Chemometric study of the contents of minerals and risk elements in some European hard cheeses

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Summary
Emmental and Edam cheeses originating from ten European countries were analysed regarding the contents of some minerals (Ca, Cu, K, Mg, Na) and risk elements (Cr, Hg, Mn, Mo, Ni, V) by atomic absorption spectrometry during two years of the production. The highest contents from the minerals were found for Ca (10 750 $mg.kg^{-1}$) and for Cu (8.96 $mg.kg^{-1}$) in Italian hard cheese samples, for K in Austrian hard cheese samples (2 588 $mg.kg^{-1}$), for Mg in German hard cheese samples (715 $mg.kg^{-1}$) and for Na in Czech hard cheese samples (10 225 $mg.kg^{-1}$). The highest contents of inorganic trace elements Ba, Cr and Mn were observed in Slovakian hard cheeses, Hg in German hard cheeses, Mo in Austrian hard cheeses, Ni in Dutch hard cheeses and V in French hard cheeses. The highest correlations were found between the following elements: Ca – Mg (r = 0.822), Cu – Ni (r = 0.787) and K – Mo (r = 0.753). Similarities in the mineral composition of cheeses produced in European countries were visualised by principal component analysis. The Ca contents in the examined cheeses that were lower than some archived data confirmed the trend of the depletion of some minerals observed recently in some food commodities.

Keywords
mineral; risk elements; Emmental; Edam; cheese; chemometry

Inorganic or aggregated forms of chemical substances in food represent a severe risk for their long-term toxicological effects. Appreciation of qualified national products, together with a guaranteed reference for consumers, has become necessary in the field of dairy products such as cheeses. Cheeses are a good source of several minerals, although the amounts of specific minerals in different cheese types vary according to manufacturing procedures, environmental conditions, and the possible contamination during several steps of their production. Generally, cheeses that are high in Ca contain other minerals, such as Mg, in appreciable amounts.

Trace elements in cheese have been determined mainly for descriptive purposes [1–3]. Minerals Na, K, Mg, Ca and trace elements Co, Cr, Fe, Rb, Se, Zn were determined in some dairy products in order to evaluate the contribution of this food group to the quality of the Italian diet. The results obtained confirmed the importance of cheese in the Italian diet to satisfy the recommended daily intake of Ca, while suggesting that special attention should be exerted in the choice of cheeses with low contents of Na in order to minimize the possible negative effects on blood pressure [2].

Samples of milk, curd, whey, cheese after moulding, cheese after salting, commercial cheese (Pecorino), ricotta, scotta and brine were analysed for contents of Al, Ba, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Pt, Sr and Zn for seven complete cycles of cheese production. Samples of curd, whey, brine and waste product (i.e. scotta) were collected and analysed in addition to the cheese and milk to assess the distribution of each element in the main product, by-products and waste products during cheesemaking. The results indicated no toxicological risk and showed that, on the contrary, Pecorino may be a good source of several essential elements [4].

Pb, Cd, Fe, Cu and Zn contents of Kasar cheese sold in the markets of Ankara, Turkey, were determined over 12 months. A total of 240 samples comprising 10 different brands were analysed. The mean (range) of Pb, Cd, Fe, Cu and Zn contents were 86 (10–421) $\mu g.kg^{-1}$, 1.8 (0.3–8.3) $\mu g.kg^{-1}$, 4.2 (1.0–14.1) $mg.kg^{-1}$, 0.7 (0.3–1.6) $mg.kg^{-1}$ and

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37.7 (26.5–63.0) $mg.kg^{-1}$, respectively. It was concluded that Kasar cheese is not a significant contributor to the intake of investigated heavy metals [5].

The results obtained from the assessment of the contents of selected trace elements such as Al, Ba, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Pt, Sr and Zn in raw cow's milk and cheese showed considerable differences among the levels of trace elements in raw milk samples collected during different periods of the same year. Furthermore, differences occurred also among the trace element contents of raw milk and related products. All this provided evidence that animal feeding, year period of sample collection, environmental conditions and manufacturing process all played a role in the distribution of trace elements [6, 7].

The results for Pb, Cd and Cr in Danish milk and milk products were in the parts per billion or parts per trillion range and compared well with literature data. The intake of Pb, Cd and Cr from milk and milk products was less than 4% of the total Danish dietary intake of these elements. It was concluded that the contribution from milk and milk products to the total intake of Pb and Cd was toxicologically insignificant and that milk and milk products were only a minor source of the essential element Cr [8].

Concentrations of Fe, Mn, Zn, Cu, Pb, Cr, Ni, Na, K, Ca and Mg in cheese samples were analysed using flame and graphite furnace atomic absorption spectrometry after microwave digestion [9]. The order of levels of the elements in the samples was determined to be Na > Ca > K > Mg > Zn > Fe > Pb > Mn > Cr > Ni. The concentration ranges in the samples were found to be 4.1–12.5, 0.28–1.1, 8.8–13.2, 0.10–0.27, 0.14–1.2, 0.02–0.62, 0.18–0.34, 3957–6558, 305–362, 3473–4556 and 28.9–127 $mg.kg^{-1}$ Fe, Mn, Zn, Cu, Pb, Cr, Ni, Na, K, Ca and Mg, respectively [9].

Some analytical aspects of sample preparation and mineralization were investigated to determine the concentration of Ca, Cr, Cu, Fe, K, Mg, Mn, Na, P and Zn in dairy products by inductively coupled plasma optical emission spectrometry (ICP OES) technique. A comparison of the results obtained from this methodology was carried out with the other results from dry ashing digestion and instrumental neutron activation analysis (INAA) technique that do not require pre-treatment procedure [10].

Almost no information is available about the contents of minerals and risk elements in European Emmental or Edam hard cheeses. Twenty Emmental cheeses from six European regions (Allgäu, Bretagne, Finland, Savoie, Switzerland and Vorarlberg) were analysed for stable isotope ratios, as well as for contents of major elements (Ca, Mg, Na, K) and trace elements (Cu, Mn, Mo, I) [11].

Commission Regulation (EC) No 1881/2006 of 19 december 2006 did not yet establish the specific maximum levels for above mentioned elements in cheeses [12]. The older FAO/WHO Codex Alimentarius standards recommended the authorized addition of $CaCl_2$ to milk for Emmental and Edam cheese production at a level of 200 $mg.kg^{-1}$ [13, 14]. Ca minimal level according to Codex Standard for Emmental cheese should be 8 000 $mg.kg^{-1}$ and addition of $CuSO_4$ at a level resulting in maximally 15 mg of Cu per kg of cheese [13]. New maximum and guideline levels for contaminants in foods should be developed after the finalization of the FAO/WHO Codex Alimentarius food category system.

The present work reports the data on the contents of some minerals (Ca, Cu, K, Mg, Na) and risk elements (Ba, Cr, Hg, Mn, Mo, Ni and V) in 278 Emmental and Edam hard cheeses originating from 10 European countries, produced in 2006 and 2007. The data obtained were compared to those available in the literature and to the archive data with the aim to confirm the hypothetical trends of the decrease of some minerals and their depletion in some food commodities [15, 16]. Results were obtained in frames of the study on geographical authentication of European hard cheeses based upon elemental markers.

MATERIAL AND METHODS

Samples

A number of 192 samples of European Emmental and Edam hard cheeses (Slovakia – 80, Germany – 20, Italy – 6, Austria – 20, Hungary – 14, Czech Republic – 8, Poland – 18, United Kingdom – 6, France – 8, and Netherlands – 12) was obtained from the retail network and analysed in 2006. In 2007, similarly 86 samples (Slovakia – 14, Germany – 10, Italy – 6, Austria – 10, Hungary – 8, Czech Republic – 8, Poland – 10, United Kingdom – 6, France – 4, and Netherlands – 10) were analysed. All samples were analysed for the contents of minerals (Ca, Cu, K, Mg, Na) and risk elements (Ba, Cr, Hg, Mn, Mo, Ni, V).

Reagents

All chemicals were of analytical grade. Stock solutions of each metal Ba, Ca, Cr, Cu, Hg, K, Mg, Mn, Mo, Na, Ni, and V at a concentration of 1.00 $g.dm^{-3}$ were from Merck (Darmstadt, Germany). Working standard solutions were prepared by suitable dilution of stock solutions. Nitric acid of suprapure quality was purchased from Merck. CsCl 99% as ionic suppressor was obtained from Serva (Heidelberg, Germany) and $LaCl_3$ 5% as ionic suppressor was delivered from Slovak Institute of Metrology (Bratislava, Slovakia). Ultra pure water from Milli-Q system (Analyst HP, Wolf, United Kingdom) with a conductivity of 18 MΩ was used for the preparation of solutions.

Atomic absorption spectrometry

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 involving atomic absorption spectrometry (AAS). Metals Ca, K, Mg, Mn, Na were determined by AAS using an air/acetylene flame. Metals Ba, Cr, Cu, Mo, Ni and V were measured on graphite tube atomizer. All results were expressed as the average of triplicate measurements. The instrumental conditions for the determination are shown in Tab. 1 and validation parameters for the determination of elements in samples are shown in Tab. 2. The accuracy of the results was verified by the standard addition method, because certified reference materials for

Tab. 1. Instrumental conditions for determination of some elements by AAS.

Element	Wavelength [nm]	Lamp current [mA]	Technique by AAS	Gas	Signal type	Suppressor modifier
Ba	553.6	25	GF	Argon	AA	No
Ca	422.7	15	Flame	C_2H_2 – air	AA	0.1% $LaCl_3$
Cr	357.9	25	GF	Argon	AA-BG	No
Cu	324.8	15	GF	Argon	AA.-BG	No
K	769.9	15	Flame	C_2H_2 – air	AA	0.5% CsCl
Mn	279.5	20	Flame	C_2H_2 – air	AA	No
Mg	285.2	15	Flame	C_2H_2 – air	AA-BG	0.1% $LaCl_3$
Mo	313.3	20	GF	Argon	AA-BG	No
Na	589.0	15	Flame	C_2H_2 – air	AA	0.5% CsCl
Ni	232.0	25	GF	Argon	AA-BG	No
V	318.4	25	GF	Argon	AA-BG	No

GF - graphite furnace, AA - atomic absorption, BG - background correction.

Tab. 2. Validation parameters for the determination of some elements in cheese by GF-AAS and flame.

Element	*LOD* [mg.kg^{-1}]	*LOQ* [mg.kg^{-1}]	*R* [%]	U_A [%]	U_B [%]	U_C [%]
Ba	0.002	0.005	103	8.5	10.2	13.3
Ca	0.030	0.100	99	3.3	6.0	6.8
Cr	0.002	0.005	102	3.2	4.5	5.5
Cu	0.004	0.010	109	0.8	6.9	6.9
Hg	0.0001	0.0002	100	1.4	12.6	12.7
K	0.020	0.060	101	0.5	10.3	10.3
Mn	0.020	0.080	101	4.3	5.1	6.6
Mo	0.002	0.004	96	4.5	8.4	9.5
Mg	0.005	0.020	85	1.2	3.3	3.5
Na	0.030	0.090	104	3.0	5.6	6.4
Ni	0.010	0.020	103	1.0	14.4	14.5
V	0.004	0.007	102	1.2	6.2	6.3

LOD - limit of detection, *LOQ* - limit of quantification, U_A - uncertainty of A – type, U_B - uncertainty of B –type, U_C - combined uncertainty, *R* - recovery.

Tab. 3. Contents of some mineral elements in European Emmental and Edam cheeses.

Element	Value	SK	D	I	A	H	CZ	PL	UK	F	NL
		Contents [mg.kg-1]									
2006											
Cu	x_{mean}	1.24	0.860	4.23	2.06	1.42	1.43	1.11	0.717	0.761	0.778
	s_x	0.32	0.180	3.07	0.44	0.89	0.32	0.53	0.055	0.087	0.113
	x_{min}	0.689	0.626	1.21	1.43	0.858	1.16	0.532	0.677	0.639	0.637
	x_{max}	2.07	1.18	7.34	2.59	3.40	1.85	2.00	0.780	0.844	0.949
Ca	x_{mean}	6877	9050	9299	8798	8604	8743	8325	7505	8378	7465
	s_x	1478	392	1491	744	734	490	696	630	1656	1109
	x_{min}	4540	8307	7771	7554	7754	8310	7439	6827	6429	6181
	x_{max}	9588	9634	10750	9909	9617	9302	9295	8073	10195	9093
K	x_{mean}	1241	1091	1179	1261	1129	887	1082	1156	978	1028
	s_x	374	306	306	210	193	107	109	106	83	137
	x_{min}	809	827	1136	969	945	766	881	1038	868	828
	x_{max}	2386	1824	1249	1597	1405	1022	1233	1244	1068	1193
Mg	x_{mean}	376	432	507	459	485	375	382	406	427	449
	s_x	61	69	11	54	29	29	55	21	30	38
	x_{min}	238	373	497	395	448	349	327	389	402	415
	x_{max}	591	582	518	528	518	416	445	429	468	507
Na	x_{mean}	6075	6538	6181	2246	2844	8396	7052	7154	3458	5754
	s_x	1226	1991	571	661	435	1372	1874	1863	1442	1653
	x_{min}	4690	3883	5557	1619	2071	7118	5013	5002	2106	4184
	x_{max}	10060	9291	6677	3448	3181	10225	9745	8243	5183	7155
2007											
Cu	x_{mean}	1.08	1.14	7.66	2.58	1.16	0.925	0.829	0.685	0.699	0.841
	s_x	0.216	0.839	0.926	1.49	0.180	0.131	0.232	0.123	0.121	0.273
	x_{min}	0.815	0.780	6.89	1.64	0.933	0.768	0.469	0.549	0.562	0.570
	x_{max}	1.57	2.68	8.96	5.64	1.54	1.15	1.12	0.870	0.846	1.38
Ca	x_{mean}	7314	8111	8668	7824	7878	7512	7061	6216	7869	7046
	s_x	504	741	661	649	367	351	546	394	421	484
	x_{min}	6516	7132	8081	7087	7456	6957	6077	5896	7486	6454
	x_{max}	7980	9158	9890	8852	8460	7991	8240	6894	8268	7700
K	x_{mean}	1033	1126	1297	1551	999	1177	827	858	872	1061
	s_x	386	271	270	702	159	262	270	151	156	259
	x_{min}	669	793	1110	828	678	961	581	719	734	810
	x_{max}	1950	1629	1797	2588	1130	1615	1258	1090	1082	1542
Mg	x_{mean}	459	576	491	414	487	450	387	297	392	354
	s_x	58	101	120	110	73	36	53	119	112	78
	x_{min}	386	426	369	303	367	417	320	176	297	230
	x_{max}	578	715	693	626	518	518	469	473	524	452
Na	x_{mean}	4968	4501	5188	3239	3076	4954	4502	4300	3526	4123
	s_x	159	559	232	839	625	920	557	346	207	471
	x_{min}	4679	3342	4864	2153	2330	3398	3517	3947	3350	3536
	x_{max}	5189	4988	5471	4989	4173	5565	5026	4757	3826	4779

Country of origin: SK – Slovakia, D – Germany, I – Italy, A – Austria, H – Hungary, CZ – Czech Republic, PL – Poland, UK – United Kingdom, F – France, NL – Netherlands. s_x – standard deviation.

Tab. 4. Contents of some risk elements in European Emmental and Edam cheeses.

Element	Value	Country of origin									
		SK	D	I	A	H	CZ	PL	UK	F	NL
		Contents [mg.kg^{-1}]									
2006											
Ba	x_{mean}	3.48	3.12	2.64	2.82	2.95	2.38	3.89	1.89	1.35	1.36
	s_x	0.83	0.73	1.13	1.13	0.69	0.15	1.11	0.44	0.42	0.49
	x_{min}	2.41	2.59	1.81	1.56	1.88	2.23	2.49	1.51	1.00	1.00
	x_{max}	6.01	4.43	3.93	5.21	3.90	2.59	5.81	2.37	1.94	2.34
Cr	x_{mean}	0.228	0.292	0.351	0.348	0.326	0.353	0.320	0.357	0.290	0.396
	s_x	0.067	0.096	0.033	0.061	0.030	0.013	0.030	0.065	0.054	0.049
	x_{min}	0.143	0.165	0.323	0.279	0.286	0.334	0.283	0.311	0.257	0.341
	x_{max}	0.460	0.381	0.387	0.487	0.364	0.364	0.377	0.432	0.371	0.468
Hg	x_{mean}	0.003	0.010	0.012	0.011	0.013	0.012	0.009	0.012	0.005	0.017
	s_x	0.005	0.008	0.009	0.007	0.007	0.004	0.006	0.006	0.006	0.008
	x_{min}	0.001	0.002	0.002	0.003	0.001	0.007	0.001	0.005	0.001	0.001
	x_{max}	0.018	0.026	0.020	0.019	0.021	0.015	0.017	0.016	0.015	0.023
Mo	x_{mean}	0.071	0.055	0.099	0.095	0.093	0.052	0.049	0.033	0.061	0.041
	s_x	0.097	0.021	0.014	0.017	0.016	0.017	0.018	0.021	0.051	0.029
	x_{min}	0.024	0.045	0.086	0.060	0.075	0.031	0.026	0.017	0.013	0.017
	x_{max}	0.127	0.085	0.114	0.120	0.119	0.069	0.066	0.057	0.128	0.082
Mn	x_{mean}	0.769	0.551	0.676	0.558	0.525	0.388	0.801	0.735	0.569	0.616
	s_x	0.327	0.152	0.215	0.138	0.126	0.203	0.177	0.299	0.176	0.225
	x_{min}	0.173	0.254	0.438	0.387	0.330	0.187	0.562	0.483	0.418	0.351
	x_{max}	1.52	0.781	0.857	0.825	0.697	0.597	1.17	1.07	0.791	0.847
Ni	x_{mean}	0.213	0.316	0.547	0.289	0.313	0.309	0.242	0.290	0.181	0.387
	s_x	0.117	0.179	0.258	0.098	0.098	0.165	0.049	0.118	0.051	0.238
	x_{min}	0.070	0.148	0.307	0.194	0.203	0.216	0.181	0.210	0.112	0.149
	x_{max}	0.552	0.609	0.819	0.457	0.481	0.556	0.325	0.426	0.235	0.839
V	x_{mean}	0.124	0.098	0.130	0.140	0.176	0.180	0.134	0.255	0.257	0.131
	s_x	0.075	0.032	0.092	0.061	0.071	0.049	0.064	0.105	0.125	0.033
	x_{min}	0.023	0.059	0.059	0.051	0.117	0.143	0.019	0.137	0.134	0.093
	x_{max}	0.273	0.146	0.234	0.283	0.317	0.249	0.224	0.341	0.379	0.185
2007											
Ba	x_{mean}	2.14	2.98	2.63	3.28	2.10	3.13	3.26	2.25	1.91	2.53
	s_x	0.211	0.654	0.266	0.717	0.413	0.605	0.566	0.464	0.106	0.396
	x_{min}	1.89	2.22	2.31	2.18	1.57	2.33	2.46	1.81	1.76	2.00
	x_{max}	2.46	4.13	3.01	4.52	2.70	4.25	4.24	3.06	2.01	3.12
Cr	x_{mean}	0.503	0.315	0.277	0.392	0.441	0.178	0.270	0.353	0.245	0.287
	s_x	0.044	0.178	0.064	0.097	0.089	0.104	0.049	0.093	0.044	0.030
	x_{min}	0.410	0.095	0.189	0.274	0.279	0.080	0.163	0.209	0.205	0.248
	x_{max}	0.578	0.520	0.356	0.540	0.536	0.340	0.317	0.449	0.286	0.345
Hg	x_{mean}	0.0011	0.0047	0.0103	0.0098	0.0091	0.0036	0.0087	0.0066	0.0087	0.0099
	s_x	0.0009	0.0045	0.0069	0.0072	0.0074	0.0032	0.0076	0.0047	0.0072	0.0056
	x_{min}	0.0001	0.0014	0.0011	0.0008	0.0015	0.0004	0.0008	0.0030	0.0019	0.0013
	x_{max}	0.0038	0.0132	0.0170	0.0180	0.0177	0.0103	0.0210	0.0115	0.0162	0.0183

Tab. 4. *continued*

Element	Value	Country of origin									
		SK	D	I	A	H	CZ	PL	UK	F	NL
		Contents [mg.kg^{-1}]									
Mo	x_{mean}	0.016	0.059	0.071	0.090	0.076	0.034	0.032	0.049	0.040	0.069
	s_x	0.009	0.027	0.030	0.042	0.040	0.026	0.019	0.024	0.019	0.030
	x_{min}	0.007	0.026	0.042	0.030	0.026	0.010	0.012	0.014	0.016	0.041
	x_{max}	0.034	0.098	0.118	0.156	0.141	0.079	0.054	0.077	0.060	0.114
Mn	x_{mean}	0.314	0.305	0.298	0.350	0.394	0.211	0.462	0.347	0.186	0.189
	s_x	0.129	0.070	0.068	0.090	0.140	0.053	0.182	0.152	0.046	0.083
	x_{min}	0.226	0.188	0.204	0.193	0.274	0.141	0.299	0.208	0.141	0.121
	x_{max}	0.497	0.429	0.396	0.482	0.682	0.305	0.614	0.577	0.248	0.339
Ni	x_{mean}	0.309	0.231	0.256	0.291	0.316	0.231	0.263	0.098	0.101	0.137
	s_x	0.081	0.096	0.091	0.070	0.059	0.085	0.085	0.044	0.026	0.088
	x_{min}	0.201	0.118	0.177	0.139	0.259	0.123	0.174	0.051	0.070	0.048
	x_{max}	0.444	0.375	0.422	0.383	0.427	0.345	0.458	0.174	0.132	0.337
V	x_{mean}	0.235	0.166	0.151	0.046	0.109	0.191	0.121	0.039	0.065	0.087
	s_x	0.066	0.063	0.082	0.027	0.026	0.065	0.087	0.014	0.017	0.056
	x_{min}	0.169	0.078	0.073	0.032	0.060	0.124	0.039	0.025	0.053	0.038
	x_{max}	0.314	0.290	0.286	0.101	0.144	0.275	0.282	0.061	0.089	0.194

SK – Slovakia, D – Germany, I – Italy, A – Austria, H – Hungary, CZ – Czech Republic, PL – Poland, UK – United Kingdom, F – France, NL – Netherlands. s_x – standard deviation.

the determination of elements in cheese were not available. The recovery of the method was assessed in the matrix by the analysis of fortified samples. Fortification of samples was performed before microwave digestion using solutions of selected elements. Mean recoveries of the elements are presented in Tab. 2. The accuracy of the method was tested by the determination of Ba, Ca, Cr, Cu, Hg, K, Mg, Mn, Mo, Na, Ni, and V concentration in the reference material NCS ZC 73008 (rice) with the recovery ranging from 96% to 107% and in NCS ZC 73013 (spinach; both from National Analysis Center for Iron and Steel, Beijeng, China) with the recovery ranging from 98% to 114%. For the determination of Hg in cheeses, atomic absorption spectrometer AMA 254 (Altec, Prague, Czech Republic) was used.

Digestion of cheese

Samples of Emmental and Edam cheeses (0.5 g) were digested by the microwave digestion system Milestone MLS 1200 MEGA (Sorisole, Italy) with 4 ml of 65 % HNO_3 and 0.5 ml H_2O_2. The microwave digestion programme 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 digested samples were adjusted to volumes of 10 ml with ultra pure water and used for further analyses. All samples were tested in triplicate.

Statistics

Principal component analysis (PCA) was carried out using a statistical programme Unistat (Unistat, London, United Kingdom) Basic descriptive statistics was carried out by Office Excel 2003 (Microsoft, Redmond, Washington, USA).

RESULTS AND DISCUSSION

Minimal, maximal and mean concentrations of some mineral elements (Ca, Cu K, Mg and Na) determined in 192 cheese samples originating from 10 European countries in 2006 and 86 cheese samples in 2007 are shown in Tab. 3. Similarly, results from the determination of some trace anorganic elements (Ba, Cr, Hg, Mo, Mn, Ni and V) from these two production periods are listed in Tab. 4. The concentrations of the minerals and trace elements in all cheeses examined in this work varied considerably among the European countries and years of production as can be seen from the following ranges in mg.kg^{-1}: Cu (0.47–8.96), Ca (4 540–10 750), K

(581–2 588), Mg (176–715), Na (1 619–10 225), Ba (1–6.01), Cr (0.08–0.58), Hg (0.0001–0.026), Mo (0.007–0.156), Mn (0.121–1.52), Ni (0.048–0.839) and V (0.019–0.379).

All elements showed significant concentration differences according to the country of origin of the cheese. The highest Ca contents of Emmental and Edam cheeses from the ten European countries were found in Italian hard cheeses (10 750 mg.kg^{-1}), and the lowest contents of this essential element were determined in Slovakian cheeses (4 540 mg.kg^{-1}) in 2006 (Tab. 3). The high contents of Ca related to the fact that no curd washing could be applied in the cheese-making technology [11]. In most cases, the cheese samples did not meet the older recommendation of the Codex standard on the minimal contents of Ca in cheeses (8 000 mg.kg^{-1}) [13] with the only exception of German and Czech cheeses in 2006 and the Italian ones in 2007.

Cheese products normally contain detectable Cu levels, as a consequence of the contents of this element in milk, which was in contact with metallic materials. Some hard cheeses are manufactured in stainless-steel vats instead of the traditional copper vats encountered in most European regions [11]. The highest Cu contents were found in Italian samples (8.96 mg.kg^{-1}) in both years of cheese production and the lowest contents in the Polish cheeses (0.469 mg.kg^{-1}). All hard cheese samples met the limitation of Codex Standard [13] on maximally 15 mg of Cu per kg of cheese.

In 2007, the highest contents of K were observed in Austrian hard cheeses (2 588 mg.kg^{-1}), so far the lowest contents were determined in Polish cheeses (581 mg.kg^{-1}). Mg contents were the highest in German hard cheeses (715 mg.kg^{-1}), and the lowest concentrations were found in British samples (176 mg.kg^{-1}). Contents of Na, which originates mainly from the cheese salt bath, was found the highest in a Czech sample (10 225 mg.kg^{-1}) and the lowest value of 1 619 mg.kg^{-1} was determined in an Austrian cheese of 2006.

The highest contents of inorganic trace elements Ba, Cr and Mn were observed in Slovakian hard cheeses, Hg in German, Mo in Austrian, Ni in Dutch and V in French hard cheeses. The ranges of the elements in European Emmental and Edam cheeses determined in this study appear to be similar to the results quoted by the literature (Tab. 5).

A statistical analysis performed on all the average data showed the highest correlation between the following elements: Ca – Mg (0.822), Cu – Ni (0.787) and K – Mo (0.753). Direct correlation was found between minerals Cu – Ca (0.625), Cu – K (0.594) and Cu – Mg (0.542) as well as one inverse

Tab. 5. References on the contents of minerals and risk elements in some types of European hard cheeses.

Element	Contents [mg.kg^{-1}] (range or mean)	Reference
Ca	8 100–12 200	13*
	1 030	4
	3 473–4 556	9
	8 929–10 498	2
	2 153	14
	4 540–10 750	**
Cu	0.1–0.27	9
	> 1–13	2
	0.31–1.23; 0.537	3
	0.22	14
	0.469–8.96	**
K	550	4
	305–349	9
	800–980	2
	980	14
	581–2 588	**
Mg	469–496	13*
	300	4
	28–120	9
	340–390	2
	74.5	14
	176–715	**
Na	1 800	4
	3 957–6 558	9
	1 316–2 561	2
	283	14
	1 619–10 225	**
Cr	0.01–0.05; 0.028	3
	0.01	4
	0.04–0.62	9
	0.07	14
	0.08–0.578	**
Hg	0.001	4
	0.0001–0.026	**
Mo	0.07–0.15	2
	0.007–0.086	**
Mn	0.178–0.404; 0.26	3
	0.21–0.4	2
	0.28–1.1	9
	0.35	14
	0.121–1.52	**
Ni	0.18–0.34	9
	0.028–0.131; 0.06	3
	0.07–0.839	**

* – archived data from 1940s, ** – our results.

correlation between Na and Mo (–0.649). Some positive correlations were found also between the minerals and trace elements: Cu – Mo (0.625), Ca – Mo (0.646), Ca – Ni (0.559), K – Ni (0.620), Mg – Mo (0.677), Mg – Ni (0,695), and Mo – Ni (0.657). No significant correlations were observed between the other elements.

PCA is a multivariate analytical statistical technique widely used to reduce dimensionality of the data, which retains most of the original variability in the data set. The method utilizes linear combinations of original dependent variables to a smaller set of new uncorrelated variables called principal components or, in the case of factor analysis, to a new set of variables called factors, based on patterns of correlation among the original variables. Average values of all measured data of mineral elements in European Emmental and Edam cheeses are well visualized on the plot of PCA (Fig. 1). This plot describes the relationship among minerals in cheeses (plot A, Fig. 1), as well as the similarities of some European countries in mineral composition of the examined cheeses (plot B, Fig. 1). The first and the second principal component describe 77% of the total variation in the cheese mineral element composition. Ca and Na had the highest impact on the cheese differentiation (plot A, Fig. 1) according to country of origin (plot B, Fig. 1). PCA pointed out similarities in mineral composition of Emmental and Edam cheeses of these European countries: Italy and Germany, namely in the contents of Ca, Hungary and Austria in Na and, thanks to the contents of other minerals, Dutch and French cheeses were well differentiated from those originating in remaining countries.

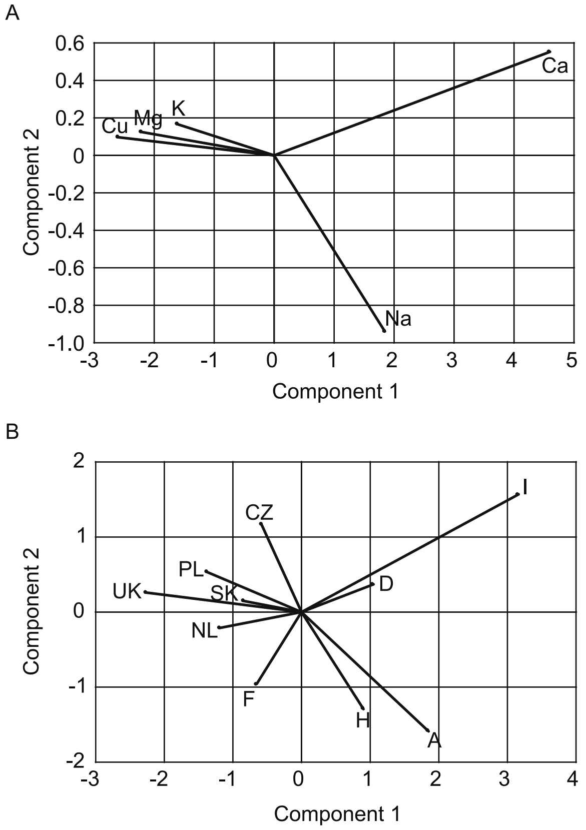

Fig. 1. Principal component analysis of mineral elements in European Emmental and Edam cheeses.
Biplot of loadings (A) and scores (B). Country of origin: A – Austria, CZ – Czech Republic, F – France, UK – United Kingdom, D – Germany, H – Hungary, I – Italy, NL – Netherlands, PL - Poland, and SK – Slovakia.

Recently, information on the depletion and decrease of some essential minerals, such as Ca, Mg and Fe in fruit, vegetable, meat and dairy products appeared in the literature [15–18]. This was based on the comparison the current and older data from the half of the previous century. Published data demonstrate that there has been a significant loss of minerals and trace elements in some foods over that period of time. For example, the loss of Ca from cheeses averaged over 15%, in Parmesan cheese the loss was as high as 70%, implying a considerable dilution or some other significant shift in the ingredients to account for this change. Cu and Mg also showed losses in dairy foods [16]. From the comparison of our Ca and Mg data to the range of the archive data [15] (Tab. 5), a significant decrease of Ca contents in cheeses can be seen. Some trends in the nutrient decline in some food commodities were noticed in the U.S. Department of Agriculture's nutrient database [18]. Authors attributed the decline in the nutrient density to a genetics-driven "dilution effect". Other possible explanations include gradual depletion of soil micronutrients and the organic matter, changes in pest complexes and levels, and the impact of farming systems. It was hypothesized that the above mentioned depletion of Ca contents in cheeses results from modification or changes of the crude milk composition before the cheese making process and/or from the cheese production technology.

CONCLUSION

Obtained results from the determination of some minerals and trace elements in Emmental and Edam type hard cheeses originating from 10 European countries showed a wide variability. This dispersion of element concentrations could be used for differentiation of cheeses and their geographical authentication by multivariate procedures. The found lower range of Ca contents, in comparison to some archived data, confirms the trend of the depletion of some minerals in some food commodities.

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