THE COMPARISON BETWEEN SLOVENE AND CENTRAL EUROPEAN MINERAL AND THERMAL WATERS

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Received 03-06-2002

Abstract
This study gives an insight into the diversity of Slovene mineral and thermal waters as an important natural resource, furthermore, it compares Slovene waters to Central European waters. The evaluation of Slovene mineral waters is based on the data obtained at our Faculty during a longer period. In order to compare the two groups of waters building of computer data bases was required. The computer data base on Slovene mineral waters includes 118 different waters and nearly 10,000 data items. The data base for Central European waters is based on the monograph written by Carlé, comprising 15,000 data for 702 sampled waters. Among European waters 143 different balneological types were recognised. Slovene mineral waters qualified for 20 categories. Two types of Slovene mineral waters, i.e. NA-CA-MG-SO4-HCO3-CO2 and MG-NA-HCO3-SO4-CO2, had no exact match among European waters. For more precise evaluation of European and Slovene mineral waters a triangular diagram was selected and modified so as to allow for the four parameters of each water to be read simultaneously from the graph. Triangular diagrams show that European and Slovene mineral waters are comparable if the relative cationic composition of waters is considered. Hydrogen carbonate significantly predominates in anionic composition of Slovene mineral waters, while triangular diagrams for European mineral waters show that any proportion of chloride, sulphate and hydrogen carbonate is naturally possible.

Introduction

In contrast to drinking water, natural mineral water is defined as "microbiologically wholesome water, originating in an underground water table or deposit and emerging from a spring tapped at one or more natural or bored exits (Directive 80/777/EEC and 96/79/EEC). Mineral waters are mostly characterised by higher mineral contents. As such they are valuable as an additional source of some physiologically important elements or ions. The bio-availability of magnesium[1] and calcium[2] from mineral water are of wider interest.

Mineral waters are not meant to be the main source for daily water intake in human. In contrast with tap and spring water higher concentration of some ions in mineral waters are acceptable if hydro-geologically originated. No chemical additions are allowed except the removal or/and addition of carbon dioxide. Like any other product for human consumption mineral water needs to be periodically tested for microbiological and chemical composition. Water treatment is limited to aeration and filtration. Water disinfection is not acceptable. As a consequence the microbiological and virological aspects are very delicate: an extreme case was the epidemic of cholera in Portugal in 1974 which was transmitted by bottled mineral water.[3]

The evaluation of matrix effect is of great importance in the development of analytical methods for mineral water testing. However, authors generally focus on a particular water sample, and use it as an example for wider application of a proposed analytical method, while natural diversity in the composition of mineral waters is rarely taken in to account in developing analytical methods.[4] One of the reasons is the lack of surveys on the composition of natural mineral waters at national and international level. The information in this field is rather dispersed. One way of combating this problem was used by Misund *et al*[5] who obtained 56 different samples of mineral waters during their travels to European countries. Bottle labels were used as a source of basic information on a particular water sample and sixty-six chemical elements were determined with ICP-AES, ICP-MS and ion chromatography. Bottled mineral waters are a subcategory of mineral waters. They do not represent mineral waters as a whole since not all mineral waters are potable and even not all potable waters are bottled. Several mineral waters are used therapeutically in numerous spas, and some others, mainly brines, might become technologically exploited. Chemical characteristics and the abundance of a water source determine the use of water and potential economical benefits.

Slovenia is rich in mineral, thermal and thermo-mineral waters. The most abundant are mineral waters in North-Eastern part of Slovenia which is a transition region between Pannonia lowlands in the East, and Southern Alps in the West. The most important tectonic structure is the Mura basin (Fig. 1, an asterisk), which consists of clastic sediments from the Tertiary and Quarternary age. The Mura basin forms a part of much larger Zala basin, which extends from South-Western Hungary to northern Croatia, and belongs to a widespread system of Pannonian basin.[6]

Mura basin in north-eastern Slovenia is made up of two depressions, developed during the late Neogene and Early Pliocene periods. The Radgona depression is in the Northern part of the basin and reaches depths of about 2 km. The adjacent Ljutomer depression is over 4 km deep. Thermal waters from this aquifer are used in balneology, and in the town of Murska Sobota also for local district heating. Some resources indicate the signs of overexploitation.[7]

Chemical analyses of Slovene mineral waters were performed at the Faculty of Chemistry and Chemical Technology (University of Ljubljana) during longer period, starting after the second World war and extending into the late nineties of the last century. More than 100 different underground waters were analysed. The chemical composition of several of them was periodically checked enabling the insight into their composition over decades. The data on Slovene natural resources were organised and preserved in the form of a computer database. The aim of this study was to give a concise overview of chemical characteristics of Slovene mineral waters. The other objective was to evaluate Slovene mineral waters within the wider Central European context.

Information sources and data bases for European and Slovene mineral waters

In order to identify the main characteristics of European and Slovene mineral, thermal and thermomineral waters and to compare the two groups, two extensive computer databases were built: one for Slovene and one for European waters. The databases contain data on the origin of water, concentration of the constituents (including anions, cations, non-ionic species and gases), physical data and some descriptive parameters, which gives 53 different categories of data in total.

The computer data base on Slovene mineral waters includes nearly 10,000 data items. For each water source the most up-to-date analysis was taken in to consideration. There are 118 different sources of mineral waters. The majority, 99 mineral waters were from north-eastern part of Slovenia, among them 76 from the Radenska region. The remaining 19 waters from other Slovene locations are as follows: eight water sources from Rogaška Slatina, three from Dolenjske toplice, two from Dobrna, Laško, Medija - Izlake, one from Ptuj, and one from Krakovski Gozd.

The data for another data base were drawn from the monography by Carlé which contains data on the composition of more than 700 Central European mineral and thermal waters (including a wide spectra of waters from potable waters to brines). The data for 702 waters were entered into the computer database comprising of more than 15,000 data items organised into 34 categories on chemical composition of waters and some additional parameters. Countries of origin of waters and the number of waters per country are shown in Fig. 1.

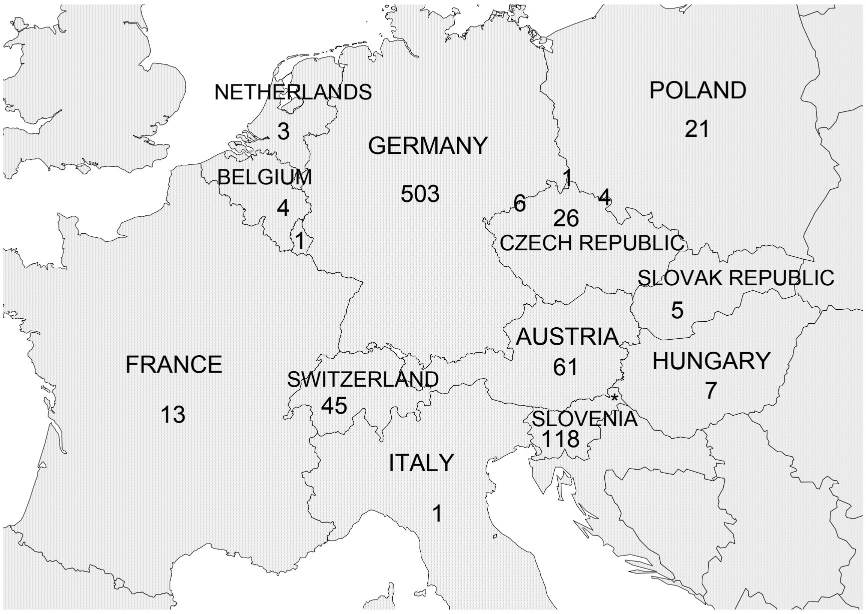

Fig. 1. The geographic origin of waters included in the computer databases (an asterisk marks the location of the Mura basin).

Both computer databases were built up using dBase program and were later transferred to Excel. For the analysis, comparison and graphic representation of data on European and Slovene mineral waters computer programs Statgraphics and Excel were used.

Results and discussion

In order to evaluate the basic characteristics of the results for the main physical and chemical parameters in European and Slovene mineral waters descriptive statistics was used. The comparison of minimum, maximum, mean and median values of the Slovene and European mineral waters is summarised in Table 1. The heading "Counts" stands for the number of statistically evaluated results. In spite of a high number of Slovene waters (118), the value of counts is frequently lower. The reason is either the lack of particular data for some waters or the zero value which was omitted from the statistical evaluation. The same principle was applied in analysing the data on European waters.

Table 1. The comparison of the results of descriptive statistics for the main chemical and physical parameters in Slovene (SI) and European (EU) mineral waters (concentrations are in mg/L).

	Li^+	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Fe	F^-
Minimum SI	0.01	0.1	0.3	0.1	1	3.9	0.04	0.05	0.05
Minimum EU	0.01	0.01	0.8	0.2	0.02	1.84	0.02	0.01	0.04
Maximum SI	9.5	34.1	5250	520	1255	509	37	51.3	7.6
Maximum EU	163	252	122500	5493	5430	28826	1223	12831.4	84.8
Mean SI	0.93	3.94	877	81.8	94.0	170	2.56	6.96	0.858
Mean EU	3.32	5.59	5684	105.8	176.3	549	27.14	33.11	2.028
Median SI	0.505	2.23	532	50	55.8	153	1.5	4.85	0.61
Median EU	0.735	1.07	573	24.9	64.1	259	3.745	2.5	0.66
Counts SI	112	113	118	115	118	118	113	118	111
Counts EU	264	335	702	614	697	700	248	620	152

	Cl^-	Br^-	I^-	SO_4^{2-}	HPO_4^{2-}	NO_2^-	NO_3^-	HCO_3^-	CO_3^{2-}
Minimum SI	0.7	0.01	0.01	0.9	0.02	0.01	0.01	69	
Minimum EU	0.14	0.01	0.001	0.86	0.01	0.003	0.02	5	0.09
Maximum SI	5735	10.85	9	2153	3.6	0.14	57.4	8996	
Maximum EU	197426	4551	98.5	52890	53.8	15.7	298.5	9319.1	642
Mean SI	319	0.669	0.418	178	0.517	0.022	1.55	2740	
Mean EU	9211	44.1	2.005	1182	0.802	1.107	8.64	975	85.6
Median SI	66.4	0.17	0.11	42.8	0.26	0.02	0.1	2511	
Median EU	344	1.86	0.09	339	0.145	0.235	2.385	549.8	38.4
Counts SI	118	107	106	118	105	37	107	118	
Counts EU	700	261	238	689	298	50	226	694	20

	HS^-	H_2SiO_3	HBO_2	TDS	CO_2	H_2S	T [°C]		
Minimum SI	0.05	2.7	0.08	152	16		8.2		
Minimum EU	0.11	0.49	0.02	10.9	1.1	0.01	4		
Maximum SI	1.11	197	56.2	15938	4495		70.8		
Maximum EU	376.8	338.1	665.3	773757	8328	77.18	75		
Mean SI	0.62	48.16	13.3	4471	1768		23.1		
Mean EU	14.37	29.73	19.1	18702	963.7	8.25	16.9		
Median SI	0.7	44.25	9.71	3752	1828		18		
Median EU	3.04	21	3.44	3178	391	1.8	12.8		
Counts SI	3	118	96	114	98		93		
Counts EU	64	575	179	697	536	103	609		

To get an insight into natural diversity in the composition of mineral waters the balneologic types were identified for all European and Slovene mineral waters. The type of water is defined by all ionic constituents which contribute at least 20 miliequivalent % to the total anionic or cationic composition of water. In order to present the composition of water as precisely as possible cations or anions are listed in the decreasing order, starting with the most prevailing one. Besides this the presence of carbon dioxide with concentration higher than 250 mg/L was given by adding a symbol

Table 2. Types of European (EU) and Slovene (SI) mineral waters.

N	Type	EU/SI	N	Type	EU/SI	N	Type	EU/SI
1	CA-CL	1	49	CA-NA-SO4-HCO3	5	97	NA-CA-SO4-CL	5
2	CA-FE-HCO3-SO4-CO2	1	50	CA-NA-SO4-HCO3-CO2	2	98	NA-CA-SO4-CL-CO2	1
3	CA-FE-SO4	1	51	CA-SO4	22	99	NA-CA-SO4-CL-HCO3-CO2	1
4	CA-HCO3	8	52	CA-SO4-CL	1	100	NA-CA-SO4-HCO3	2
5	CA-HCO3-CL	1	53	CA-SO4-CL-CO2	1	101	NA-CA-SO4-HCO3-CL-CO2	2
6	CA-HCO3-CO2	16/1	54	CA-SO4-CL-HCO3-CO2	1	102	NA-CL	122
7	CA-HCO3-SO4	2	55	CA-SO4-CO2	2	103	NA-CL-CO2	38
8	CA-HCO3-SO4-CO2	1	56	CA-SO4-HCO3	8	104	NA-CL-CO3	1
9	CA-MA-SO4-HCO3-CO2	1	57	CA-SO4-HCO3-CO2	5	105	NA-CL-HCO3	19/4
10	CA-MG-HCO3	11/12	58	FE-SO4	1	106	NA-CL-HCO3-CO2	8
11	CA-MG-HCO3-CL	1	59	K-NA-CA-HCO3-CL	1	107	NA-CL-HCO3-SO4	2
12	CA-MG-HCO3-CO2	22/11	60	K-NA-MG-SO4-CL	1	108	NA-CL-SO4	10
13	CA-MG-HCO3-SO4	8	61	MG-CA-HCO3	1	109	NA-CL-SO4-CO2	6
14	CA-MG-HCO3-SO4-CL	2	62	MG-CA-HCO3-CO2	5	110	NA-CL-SO4-HCO3	1
15	CA-MG-HCO3-SO4-CO2	8	63	MG-CA-HCO3-SO4	2	111	NA-CO3	1
16	CA-MG-NA-HCO3	2/1	64	MG-CA-NA-HCO3	1	112	NA-CO3-SO4	1
17	CA-MG-NA-HCO3-CO2	2/5	65	MG-CA-NA-HCO3-CO2	1	113	NA-HCO3	14/3
18	CA-MG-NA-HCO3-SO4	2	66	MG-CA-SO4	1	114	NA-HCO3-CL	16/5
19	CA-MG-NA-HCO3-SO4-CO2	1	67	MG-CA-SO4-HCO3	1	115	NA-HCO3-CL-CO2	10
20	CA-MG-NA-SO4	2	68	MG-HCO3-CO2	1	116	NA-HCO3-CL-SO4	1
21	CA-MG-NA-SO4-HCO3-CO2	1	69	MG-NA-CA-HCO3-CL-CO2	1	117	NA-HCO3-CO2	17/42
22	CA-MG-SO4	16	70	MG-NA-CA-HCO3-CO2	2/1	118	NA-HCO3-F	1
23	CA-MG-SO4-HCO3	11	71	MG-NA-HCO3-CO2	2/1	119	NA-HCO3-SO4	3
24	CA-MG-SO4-HCO3-CL	1	72	MG-NA-SO4	2	120	NA-HCO3-SO4-CO2	5/1
25	CA-MG-SO4-HCO3-CO2	1	73	MG-NA-SO4-CL	1	121	NA-MG-CA-CL-HCO3	1
26	CA-NA-CL	1	74	MG-NA-SO4-CO2	2	122	NA-MG-CA-HCO3	1/1
27	CA-NA-CL-SO4	1	75	NA-CA-CL	18	123	NA-MG-CA-HCO3-CL-CO2	1
28	CA-NA-CL-SO4-HCO3	1	76	NA-CA-CL-CO2	8	124	NA-MG-CA-HCO3-CO2	1
29	CA-NA-CL-SO4-HCO3-CO2	1	77	NA-CA-CL-HCO3	6	125	NA-MG-CA-HCO3-SO4	1
30	CA-NA-HCO3	2	78	NA-CA-CL-HCO3-CO2	10	126	NA-MG-CA-SO4	1
31	CA-NA-HCO3-CL-CO2	1	79	NA-CA-CL-HCO3-SO4-CO2	1	127	NA-MG-CL	1
32	CA-NA-HCO3-CL-SO4-CO2	1	80	NA-CA-CL-SO4	15	128	NA-MG-CL-CO2	1
33	CA-NA-HCO3-CO2	8/3	81	NA-CA-CL-SO4-CO2	5	129	NA-MG-CL-HCO3	1
34	CA-NA-HCO3-SO4	3	82	NA-CA-CL-SO4-HCO3-CO2	6	130	NA-MG-CL-SO4	1
35	CA-NA-HCO3-SO4-CL-CO2	1	83	NA-CA-HCO3	4/2	131	NA-MG-HCO3-CL-CO2	5
36	CA-NA-HCO3-SO4-CO2	8	84	NA-CA-HCO3-CL	1	132	NA-MG-HCO3-CO2	6
37	CA-NA-MG-CL-HCO3	1	85	NA-CA-HCO3-CL-CO2	4	133	NA-MG-HCO3-SO4-CL	1
38	CA-NA-MG-CL-SO4-HCO3-CO2	1	86	NA-CA-HCO3-CL-SO4-CO2	1	134	NA-MG-HCO3-SO4-CO2	3
39	CA-NA-MG-HCO3	1	87	NA-CA-HCO3-CO2	15/16	135	NA-MG-SO4-CO2	1
40	CA-NA-MG-HCO3-CL	1	88	NA-CA-HCO3-SO4-CL	1	136	NA-SO4-CL	7
41	CA-NA-MG-HCO3-CO2	1/1	89	NA-CA-HCO3-SO4-CO2	3	137	NA-SO4-CL-CO2	2
42	CA-NA-MG-HCO3-SO4	1	90	NA-CA-MG-HCO3	1/2	138	NA-SO4-CL-HCO3-CO2	2
43	CA-NA-MG-SO4-CL	3	91	NA-CA-MG-HCO3-CL-SO4-CO2	1	139	NA-SO4-CO2	1
44	CA-NA-MG-SO4-HCO3	1	92	NA-CA-MG-HCO3-CO2	8/1	140	NA-SO4-HCO3	7
45	CA-NA-SO4	2	93	NA-CA-MG-HCO3-SO4	1	141	NA-SO4-HCO3-CL	2
46	CA-NA-SO4-CL	5	94	NA-CA-MG-HCO3-SO4-CL	1	142	NA-SO4-HCO3-CL-CO2	3
47	CA-NA-SO4-CL-CO2	2	95	NA-CA-MG-HCO3-SO4-CO2	1/1	143	NA-SO4-HCO3-CO2	1
48	CA-NA-SO4-CL-HCO3	1	96	NA-CA-SO4	6			

CO2 at the end of the type name. With this procedure 143 different types of European mineral waters were identified and classified accordingly as shown in Table 2. The frequency of European and Slovene mineral waters (EU/SI) was given for each water type. Slovene mineral waters qualified for 20 categories of European mineral waters. For Slovene mineral waters, one water of the NA-CA-MG-SO4-HCO3-CO2 type and three waters of the MG-NA-HCO3-SO4-CO2 type had no exact match within the group of European waters.

The identification of a type of mineral water is a descriptive parameter, which classifies water samples and gives the first information on the possible use of the water. The type of water does not represent the composition of a water sample in more details. The type of water is not precise enough to adequately represent the matrix of water which is important when developing or applying an analytical method. Waters of the same type can still have a significantly different composition concerning even the major constituents.

For more precise evaluation of the diversity in the composition of European and Slovene mineral waters and for the comparison of the two groups a triangular diagram is frequently selected. Each side of the triangle stands for a relative amount of one of the three main cations or anions expressed in miliequivalent % but the relative amount of only two constituents is adequately represented. The relative amount of the third ion is not represented realistically, however the difference to achieve a 100 percent in the total anionic or cationic composition is given. In order to improve the insight into the composition of mineral waters we modified the triangular diagram so that each water is represented with three points, each point being determined by the relative amount of the pair of ions. By this approach the graph becomes four-dimensional: thus the graph shows the actual relative amount of the three ions and additionally the contribution of the remaining cations or anions represented by the size of an even-sided triangle related to particular water sample.

Fig. 2 shows the comparison of cationic composition of European and Slovene mineral waters while Fig. 3 relates to anionic composition of mineral waters. The graphs are of the three types: The first type of graph (EU 1 or SI 1) represents the waters in which the remaining cations or anions which are not represented individually contribute

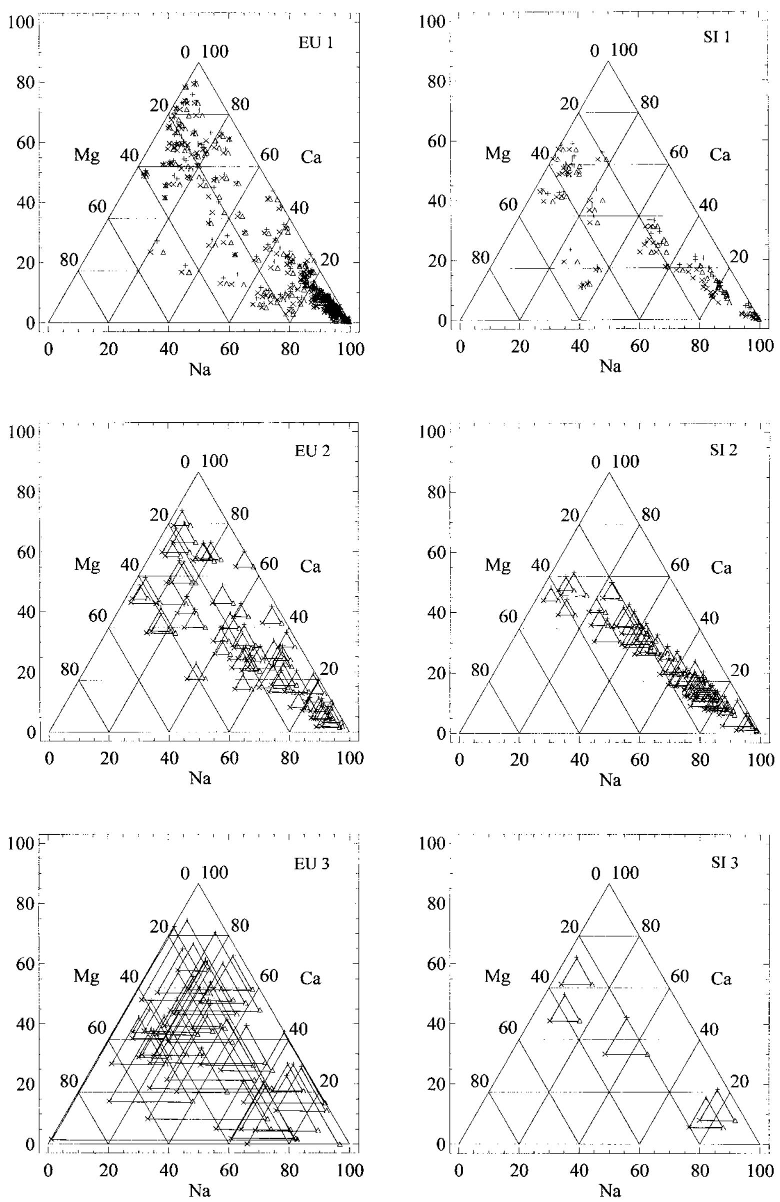

Fig. 2. The comparison of cationic composition of European (EU) and Slovene (SI) mineral waters. EU 1 and SI 1 represent the waters in which cations which are not represented individually contribute to the total cationic contents 5% at most. For EU 3 or SI 3 the contribution of the remaining ions is greater than 10%. EU 2 or SI 2 include waters which fall between the two mentioned categories. The results are expressed in miliequivalent %. The open triangle represents a relative amount of magnesium and calcium, + shows a relative amount of sodium and magnesium, x stands for sodium and calcium.

to the total cationic or anionic contents 5% at most. For the third type of graph (EU 3 or SI 3) the contribution of the remaining ions is greater than 10%. The second type of graph (EU 2 or SI 2) includes waters which fall between the two described categories. The plus in Fig. 2 or 3 represents the relative amount of sodium and magnesium or relative amount of chloride and sulphate while the cross sign stands for sodium and calcium or chloride and hydrogen carbonate. An open triangle represents a relative amount of magnesium and calcium or sulphate and hydrogen carbonate.

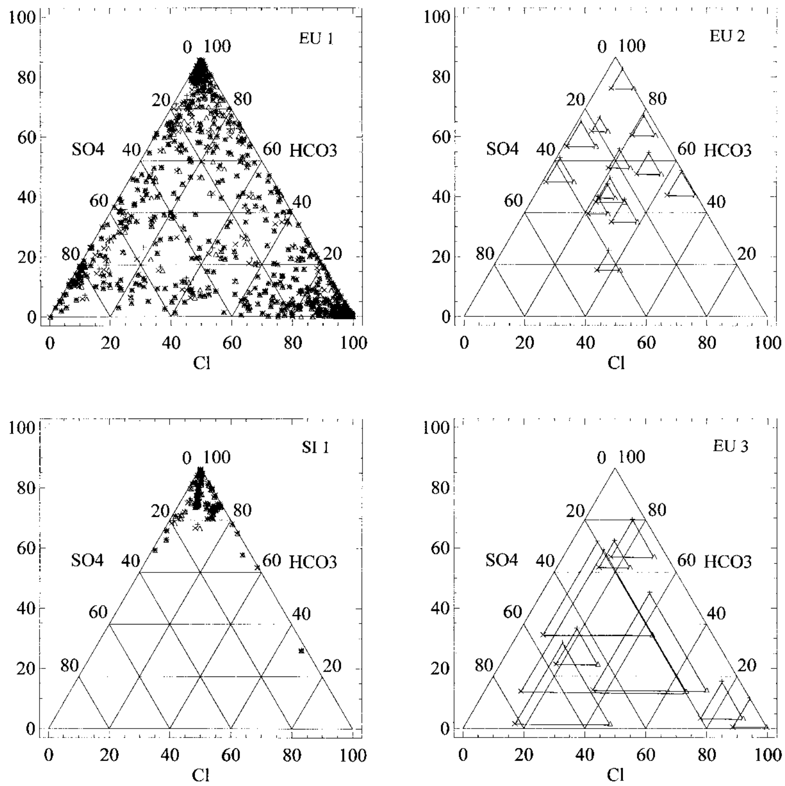

Fig. 3. The comparison of anionic composition of European (EU) and Slovene (SI) mineral waters. EU 1 and SI 1 represent the waters in which anions which are not represented individually contribute to the total anionic contents 5% at most. For EU 3 or SI 3 the contribution of the remaining ions is greater than 10%. EU 2 or SI 2 include waters which fall between the two mentioned categories. The results are expressed in miliequivalent %. The open triangle represents a relative amount of sulphate and hydrogen carbonate, + shows a relative amount of chloride and sulphate, x stands for chloride and hydrogen carbonate.

A brief comparison of Figures 2 and 3 shows that while nearly any anionic composition is naturally possible there are natural limitations for cationic composition resulting in the lack of waters with the relative amount of magnesium exceeding the limit of 50%. In contrast with European mineral waters Slovene mineral waters show a much greater variety in cationic than in anionic composition. The cationic composition of Slovene mineral waters is comparable to European waters while in anionic composition of Slovene mineral waters hydrogen carbonate strongly predominates, in addition, there are only few waters with very low sulphate contents and higher chloride contents extending from 20 to 70%. The distribution of Slovene water samples in Fig. 3 shows some regularities, several waters are distributed along the straight line.

Conclusions

On the one hand, this study was concerned primarily with showing, for the first time, the diversity of Slovene mineral waters as an important natural resource, based on the data obtained at our Faculty. On the other hand this research defined matrix effects that an analytical chemist has to consider when developing analytical methods for mineral waters.

Acknowledgement

The author wishes to thank the Ministry of Education, Science and Sports of the Republic of Slovenia and the company Radenska d.d. for financial support to the project L1-0590-0103 "Slovenske mineralne vode in njihova umestitev v evropski okvir".

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Povzetek

V prispevku je prikazana raznolikost v kemijski sestavi slovenskih mineralnih in termalnih vod in podana primerjava z vodami Srednje Evrope. Ovrednotenje slovenskih mineralnih vod temelji na kemijskih analizah, ki so bile narejene na Fakulteti za kemijo in kemijsko tehnologijo skozi daljše obdobje. Da bi bilo mogoče primerjati obe skupini vod, sta bili zgrajeni računalniški podatkovni bazi. Podatkovna baza o slovenskih mineralnih vodah obsega približno 10 000 podatkov, povezanih z 118 različnimi vodami. Podatkovna baza o srednje evropskih vodah temelji na Carlé-jevi monografiji in vključuje 702 vodi ter približno 15 000 podatkov. Za evropske vode je bilo ugotovljenih 143 različnih balneoloških tipov. Slovenske vode se uvrščajo v 20 razredov. Dva tipa slovenskih vod nimata natančne primerjave med evropskimi. Za natančnejšo primerjavo slovenskih in evropskih mineralnih vod je uporabljen trikotniški diagram, ki je bil prilagojen tako, da je mogoče za vsako vodo odčitati štiri temeljne podatke o njeni kemijski sestavi. Trikotniški diagrami so pokazali, da so glede kationske sestave slovenske vode primerljive z evropskimi. Hidrogenkarbonat izrazito prevladuj v anionski sestavi slovenskih mineralnih vod. Diagrami za evropske vode nasprotno kažejo, da je naravno mogoče poljubno razmerje med kloridom, sulfatom in hidrogenkarbonatom.