 ± 0.005	0.173 ± 0.066	0.9998
TU	Soil	2	445 ± 6	41.0 ± 28.8	84.5 ± 40.9	0.092 ± 0.005	8800 ± 3535	2223 ± 2050	58.0 ± 47.1	112 ± 74	–
	Grass	3	24.5 ± 8.0	6.91 ± 2.00	0.612 ± 0.240	0.0074 ± 0.0014	1653 ± 328	44.5 ± 13.2	2.78 ± 1.38	1.65 ± 1.34	0.9754
	Bryndza	6	3.43 ± 0.47	0.711 ± 0.053	0.197 ± 0.060	0.0006 ± 0.0002	309 ± 49	0.266 ± 0.091	0.448 ± 0.094	0.138 ± 0.064	0.9696
TI	Soil	3	430 ± 18	15.0 ± 1.1	72.0 ± 1.0	0.063 ± 0.004	6400 ± 150	908 ± 18	25.0 ± 1.3	74.5 ± 2.7	–
	Grass	3	62.4 ± 3.1	7.75 ± 0.78	1.02 ± 0.43	0.0087 ± 0.0004	2095 ± 110	226 ± 55	2.69 ± 0.46	0.454 ± 0.263	0.9990
	Bryndza	8	3.10 ± 0.61	0.873 ± 0.113	0.264 ± 0.021	0.0002 ± 0.0001	293 ± 3	0.692 ± 0.350	0.329 ± 0.071	0.112 ± 0.074	0.9903
HS	Soil	3	385 ± 29	15.0 ± 1.7	67.3 ± 3.2	0.075 ± 0.007	3917 ± 503	940 ± 115	22.7 ± 1.5	55.3 ± 8.1	–
	Grass	3	37.8 ± 7.2	8.09 ± 0.37	1.80 ± 0.36	0.0106 ± 0.0013	1681 ± 191	129 ± 77	3.63 ± 0.54	1.34 ± 0.37	0.9860
	Bryndza	4	2.14 ± 0.29	0.686 ± 0.039	0.373 ± 0.012	0.0003 ± 0.0001	284 ± 7	0.160 ± 0.099	0.480 ± 0.043	0.066 ± 0.016	0.9713
VF	Soil	3	415 ± 19	40.0 ± 0.6	136 ± 4	0.149 ± 0.006	8633 ± 502	1492 ± 40	66.3 ± 3.8	167 ± 7.8	–
	Grass	3	44.6 ± 4.9	7.72 ± 1.29	1.34 ± 0.39	0.0070 ± 0.0008	2047 ± 254	110 ± 44	3.45 ± 0.49	2.03 ± 0.32	0.9935
	Bryndza	6	1.29 ± 0.09	0.713 ± 0.123	0.111 ± 0.085	0.0003 ± 0.0002	208 ± 13	0.060 ± 0.001	0.203 ± 0.019	0.063 ± 0.051	0.9862
JA	Soil	3	356 ± 26	163 ± 63	743 ± 159	0.926 ± 0.295	8867 ± 1767	803 ± 253	217 ± 106	74.2 ± 19.8	–
	Grass	3	47.8 ± 2.1	20.6 ± 6.5	2.27 ± 0.95	0.0364 ± 0.0183	1884 ± 108	34.8 ± 6.6	4.94 ± 0.50	0.305 ± 0.268	0.9959
	Bryndza	6	3.03 ± 0.27	0.942 ± 0.062	0.053 ± 0.006	0.0002 ± 0.0001	307 ± 18	0.060 ± 0.001	0.360 ± 0.104	0.162 ± 0.012	0.9951
ZS	Soil	3	483 ± 36	20.7 ± 1.5	50.7 ± 4.7	0.081 ± 0.026	11783 ± 5639	1130 ± 286	19.3 ± 1.5	165 ± 10	–
	Grass	3	43.9 ± 4.2	6.63 ± 1.43	0.505 ± 0.068	0.0105 ± 0.0035	1698 ± 139	50.0 ± 7.9	2.69 ± 0.36	1.83 ± 0.46	0.9979
	Bryndza	10	4.35 ± 0.77	0.698 ± 0.090	0.116 ± 0.095	0.0004 ± 0.0001	306 ± 19	0.060 ± 0.001	0.501 ± 0.159	0.205 ± 0.093	0.9957

(ČK – Červený Kameň, LM – Liptovský Mikuláš, RU – Ružomberok, TU – Turčianske Teplice, TI – Tisovec, HS – Horná Súča, VF – Veľká Franková, JA – Jaklovce, and ZS – Zvolenská Slatina).

Table 5
Correlation of elemental markers between the soils and Bryndza sheep cheese-making products (five samples of each matrix) from cheese producers Červený Kameň (ČK) and Liptovský Mikuláš (LM)

Sample	Coefficient of correlation	
	Producer (ČK)	Producer (LM)
Grass	0.9565	0.9999
Milk	0.9431	0.8246
Boiled sheep whey	0.9419	0.9887
Bryndza	0.9426	0.9995
Whey	0.9428	0.9995
Lumpy sheep cheese	0.9429	0.9996

Table 6
Correlations of elemental Bryndza cheese markers of origin

Markers	Ba	Cu	Cr	Hg	Mg	Mn	Ni	V
Ba	1							
Cu	0.5359	1						
Cr	0.4361	0.9613	1					
Hg	0.4824	0.9521	0.9544	1				
Mg	0.7799	0.3562	0.2642	0.4173	1			
Mn	0.7783	0.4706	0.3149	0.2583	0.4554	1		
Ni	0.5478	0.9742	0.9615	0.8960	0.3128	0.5472	1	
V	0.8946	0.4921	0.3847	0.3578	0.5929	0.8658	0.5517	1

follows from the averaged results obtained, the Ba, Cr, Mn, Mg, Ni and V markers were accumulated mainly in the final Bryndza and lumpy cheese, lower content was detected in the whey and boiled sheep whey (Figs. 1–3). In the case of Cu ions presence (Fig. 2), its main portion was accumulated in the boiled sheep whey, where its content was most probably affected by leaching of the copper ions from copper tub used in a traditional Bryndza cheese-making technology in the shepherds' chalets.

As follows from canonical discriminant analysis of Slovak Bryndza sheep cheese (Fig. 4), the increased concentration of elemental markers of origin as a result of technology used for Bryndza production did not negatively affect their geographical authentication. More than 90% accuracy was achieved using the classification procedure based on the canonical discriminant analysis of all Bryndza

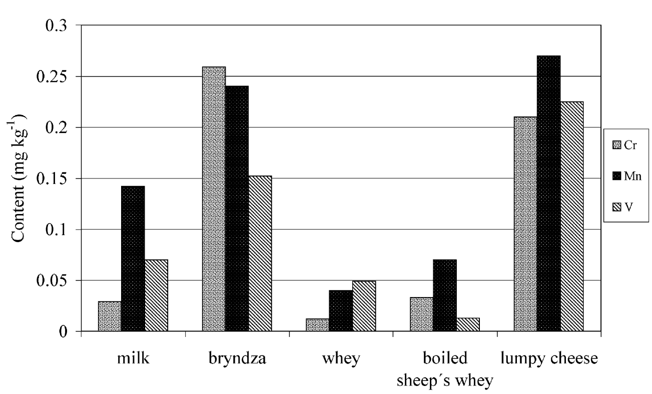

Fig. 1. Average distribution of Cr, Mn, and V in the process of Bryndza sheep cheese production. The analysed products were obtained from Červený Kameň and Liptovský Mikuláš regions.

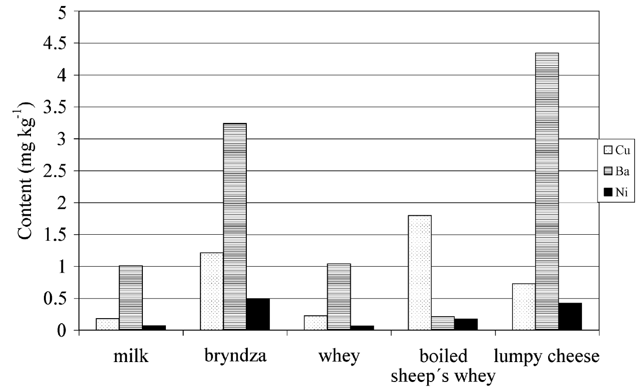

Fig. 2. Average distribution of Ba, Cu, and Ni in the process of Bryndza sheep cheese production. The analysed products were obtained from Červený Kameň and Liptovský Mikuláš regions.

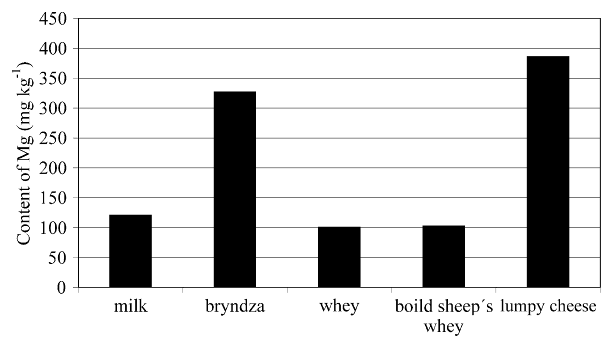

Fig. 3. Average distribution of Mg in the process of Bryndza sheep cheese production. The analysed products were obtained from Červený Kameň and Liptovský Mikuláš regions.

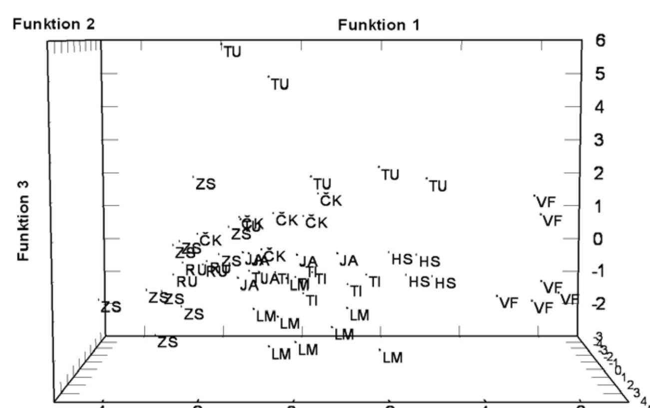

Fig. 4. Canonical discriminant analysis of Slovakian Bryndza sheep cheese (number of samples – 58; markers of origin: Ba, Cu, Cr, Hg, Mg, Mn, Ni and V; producers: ZS – Zvolenská Slatina, ČK – Červený Kameň, RU – Ružomberok, TU – Turčianske Teplice, JA – Jaklovce, LM – Liptovský Mikuláš, TI – Tisovec, HS – Horná Súča and VF – Veľká Franková).

cheese samples. Using the same approach, seven producers from nine were correctly classified. These results are of high importance, especially if the small geographical area and major geochemical similarities of Slovakia regions is taken into account. Moreover, as we previously showed, some of the markers of origin (Cr, Hg, Mn, and V) enabled the successful multiregional differentiation of Slovak Bryndza cheeses from Polish and Romanian variety (Koreňovská & Suhaj, 2007).

4. Conclusion

Significant elemental marker correlations were found between pasture soils, grasses, milk and cheese products and by-products from nine Slovak Bryndza sheep cheese producing regions. The Bryndza cheese-making process did not significantly affect the mutual markers correlations nor subsequent traceability of this typical Slovak cheese, based on the method of canonical discriminant analysis. Canonical discriminant analysis of cheeses based on Ba, Cu, Cr, Hg, Mg, Mn, Ni and V markers is a powerful tool which enables the effective and high-reliable identification of Bryndza cheese originated both from Slovak regions as well as from other Central European countries.

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