Assessment of some European goats' cheeses by multivariate elemental data comparison

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Summary

Based on statistical evaluation of the contents of 12 mineral and trace elements (Ba, Ca, Cu, Cr, Hg, K, Mg, Mn, Mo, Na, Ni and V) determined by atomic absorption spectrometry, differentiation and classification of 158 European commercial caprine hard cheeses originating from 10 countries were carried out involving the cluster, principal component, factor and discriminant analyses. Cluster analysis grouped the samples into several sub-clusters in principle corresponding well with the country or region of sample origin. Similar clustering tendency of samples was revealed also by principal component and factor analyses. The best classification of caprine cheeses according to their country of origin was achieved by K-th nearest neighbour discrimination, with 100% correctly classified samples at $K = 1$, and 87.9% correctness in cross-validation tests. When processed by canonical discriminant analysis, 87.5% recognizability and 80.4% successfulness in cross-validation tests was achieved. Results obtained indicated that caprine cheeses originating from Germany, Italy, Croatia, Spain and Portugal could be 100% correctly traced according to their country of origin on the basis of multivariate analysis of elemental markers. In this context, Cr, Mo, Mn, Hg, Ca, Na, V and Ba were recognized as the most significant elemental markers providing the highest discrimination power for caprine cheeses geographical distinguishing.

Keywords

caprine cheeses; elemental data; multivariate analysis; classification

Cheese authenticity is currently of increasing interest for the dairy sector. Caprine milk has been recommended as an ideal substitute for bovine milk, especially for those who suffer from cows' milk allergy. Goats' milk contains more calcium, phosphorus and magnesium than cows' milk [1]. Although goats' milk has been receiving increasing attention from consumers and the effects of different technological treatments on mineral content are well known [2], most of the interest in cows' milk is focused on cheesemaking. Individual cheeses have distinct characteristics and enhanced quality, and are defined according to their geographical area of production. The legislation restrictions and the demands on manufacturers and producers to be capable to demonstrate traceability along the food chain, together with raised consumers' awareness in food products, has focused the renewed interest in food authenticity determination problems [3, 4].

In this context, the ability to determine unambiguously the geographical origin of milk products is a logical consequence, and is currently of major concern for researchers, industries and policymakers [5].

In the recent years, an increased interest in the development of reliable methods for determination of geographical origin of agricultural products has been noticed. As one of the most promising methods, trace element analysis is used for this purpose. A number of recently published papers deal with the use of naturally abundant isotopes variation and elemental concentrations as geographic tracers to determine the provenance of food [6–18]. Results obtained from the geographical characterization of mozzarella cheeses originating from two areas of Southern Italy proved that $^{13}C/^{12}C$ and $^{15}N/^{14}N$ isotopic ratios as well as NMR data enabled the successful discrimination of mozzarella samples [7]. Pillonel et al. analysed stable isotope ratios as well as specific elements contents in twenty Emmental cheeses from six European regions [8, 9]. Based on Mo and Na concentrations, the groups of "Swiss", "Vorarlberg" and "Allgäu" cheeses were separated. Multiple-collector inductively coupled plasma mass spec-

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trometry was used for the determination of variations in the $^{87}Sr/^{86}Sr$ isotope abundance ratios, in order to classify Emmental-type cheeses from Alps, Bretagne, Finland, Canada and Australia according to their origin [10]. For the authentication of French and Swiss Emmental cheeses, Na, Zn, Mg and ratios of some stable isotopes, were successfully applied, while the differentiation of Italian ewes' and cows' cheeses was based on the monitoring of Li, K, Mn, Se, Rb and Cs elemental markers presence [11]. The contents of Ca, P, K, Mg, Mn, Zn, Cu and Fe were analysed in 42 mature cheeses made from raw ewes' milk in different Mediterranean areas and used for their geographical indication [12]. From the elements analysed, Al, Ca, Mg, Mn, Fe, Co, Sr, Mo and some rare earth ones were found to be the most characteristic markers for this purpose.

Processing of analytical data by multivariate statistics represents a method of choice for the discrimination of cheeses according to their geographical origin, but also according to their varieties or their quality. It has found application even in the cheese maturation control. Pillonel et al. used discriminant analysis for the geographical classification of European Emmental cheeses and, after optimization, their statistical calculation models achieved 100% correct classification and discrimination [13].

Other methods with a potential application in analytical traceability (e.g., multi-isotopic, spectroscopic, molecular biological) coupled with chemometric tools allowing the authentication of cheeses and other food products, were reviewed [6, 14–18].

As follows from the presented overview, the specific elements analysis was previously successfully used for geographical tracing of cows‘ or ewes‘ cheeses. However, there is still a lack of information on the geographic origin authentification of goats‘ cheeses, since few papers containing chemo-metric data were published [19–24]. The geographical recognition and prediction of selected commercial European goats' cheeses performed by multivariate statistics of elemental data are presented in this article to fill in this gap.

MATERIALS AND METHODS

Samples

A set of 158 samples of selected European commercial goats' hard cheeses originating from 10 countries (Slovakia, 38; Germany, 6; Italy, 6; Austria, 18; Czech Republic, 28; France, 22; The Netherlands, 24; Croatia, 6; Spain, 6 and Portugal, 4) was obtained from the retail network in 2007 and 2008. The declared dry matter contents in majority of European cheeses varied from 42% to 48% with the exception of higher contents in some samples from France (58%), Portugal (60%) and Italy (65%). Fat contents varied from 42% to 50% with the exception of 12 Czech samples where the fat content was about 18%. All the samples were analysed for the contents of twelve elemental markers, i.e., Ba, Ca, Cu, Cr, Hg, K, Mg, Mn, Mo, Na, Ni and V. The geographical origin of the cheeses was declared on the labels. Markers' selection was based on our previous experience with authentication of European cows' and ewes' hard cheeses, and partially on the distribution of mineral and trace elements in the European topsoil [25–30].

Digestion of cheeses

Each sample of cheese (0.5 g) was digested with 4 ml of 65% HNO_3 and 0.5 ml H_2O_2 in Milestone MLS 1200 MEGA (Sorisole, Italy) microwave digestion system using the following digestion programme: 250 W (1 min), 0 W (1 min), 250 W (5 min), 400 W (5 min), and 650 W (5 min). The digested samples were adjusted to 10 ml volume with ultra-pure water and used for further analysis.

Atomic absorption spectrometry (AAS) conditions

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. Metals Ca, K, Mg, Mn, Na were determined from atomic spectrometry using an air/acetylene flame. Metals Ba, Cr, Cu, Mo, Ni and V were detected on graphite tube atomizer. Results were expressed as the average of triplicate measurements. Further instrumental conditions and analytical and validation parameters of the used methods were previously described [26–29].

Statistics

From multidimensional pattern recognition techniques, the cluster analysis (CA), principal component analysis (PCA), factor analysis (FA) and canonical discriminant analysis (CDA) were used. The methods are designed in a way that enables the enhancement of hidden properties of the original data and allows the reduction of multi-dimensional data set to only a few dimensions, which can sufficiently explain all the original data. Two parameters are of crucial importance in CDA – the recognition ability (determined as the percentage of correctly classified samples in the

Tab. 1. Comparison of marker element contents in goats' cheeses of different origin (samples were collected in 2007 and 2008).

Marker	Value [mg·kg^{-1}]	Country of origin									
		S (*n* = 38)	G (*n* = 6)	I (*n* = 6)	A (*n* = 18)	C (*n* = 28)	F (*n* = 22)	N (*n* = 24)	CR (*n* = 6)	E (*n* = 6)	P (*n* = 4)
Ba	Mean	3.209	3.02	4.87	2.274	4.126	0.871	2.452	1.59	0.435	0.340
	s_x	1.046	0.88	0.383	0.591	1.234	0.429	0.763	0.144	0.163	0.049
	Median	2.870	3.48	4.74	2.460	4.025	0.782	2.190	1.63	0.386	0.344
	x_{min}	1.880	1.88	4.46	1.220	2.200	0.404	1.670	1.38	0.306	0.284
	x_{max}	6.020	3.79	5.40	2.940	6.640	1.91	4.970	1.74	0.753	0.387
Cr	Mean	0.202	0.031	0.053	0.184	0.194	0.076	0.150	0.052	0.043	0.095
	s_x	0.164	0.008	0.007	0.166	0.138	0.057	0.170	0.019	0.011	0.017
	Median	0.217	0.031	0.055	0.064	0.284	0.055	0.053	0.055	0.039	0.097
	x_{min}	0.006	0.019	0.043	0.028	0.010	0.020	0.006	0.034	0.030	0.072
	x_{max}	0.630	0.042	0.061	0.473	0.359	0.229	0.539	0.074	0.059	0.112
Cu	Mean	0,983	1.20	1.01	0.655	0.788	1.91	1.202	0.795	1.10	0.878
	s_x	0.610	0.178	0.223	0.310	0.377	1.13	0.296	0.092	0.205	0.106
	Median	0.865	1.20	0.940	0.682	0.654	1.82	1.132	0.792	1.05	0.876
	x_{min}	0.300	0.957	0.823	0.155	0.390	0.582	0.813	0.683	0.919	0.767
	x_{max}	3.270	1.44	1.43	1.280	1.680	4.93	2.05	0.957	1.43	0.995
Hg	Mean	0.0150	0.0350	0.0098	0.0077	0.0159	0.0326	0.0254	0.0041	0.0028	0.0033
	s_x	0.0119	0.0047	0.0045	0.0039	0.0138	0.0047	0.0113	0.0014	0.0021	0.0011
	Median	0.0107	0.0347	0.0114	0.0063	0.0107	0.0314	0.0292	0.0042	0.0021	0.0033
	x_{min}	0.0011	0.0298	0.0009	0.0018	0.0001	0.0267	0.0026	0.0023	0.0011	0.0022
	x_{max}	0.0342	0.0422	0.0130	0.0164	0.0387	0.0441	0.0418	0.0057	0.0067	0.0043
Mo	Mean	0.0418	0.069	0.099	0.026	0.0381	0.017	0.036	0.060	0.026	0.019
	s_x	0.0147	0.016	0.022	0.017	0.0284	0.012	0.023	0.016	0.005	0.005
	Median	0.0425	0.066	0.096	0.021	0.0295	0.017	0.030	0.065	0.025	0.018
	x_{min}	0.0130	0.055	0.078	0.009	0.0100	0.005	0.014	0.039	0.019	0.014
	x_{max}	0.0720	0.078	0.141	0.066	0.0990	0.051	0.091	0.076	0.034	0.026
Mn	Mean	0.3412	0.430	0.421	0.401	0.655	0.468	0.395	0.041	0.965	0.366
	s_x	0.2313	0.257	0.043	0.259	0.246	0.185	0.173	0.002	0.337	0.057
	Median	0.2420	0.334	0.421	0.316	0.639	0.498	0.342	0.040	0.807	0.361
	x_{min}	0.0420	0.206	0.364	0.072	0.155	0.197	0.215	0.040	0.661	0.309
	x_{max}	0.9660	0.857	0.473	0.853	1.177	0.854	0.739	0.045	1.42	0.432
Ni	Mean	0.1359	0.208	0.272	0.187	0.184	0.182	0.199	0.175	0.188	0.120
	s_x	0.0849	0.181	0.085	0.079	0.141	0.089	0.142	0.094	0.072	0.021
	Median	0.1120	0.107	0.249	0.192	0.148	0.171	0.149	0.141	0.158	0.096
	x_{min}	0.0320	0.077	0.167	0.043	0.034	0.072	0.027	0.084	0.128	0.081
	x_{max}	0.3680	0.474	0.395	0.321	0.538	0.324	0.549	0.296	0.280	0.126
V	Mean	0.0775	0.097	0.258	0.070	0.065	0.050	0.123	0.040	0.038	0.026
	s_x	0.0399	0.027	0.068	0.037	0.035	0.027	0.059	0.017	0.020	0.015
	Median	0.0805	0.097	0.269	0.064	0.062	0.055	0.120	0.044	0.035	0.022
	x_{min}	0.006	0.065	0.157	0.014	0.013	0.006	0.013	0.017	0.014	0.012
	x_{max}	0.202	0.145	0.352	0.132	0.130	0.091	0.272	0.059	0.064	0.046

Tab. 1. *continued*

Marker	Value [mg·kg^{-1}]	Country of origin									
		S ($n = 38$)	G ($n = 6$)	I ($n = 6$)	A ($n = 18$)	C ($n = 28$)	F ($n = 22$)	N ($n = 24$)	CR ($n = 6$)	E ($n = 6$)	P ($n = 4$)
Ca	Mean	5794	7476	6673	4259	5010	2642	6079	2003	1215	1091
	s_x	863	1366	213	2218	1340	1161	558	88	89	44
	Median	5641	7937	6587	4921	5333	2134	6113	1973	1195	1096
	X_{min}	4529	5721	6516	1785	1458	1606	5112	1912	1089	1042
	X_{max}	8021	9027	7063	7613	6747	5158	6949	2110	1333	1130
K	Mean	1320	832	1437	1146	1373	1199	923	1008	1084	949
	s_x	436	36	71	447	412	224	152	42	97	106
	Median	1238	838	1443	848	1213	1233	932	1044	1079	967
	X_{min}	797	787	1308	673	923	839	665	956	965	809
	X_{max}	3084	879	1504	1934	2505	1665	1267	1058	1204	1052
Mg	Mean	486	621	596	396.6	479	334	561	199	143	154
	s_x	84.2	33	18	127.5	95.6	111	78	22	19	15
	Median	491	623	589	466	463	317	563	202	136	154
	X_{min}	314	582	577	202	293	183	398	168	126	140
	X_{max}	621	653	621	588	638	562	679	223	168	167
Na	Mean	2826	4712	4441	4070	3775	4778	4968	4252	4286	4230
	s_x	990	345	129	588	927	529	500	123	151	137
	Median	3040	4641	4491	4090	3920	4622	5099	4204	4284	4274
	X_{min}	1014	4350	4279	3351	1963	3986	3424	4132	4116	4036
	X_{max}	4524	5166	4598	5027	5081	5804	5566	4408	4536	4336

n – number of samples, s_x – standard deviation, X_{min} – minimum content, X_{max} – maximum content.
S – Slovakia, G – Germany, I – Italy, A – Austria, C – Czech Republic, F – France, N – the Netherlands, CR – Croatia, E – Spain, P – Portugal.

training data set in which all the samples were of known properties for classification model) and the prediction ability (tested as the percentage of the samples correctly classified in the *K*-fold cross-validation (jack-knife) method or internal cross-validation) [18]. Statistical calculations were performed by means of the statistical software Unistat v. 5.6 (Unistat, London, United Kingdom).

RESULTS AND DISCUSSION

The concentration ranges of selected mineral and trace elements (Ba, Ca, Cu, Cr, Hg, K, Mg, Mn, Mo, Na, Ni and V) in goats' cheeses under study as well as the basic statistics providing the information about the element average content, standard deviation, median, as well as minimal and maximal concentration are presented in Tab. 1. These elements were subsequently used as markers for geographical authentification. Obtained data were in good agreement with those published previously [20–22], with the exception of a study in which the marker concentrations of goats' cheeses manufactured in USA are listed [19]. The last mentioned results indicated higher contents of Ca, Na, Cu, Mn and a lower content of K, in comparison to our samples. Furthermore, AAS results proved the presence of chromium at levels of 0.5 mg·kg^{-1} in several samples from Slovakia and the Netherlands. However, as an older EU hygienic limit for dairy products is not in force nowadays and the new one was not issued, this fact was out of our concern. In addition, the higher mercury contents of above 0.02 mg·kg^{-1} were detected in goats' cheeses from Germany, France and the Netherlands and in some samples from Czech Republic and Slovakia. The highest concentration of Ca was determined in German samples, while in Slovakian the content of K, in Dutch Mg,

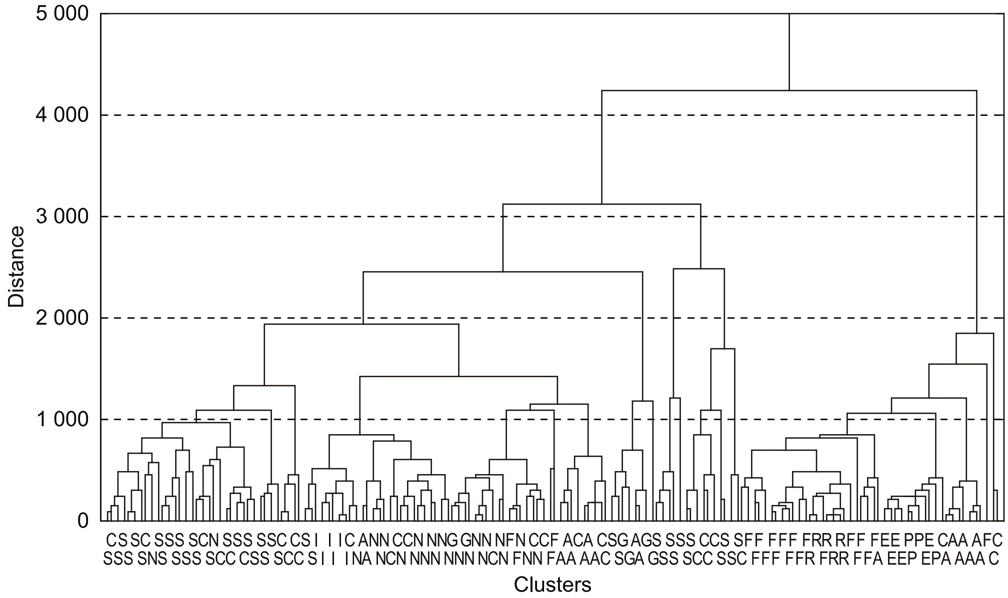

Fig. 1. Dendrogram: the similarity relationships among goats' cheeses.

Hierarchical cluster analysis with Euclidean distance measure and method of average between groups.
Country of origin: S – Slovakia, G – Germany, I – Italy, A – Austria, C – Czech Republic, F – France, N – the Netherlands, R – Croatia, E – Spain, P – Portugal. Markers of origin: Ba, Ca, Cu, Cr, Hg, K, Mg, Mn, Mo, Na, Ni and V.

Ni and V, in French Na and Cu, in Spanish Ba and Mn, and in Italian goats' cheeses Mo content were the highest. The study of the correlation between individual elemental markers in cheese samples showed only one strong correlation (r = 0.8358) between Mg and Ca and a moderate correlation between Ca and Ba (r = 0.6400). These results indicate possible effective utilization of selected markers for the purpose of recognition and prediction of the geographical origin of cheeses by mul-

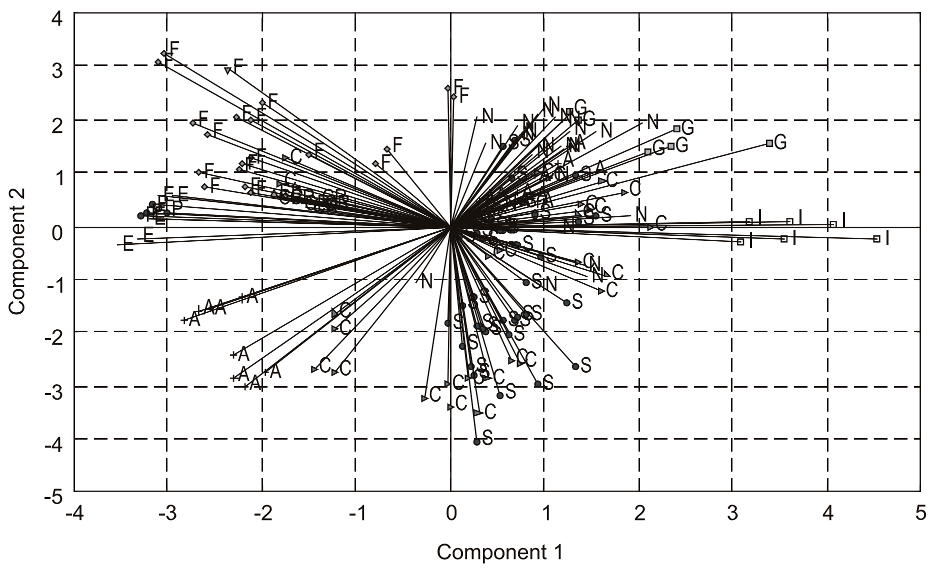

Fig. 2. Differentiation of European goats' cheeses by the principal component analysis.

Score plot on the first two principal components.
Country of origin: S – Slovakia, G – Germany, I – Italy, A – Austria, C – Czech Republic, F – France, N – the Netherlands, CR – Croatia, E – Spain, P – Portugal. Markers of origin: Ba, Ca, Cu, Cr, Hg, K, Mg, Mn, Mo, Na, Ni and V.

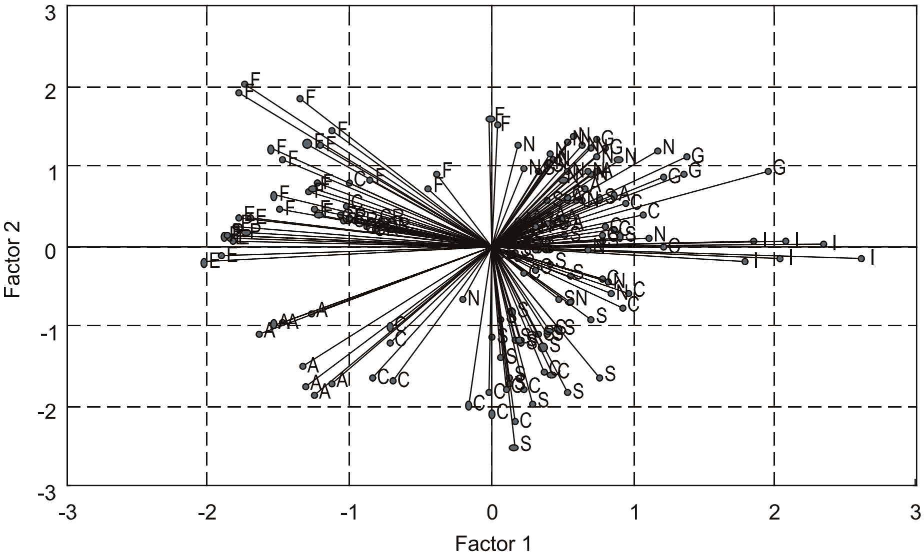

Fig. 3. Differentiation of European goats' cheeses by factor analysis with Varimax rotation.

Plot of factor scores on the first two factors.
Country of origin: S – Slovakia, G – Germany, I – Italy, A – Austria, C – Czech Republic, F – France, N – the Netherlands, CR – Croatia, E – Spain, P – Portugal. Markers of origin: Ba, Ca, Cu, Cr, Hg, K, Mg, Mn, Mo, Na, Ni and V.

tivariate statistics. The found correlations between Ca, Mg and Ba are well known, being associated with the soil geochemical composition.

Cluster analysis (CA) was applied to study the clustering tendency of elemental markers' data. As depicted in the dendrogram (Fig. 1), the samples of goats' cheeses on the top (at a distance of ~ 4100) are divided into two main clusters, which were gradually subdivided to several sub-clusters. At a distance of about 800–1000, the clusters in principle correspond to the countries of cheese samples origin. In this context, some overlap of clusters corresponds well with expected similarities in composition of cheese samples among countries, significant especially for the neighbouring ones.

As follows from the results of principal component analysis, three principal components with eigenvalues greater than 1 explain cumulatively more than 57.8% of the total variance. The first principal component is related to Ca and Mg contents, the second component is negatively associated with Cr and K concentrations, and the third principal component is related mostly to Mn content. As presented in the score plot of the first two principal components (Fig. 2), all goats' cheeses were separated into several PCA clusters. Italian (I) and French (F) samples were well separated from the rest, forming two isolated clusters; the next cluster was common for Spanish (E) and Portuguese (P) samples. The remaining cluster is the mix of Slovakian (S), Czech (C), German (G) and Dutch (N) cheese samples. Similar results were obtained also by factor analysis of marker data with Varimax rotation (Fig. 3). Factors analysis of transposition data matrix expressed by plot of factors (Fig. 4) corresponds well with the plot of factor score depicted in Fig. 3. The comparison of these two plots enables to visualize and compare how the used variables or their combination contribute to the differentiation procedure. As an illustration, for Italian cheeses differentiation, Mg and Ca markers play a significant role.

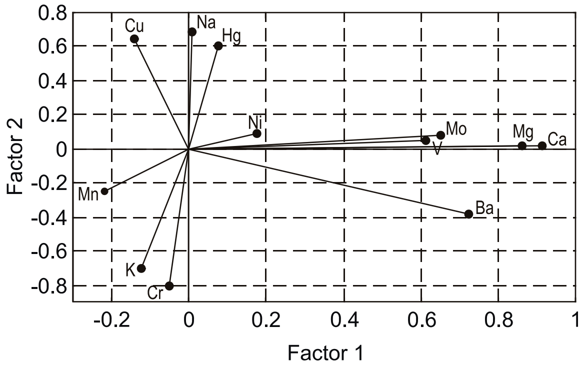

Fig. 4. Factor analysis applied on European goats' cheeses geo-reference markers.

Geo-reference markers: Ba, Ca, Cu, Cr, Hg, K, Mg, Mn, Mo, Na, Ni and V (plot of factors with Varimax rotation).

Tab. 2. Stepwise discriminant analysis of European goats' cheeses.

Variables selected	Entered at Step	*F*-to-Enter	Significance *p*-value	Wilk's Lambda
Ba	1	35.0670	0.0000	0.3192
V	2	21.1578	0.0000	0.1391
Na	3	17.3970	0.0000	0.0671
Ca	4	15.7491	0.0000	0.0339
Hg	5	12.4554	0.0000	0.0191
Mn	6	10.2884	0.0000	0.0116
Mo	7	8.3647	0.0000	0.0076
Cr	8	5.9243	0.0000	0.0055

Variables used as markers: Ba, Ca, Cr, Cu, Hg, K, Mg, Mn, Mo, Na, Ni, V. Stepwise selection criteria: tolerance = 0.001; *F*-to-Enter = 3.8416 (5.0%); *F*-to-Remove = 2.7056 (10.0%).

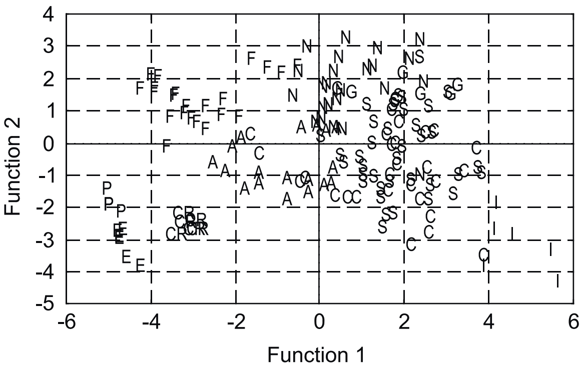

Fig. 5. Plot of discriminant score showing the first two discriminant functions obtained from canonical discriminant analysis of goats' cheeses marker data.

Country of origin: S – Slovakia, G – Germany, I – Italy, A – Austria, C – Czech Republic, F – France, N – the Netherlands, CR – Croatia, E – Spain, P – Portugal.

Three different approaches of discriminant analysis, i.e. the stepwise, *K*-th neighbour and canonical discriminant analysis, were further used for the purpose of cheese differentiation. The stepwise forward discriminant analysis was used to select the most relevant variables for classification. As follows from data (Tab. 2), eight of 12 analysed markers revealed a very high significance ($p < 0.001$) for cheeses sample differentiation. When considering the Wilks' Lambda values, these elements could be ordered as follows: Cr < < Mo < Mn < Hg < Ca < Na < V < Ba. This order corresponded well with the decreasing influence of individual elements on the discrimination procedure.

Results presented in Tab. 3 indicated that nine discrimination functions were obtained from canonical discriminant analysis, but only the first four ones enabled the significant discrimination (eigenvalues > 1, Wilk's lambda ~ 0, Chi-square test significance, $p < 0.0001$) and explained 90.2% of cumulative variance. Taking into account the coefficients of canonical discriminant functions (data not presented), the most significant contribution to discrimination in the first function was obtained from Ba, Ca and V (in a decreasing order of importance). Markers Cr, Hg, and Ca enhanced the discrimination power of the second function, and V, Na and Ca were valuable in the third one. All these markers were selected as the most important variables at the above-mentioned stepwise discrimination. The discriminant score of the first two discriminant functions obtained from canonical discriminant analysis is depicted in Fig. 5, showing the strong clustering tendency of goats' cheese samples according to the country of origin. Although the differences among goats' cheeses are not perfectly visualized using a 2D

Tab. 3. Canonical discriminant analysis of markers' data used for geographical differentiation of European goats' cheeses.

Discrim. function	Eigen-value	Percent	Cumulative	Correlation	Wilk's Lambda	Chi-Square	Degree of freedom	Significance *p*-value
1	5.7137	48.3%	48.3%	0.9225	0.0032	838.7	108	< 0.0001
2	2.2300	18.8%	67.1%	0.8309	0.0215	560.7	88	< 0.0001
3	1.7102	14.4%	81.5%	0.7944	0.0694	389.5	70	< 0.0001
4	1.0223	8.6%	90.2%	0.7110	0.1880	243.9	54	< 0.0001
5	0.6166	5.2%	95.4%	0.6176	0.3802	141.2	40	< 0.0001
6	0.3339	2.8%	98.2%	0.5003	0.6147	71.04	28	< 0.0001
7	0.1896	1.6%	99.8%	0.3992	0.8199	28.99	18	0.0486
8	0.0193	0.2%	100.0%	0.1377	0.9754	3.643	10	0.9620
9	0.0058	0.0%	100.0%	0.0762	0.9942	0.850	4	0.9316

projection, the CDA procedure possessed high scores with 87.5% of correctly classified samples at recognition ability testing (Tab. 4).

The recognition ability of the classification model at *K*-th nearest neighbour and canonical discriminant statistics was evaluated on the training data set, in which the identity of the samples was known. Afterwards, the prediction ability was tested in a jack-knife cross-validation test, in which one third of samples at a time was removed from the training data set and considered as a test set of samples with unknown attributes. The classification was repeated 3 times, so that all samples were used both in training and test positions. The averaged classification results are listed in Tab. 4. Data presented indicate that *K*-th nearest neighbour approach ($2 \leq K \leq 5$) resulted in more than 80% correct classification in the recognition ability tests. On the other hand, jack-knife test revealed the decreased classification score within the above mentioned interval of *K*. The best classification results were obtained for $K = 1$ (100% recognition and 87.9% prediction ability). The results of canonical classification summarized in Tab. 5 led to a similar conclusion as with neighbour classification at $K = 2$. Classification matrix obtained from recognition data set showed that goats' cheeses originating from Germany, Italy, Croatia, Spain and Portugal were 100% correctly classified (Tab. 5). The same results for cheeses from these countries were obtained also in the prediction ability tests. Successful differentiation was most likely related to the increased contents of dry matter in some cheeses (Italy, Portugal). For the rest of samples under study, some misclassifications were obtained (e.g., some Slovak cheeses were incorrectly recognized as Czech, Czech as French, and Austrian and Dutch as the Slovak ones). These classification errors could be attributed mostly to the small number of samples and/or to geochemical similarities between some neighbouring countries. Considering all the statistical results, the last mentioned explanation is more acceptable. Nevertheless, according to classification successfulness, the prediction ability of examined discriminant classification model was relatively high. In addition, results obtained unambiguously demonstrated that all the chosen elemental markers processed by canonical discriminant analysis meaningfully contributed to the classification efficacy, without respect to their concentration ranges. At the evaluation of the

Tab. 4. Comparison of goats' cheeses classification successfulness by K-th neighbour and canonical discrimination.

Classification method	Correctly classified [%]	
	(recognition ability)	(prediction ability - cross validation)
K-th neighbour discriminant analysis		
K = 1	100	87.9
K = 2	87.9	78.5
K = 3	86.1	76.6
K = 4	84.2	74.1
K = 5	81.0	73.5
Canonical discriminant analysis		
	87.5	80.4

Variables used: Ba, Ca, Cr, Cu, Hg, K, Mg, Mn, Mo, Na, Ni, V.

Tab. 5. Canonical discrimination and classification matrix of goats' cheeses according to the country of origin (in %).

	S	G	I	A	C	F	N	CR	E	P
S	73.68	2.63	0.00	7.89	15.79	0.00	0.00	0.00	0.00	0.00
G	0.00	100	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
I	0.00	0.00	100	0.00	0.00	0.00	0.00	0.00	0.00	0.00
A	0.00	0.00	0.00	94.44	0.00	0.00	5.56	0.00	0.00	0.00
C	14.29	3.57	0.00	7.14	67.86	7.14	0.00	0.00	0.00	0.00
F	0.00	4.55	0.00	0.00	0.00	90.91	4.55	0.00	0.00	0.00
N	8.33	4.17	0.00	0.00	0.00	0.00	87.50	0.00	0.00	0.00
CR	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100	0.00	0.00
E	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100	0.00
P	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	100

S – Slovakia, G – Germany, I – Italy, A – Austria, C – Czech republic, F – France, N – the Netherlands, CR – Croatia, E – Spain, P – Portugal.

effectiveness of individual markers, it should be taken into account that some of them may be affected by manufacturing process, for example Ca, Na, and Cu (Ca – an additive supplement, Na – cheese salting, Cu – copper vat in many traditional cheese factories). In the case when these elements were excluded from the discrimination data step by step, recognition ability of the discrimination classification worsened only by 3–8%. The rest of the used elemental markers of geographical origin were sufficient for the statistically significant differentiation of goats' cheeses (above 80% of correctly classified samples by CDA).

The effect of fat content on the differentiation was evaluated in the case of Czech samples. When 12 semi-hard samples with a low fat content (18%) were excluded from the data set consisting of cheeses with fat contents of 42–50%, the group classification of Czech samples was improved by 20%. Total classification of the European samples according to country of origin was practically unchanged and resulted in more than 80% of correctly classified cheeses in CDA recognition ability test.

CONCLUSION

This preliminary study demonstrated that multivariate analysis applied to an elemental data set is capable of extracting information that is useful for classifying European goats' cheeses according to their geographical origin. The most discriminating variables were Cr, Mo, Mn, Hg, Ca, Na, V and Ba concentrations. The results obtained may be considered a good starting point for extending this study by other types of discriminators, such as isotopes, for the enhancement of the efficacy and successfulness of geographical authentication of goats' cheeses.

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