Multivariate Data Analysis
of Natural Mineral Waters

Katja Šnuderl,[a] Marjana Simonič,[a] Jan Mocak,[b]*
Darinka Brodnjak-Vončina[a]

[a] *University of Maribor, Faculty of Chemistry and Chemical Engineering, Smetanova 17, SI-2000 Maribor, Slovenia*

[b] *University of Ss. Cyril and Methodius, Faculty of Natural Sciences, Nam. J. Herdu 2, SK-91701 Trnava, Slovakia.*
E-mail: jan.mocak @ucm.sk.

Abstract

Fifty samples of natural mineral waters from springs in Slovenia, Hungary, Germany, Czech Republic and further countries of former Yugoslavia have been analysed. The mass concentration of cations (Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, NH_4^+) and anions (F^-, Cl^-, I^-, NO_3^-, SO_4^{2-}, HCO_3^-), the spring temperature, pH, conductivity and carbon dioxide mass concentration have been measured using standard analytical methods.

Appropriate statistical methods and different chemometric tools were used to evaluate the obtained data, namely, (i) descriptive statistics, (ii) principal component analysis (PCA), (iii) cluster analysis, and (iv) linear discriminant analysis (LDA). It was confirmed that Slovenian natural mineral water samples differ most from the German ones but are relatively similar to the Czech and Hungarian ones. Water samples from Hungary are similar to waters from the eastern part of Slovenia.

Keywords: Natural mineral water, ion determination, principal component analysis, cluster analysis, linear discriminant analysis.

1. Introduction

Certain quantities of dissolved inorganic salts are present in all natural waters, therefore the waters found in nature are mineralised. Slovenia is very rich in natural mineral water sources where, according to our investigation, about 37 naturally or artificially available sources exist. The majority of locations are situated in East Slovenia.[1,2] In this paper, mineral waters from all 37 sources are examined together with 13 sources from other parts of Europe – Hungary (2 springs), Germany (4 springs), Czech Republic (2 springs) and Western Balkan countries (countries of former Yugoslavia except Slovenia – 5 springs).

The definition and the guidelines for analyses of natural mineral waters were issued by the EEC in Brussels as the Council Directive 80/777/EEC on the harmonization of the regulations covering the exploitation and marketing of natural mineral waters.[3] Mineral waters are defined as follows: (i) the waters that originate in underground water table or deposit and emerge from a spring, tapped at one or more natural or bored exits, (ii) they differ from drinking water by their mineral content, trace elements, and other constituents, and by the original state, (iii) the waters must be microbiologically wholesome, protected from all risk of pollution.

Drinking water could be considered as natural mineral water but in most cases drinking water is technologically processed and does not fulfil the condition (ii). To determine water as "natural mineral water" its temperature is very important. Waters with temperatures above 20 °C are called thermal waters. Waters with a proven physiological effect are called healing waters. Healing effects on humans have to be determined by physical-chemical analysis and confirmed by an expert balneologist.[4]

So far, the investigations have shown that mineral waters considerably differ in mineralization (expressed as conductivity) and temperature. Many studies were performed from the balneological point of view. Regardless of the total mineralization, mineral waters are classified

according to the concentration of major cations and anions (quantity share above 20 milliequivalent %).[5,6] Milliequivalents, as non-SI units, are allowed to express the results of water analysis (the balneological structure of water).[7]

In the present work, a more detailed classification and comparison of different natural mineral water samples using statistical and chemometric methods will be shown.

2. Experimental

Waters from 50 springs were analysed for the cation concentrations (Ca^{2+}, Mg^{2+}, Na^+, K^+, NH^{4+}, Fe^{2+}, Mn^{2+}) and anion concentrations (F^-, Cl^-, I^-, NO_3^-, SO_4^{2-}, HCO_3^-), pH, temperature, conductivity and CO_2 content. The results of analysis of mineral waters from Germany and Western Balkan countries were obtained from literature.[8,9]

2.1. Sampling

The ISO standard method was used for sampling.[10] Water samples were collected in polyethylene bottles. All glass and plastic ware used for sampling and analysis was rinsed with milli-Q water and filtered through glass-fibre filters. All measurements were performed the very day the samples were collected.

2.2. Instruments and Reagents

Ion chromatograph Dionex and spectrophotometer Perkin-Elmer were used for the determination of ions specified below. WTW conductivity meter and Orion pH meter were used for conductivity and pH measurements, respectively. All used reagents were analytical grade. The milli-Q system was used to prepare ion-free water.

2.3. Analytical Methods

The samples were filtered prior to the analysis. Most anions were determined by the ISO standard method using ion chromatography.[11] Ammonium and nitrate were determined spectrophotometrically. For the ammonium determination, the reaction with salicylate and hypochlorite ions in the presence of sodium nitrosopentacyanoferrate was used; 2,6-dimethylphenol was used as a reagent to determine nitrate.[12,13] Iron was also determined spectrophotometrically using the reaction of iron(II) with *o*-phenantroline; manganese was determined by the reaction of manganese(II) with ammonium peroxodisulphate in acidic solution with spectrophotometric final determination using absorption of Mn(VII) at 530 nm.[14,15] Sodium and potassium were determined using flame emission spectrometry.[16] Calcium, magnesium and sulphate were determined using EDTA titrations.[17-19] Hydrogen carbonate was determined following the standard method.[20] Conductivity and pH were measured using standard methods.[21,22]

2.4. Data Analysis

Fifty mineral water samples were characterized by 17 physical-chemical variables: pH, temperature, conductivity and CO_2 mass concentration, cation (Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, Fe^{2+}, Mn^{2+}) as well as anion mass concentration (F^-, Cl^-, I^-, NO_3^-, SO_4^{2-}, HCO_3^-). These variables, measured for all mineral water samples, create column

Table 1. Data of 50 mineral waters examined by 17 different chemical and physical measurements.

No	pH	Temp	Ca	Mg	Na	K	NH$_4$	Fe	Mn	F	Cl	I	SO$_4$	HCO$_3$	NO$_3$	CO$_2$	Cond
1	6.50	19.0	220	95.1	480	75.0	2.97	0.05	0.25	0.42	47.5	0.01	89.2	2370	0.22	4460	4943
2	6.10	26.6	129	46.2	435	39.5	3.00	3.00	0.30	1.60	60.7	0.09	9.9	1780	0.10	1290	2260
3	8.40	40.0	173	142	2215	142	2.67	3.50	0.30	1.33	160	0.44	179	7527	0.15	1160	8800
4	6.80	19.0	410	1080	1630	11.0	0.01	0.60	0.06	0.17	74.4	0.08	1845	8430	0.10	4400	6200
5	6.00	19.0	105	98.0	181	2.5	0.02	0.09	0.02	0.24	8.0	0.03	214	890	2.70	3950	1400
6	7.10	53.0	28.6	13.0	1650	31.0	3.90	0.05	0.01	7.50	470	0.01	1263	2135	0.45	277	6720
7	8.30	40.0	16.0	7.0	121	2.5	0.40	0.20	0.05	0.45	7.0	0.01	21.0	323	0.50	1	470
8	7.55	42.0	54.3	36.9	26.0	3.1	0.01	0.01	0.01	0.27	6.4	0.10	49.0	323	0.05	20	564
9	7.60	26.0	50.0	27.3	25.0	2.3	0.01	0.30	0.006	0.48	3.4	0.01	68.0	260	0.10	20	420
10	7.60	26.0	54.0	30.0	3.0	0.9	0.01	0.05	0.005	0.14	1.3	0.01	30.0	290	1.40	20	620
11	7.50	34.6	54.2	27.6	13.2	0.2	0.38	0.30	0.01	0.21	5.1	0.01	43.7	277	1.90	1	460
12	7.50	34.2	51.3	27.5	10.8	0.2	0.31	0.40	0.01	0.21	4.6	0.01	39.1	269	1.40	1	430
13	7.80	56.0	7.9	0.9	400	6.3	2.40	0.13	0.01	0.10	56.3	0.01	1.0	762	1.00	1	1360
14	7.20	72.0	17.9	8.7	3600	180	0.02	0.23	0.02	2.10	1666	1.50	210	6954	0.50	350	12100
15	7.20	72.0	76.8	27.1	4800	195	0.08	0.30	0.40	2.10	4963	7.80	214	4651	1.50	300	20200
16	7.20	71.0	91.9	19.4	2757	382	0.02	0.40	0.02	1.80	643	0.30	197	7027	0.10	250	9600
17	7.90	62.0	3.6	4.3	320	5.9	1.40	0.20	0.12	0.47	142	0.10	2.4	717	11.0	14	2030

No	pH	Temp	Ca	Mg	Na	K	NH$_4$	Fe	Mn	F	Cl	I	SO$_4$	HCO$_3$	NO$_3$	CO$_2$	Cond
18	7.90	49.0	5.3	1.3	310	9.6	3.40	0.30	0.15	1.18	16.0	0.01	1.0	830	0.10	44	1199
19	7.60	49.0	5.0	1.0	350	5.8	3.10	0.30	0.10	0.57	11.6	0.01	2.3	860	0.10	1	1100
20	6.58	48.0	28.6	12.8	950	89.0	6.30	0.18	0.05	1.29	167	0.15	50.0	2367	0.35	808	2800
21	6.90	50.0	14.4	5.7	1196	110	10.5	0.50	0.05	0.99	152	0.13	1.0	3201	0.40	350	2600
22	7.90	43.0	4.2	14.9	513	8.1	5.10	1.70	0.04	2.10	68.0	0.005	0.50	1320	4.10	1	2800
23	8.20	43.0	3.8	15.4	494	8.1	5.80	0.55	0.016	2.50	75.0	0.006	0.50	1253	4.50	1	2570
24	9.70	33.0	4.0	2.9	150	0.9	0.01	0.09	0.009	2.80	74.0	0.17	25.7	213	1.40	77	539
25	7.95	54.0	5.4	2.2	306	13.5	3.80	0.18	0.01	0.83	17.7	2.30	0.96	945	1.20	20	1360
26	8.80	56.0	11.7	3.9	2684	30.0	15.7	4.70	0.01	4.18	2259	2.70	38.7	3343	0.10	10	9800
27	8.07	54.0	5.4	1.1	318	16.5	4.00	0.10	0.01	0.86	15.9	2.70	0.96	960	5.20	9	1360
28	7.40	36.3	74.8	22.2	0.3	0.1	0.32	0.20	0.01	0.17	1.4	0.01	18.8	318	0.26	1	440
29	8.40	35.0	54.3	19.1	5.8	2.0	0.16	0.01	0.01	0.63	4.2	0.01	20.0	243	1.50	1	360
30	7.05	25.5	40.0	28.5	1.2	0.5	0.10	0.10	0.05	0.10	2.1	0.01	0.48	263	1.40	9	360
31	7.39	33.8	55.0	30.4	3.8	1.9	0.02	0.01	0.01	0.24	3.2	0.01	19.7	302	1.10	44	450
32	7.44	28.0	61.4	14.4	3.4	1.0	0.01	0.01	0.01	0.01	3.6	0.01	30.7	223	1.90	44	390
33	7.20	34.0	58.4	35.1	1.7	1.6	0.28	2.66	0.02	0.24	3.7	0.001	0.90	356	3.60	22	410
34	7.80	30.0	360	184	2630	100	1.28	0.02	0.01	3.60	4559	0.20	809	232	0.10	1	11770
35	8.80	42.0	5.3	1.8	205	8.0	0.01	0.20	0.01	0.49	2.3	0.01	1.0	577	0.01	1	766
36	7.20	29.6	59.2	33.4	12.0	1.2	0.01	0.05	0.005	0.01	2.0	0.01	8.6	348	1.00	22	440
37	7.70	81.0	36.0	13.0	8214	230	20.0	0.01	0.01	0.01	11730	0.10	128	2082	0.10	1	43200
38	6.30	19.0	283	65.8	249	16.0	0.10	3.40	0.40	2.93	181	0.16	0.23	1602	1.00	1225	2450
39	6.90	48.0	314	153	40.0	50.0	1.00	0.30	0.20	2.00	32.0	0.10	576	1135	0.10	440	2090
40	7.60	48.0	136	47.5	1810	58.0	12.0	0.15	0.10	1.40	2420	5.40	121	1650	0.10	733	5200
41	7.39	96.0	136	28.5	4000	88.5	10.6	0.40	0.10	4.10	5010	10.0	69.0	2310	0.10	94	12083
42	6.90	20.0	49.0	27.5	3.8	1.0	0.10	0.01	0.01	0.01	9.6	0.01	22.0	280	0.15	7700	460
43	6.80	20.0	58.5	26.7	5.8	1.0	0.10	0.01	0.01	0.10	14.0	0.10	20.0	283	0.38	7800	476
44	6.80	20.0	23.1	12.6	3.6	1.0	0.10	0.01	0.01	0.10	9.1	0.10	14.5	105	10.8	7900	190
45	6.80	20.0	118	67.0	5.9	1.0	0.10	0.01	0.01	0.10	4.8	0.10	30.3	710	0.30	7550	1048
46	6.80	19.0	78.0	16.2	1085	69.0	0.10	0.31	0.18	4.58	19.4	0.10	13.5	3295	1.00	3636	5217
47	6.80	19.0	85.0	60.0	589	70.0	0.10	0.02	0.04	2.07	39.0	0.10	4.0	2161	0.50	3380	3162
48	6.70	19.0	10.5	2.0	1188	55.0	0.10	0.31	0.06	4.20	68.0	0.10	177	3130	0.10	2700	4817
49	6.70	19.0	82.5	13.7	998	34.5	0.10	0.10	0.17	14.4	137	0.10	38.8	2703	0.10	2180	4413
50	6.80	19.0	25.3	20.1	370	6.5	2.00	0.10	0.01	0.30	229	1.60	53.8	716	0.10	4000	1503

vectors of the data matrix for further chemometrical analysis. All studied data are shown in Table 1. The names of the variables are listed in this table in the same form as they are used in the software calculations. Temperature is measured in °C, conductivity in μS, all 14 concentrations are expressed in mg L^{-1}.

The results of all measurements were statistically evaluated to obtain the mean and median values, standard deviations, minimal and maximal values of all measured variables and their pair correlation coefficients. Principal component analysis, cluster analysis, and linear discriminant analysis were applied for grouping the natural mineral water samples in the multidimensional space defined by the respective measured variables.

The samples of mineral water were classified according to the country of origin: 1 – Slovenia (sample no. 1–37), 2 – Czech Republic (sample no. 38, 39), 3 – Hungary (sample no. 40, 41), 4 – Germany (sample no. 42–45) and 5 – samples from the Western Balkan territory (sample no. 46–50).

All calculations were performed using Teach/Me and Statgraphics Plus software.[23,24]

3. Results and Discussion

3.1. Statistical Screening of Data

After determining the mean and median values and the standard deviations, the correlation table was calculated for all pairs of the measured variables.

The maximal pair correlation coefficient was found between the sodium mass concentration and conductivity ($r = 0.97$). This high correlation was proved also by the graph of the conductivity vs. sodium concentration dependence where some natural grouping of mineral water samples was revealed. However, such dependence is not suitable for a distinct representation of the groups of the studied mineral waters. A strong correlation ($r \geq 0.90$) was also found between the sodium and chloride ions content as well as between the chloride concentration and conductivity.

3.2. Cluster Analysis

The aim of cluster analysis (CA) is the recognition of groups of objects (clusters) based on their similarity,

which is given, by the distances between the objects in the multidimensional space of the chosen variables using appropriate metrics. The similarities among the objects and their clusters are represented by a dendrogram. It can be seen in Figure 1 that the cluster formation depends on the origin of natural mineral water samples. Close groups are formed from the water samples from Germany, Slovenia and Western Balkan territory. Water samples from the Czech Republic and Hungary are not very much different from Slovenian waters. Sample number 37 differs significantly from all other samples – as indicated by the longest distance projected to the horizontal axis. Due to a great depth of the borehole, the spring temperature and consequently the content of the dissolved salts are considerably higher.

Using Euclidean distance, five clusters plus the above mentioned sample 37 are observed in Figure 1. The samples grouped in cluster D (fourth from the top) are most similar – the samples 18–39 are connected at a low distance level. This main, largest cluster D contains most of Slovenian samples and the two examined Czech samples (38, 39). Cluster C (third from the top), containing mostly Western Balkan samples (46–49) plus one Hungarian (40) and two Slovenian samples (6, 1), and cluster E (fifth from the top), containing all German samples (42–45), one Slovenian (5) and one Western Balkan (50) sample are somewhat similar to the main cluster D. Cluster B (second from the top), containing only Slovenian samples (4, 14, 3, 16), is less similar to the main cluster D. Cluster A (first from the top), containing three Slovenian (15, 26, and 34) and one Hungarian sample (41), is least similar to other clusters. It is evident that the similarity among the samples, as expressed by the dendrogram in Figure 1, depends significantly on the geographic factor.

3.3. Principal Component Analysis

Principal component analysis (PCA) calculates latent, new variables by a combination of the original variables, representing the multidimensional data structure in an optimal way. The direction of the first principal component, PC1, to which the studied objects are projected, is calculated in the way that the maximum variance of the studied objects is preserved. Then the second principal component, PC2, orthogonal to the PC1, is calculated using the same principle so that it again preserves the maximum possible residual variance. Further principal components (PCs) can be determined just continuing this concept.[25–27] Similarly to the calculations in cluster analysis, no prior assignment of the objects to some categories is needed to calculate the principal components. The principal component analysis and most cluster analysis techniques therefore belong to the methods of unsupervised learning.
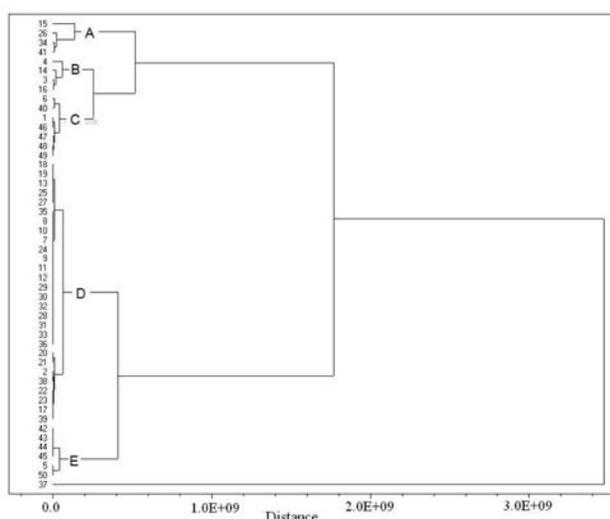
Figure 1. Complete linkage clustering (furthest neighbour) of the studied mineral water samples using Euclidean distance metrics.

PCA of the studied 50 natural mineral water samples was performed in order to get an overall impression about assembling the samples in a multidimensional space defined by the chosen physical and chemical variables. A matrix composed of 50×17 elements was created for the studied problem; 50 rows represent natural water samples and 17 columns represent the chosen variables. The original data were pre-processed using auto-scaling of the data (column standardization). With this procedure, the mean of the column elements is subtracted from all individual elements and divided by the column standard deviation. Consequently, each auto-scaled column has a zero mean and a unit variance. The percentage of the total variance, corresponding to the resulting eigenvalues and indicating information content of the individual PCs, are shown in Table 2.

It was observed on the PC2 vs. PC1 scatterplot (not shown) that the samples of mineral water from the Czech Republic, Germany and the Western Balkan territory are relatively close together, but these groups are located in the group of Slovenian samples so that no distinct assignment of the samples to the geographical territory is possible using the principal component analysis. This observation is valid irrespective of the projection plane constructed by the pair combinations of the most important principal components.

The loading/loading plot resulting from the PCA of the natural mineral water samples and showing the mutual position of 17 original variables is shown in Figure 2. It can be seen that the first principal component, PC1, is associated mainly with the sodium mass concentration (Na), conductivity (Cond) and chloride mass concentration (Cl), which are closely correlated as described above. The second principal component, PC2, is represented mainly by the calcium mass concentration (Ca), followed by the magnesium mass concentration (Mg); both negatively correlated to the PC2.

PC	Variance (%)	Variance (cumulative %)	PC	Variance (%)	Variance (cumulative %)
1	30.15	30.15	9	3.87	92.67
2	18.88	49.02	10	2.68	95.35
3	9.35	58.38	11	1.53	96.87
4	8.23	66.60	12	1.36	98.23
5	6.24	72.48	13	1.00	99.23
6	5.64	78.48	14	0.53	99.76
7	5.36	83.85	15	0.19	99.96
8	4.95	88.80	16	0.04	100.00

Note: Eigenvalues of first five principal components (PCs) were found larger than 1, which indicates that they are significant.
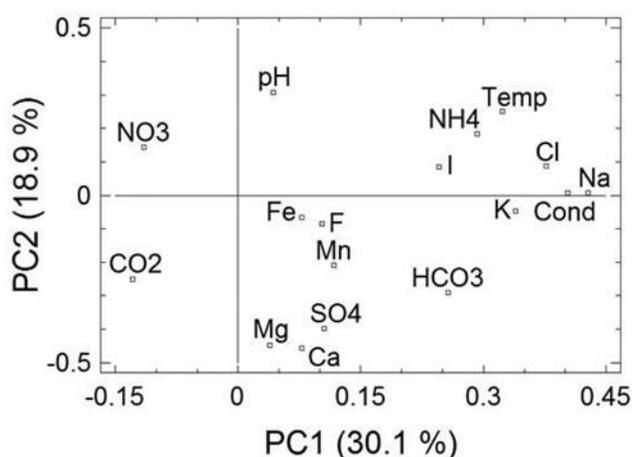
Figure 2. PCA loading/loading plot in the PC2 vs. PC1 plane using autoscaled (i.e. standardized) data.

3.4. Linear discriminant analysis

Linear discriminant analysis (LDA) belongs among the supervised pattern recognition techniques and its aim is to assign objects to one of the pre-determined classes. The procedure is designed to develop a set of discrimination functions that enable prediction of the class for any unclassified object (mineral water) based on the respective values of the chosen quantitative variables.[28]

Fifty objects and selected predictor variables were used to develop a linear discriminant model discriminating five classes representing 5 geographical territories (1 – Slovenia, 2 – Czech Republic, 3 – Hungary, 4 – Germany, 5 – Western Balkan). Four discrimination functions were calculated and all were statistically significant at the 95% confidence level (with the *p*-values less than 0.05). For discrimination of the samples according to the country of origin, the LDA yielded a 98% classification success when using all 17 originally available variables. However, it was discovered by stepwise variable selection that actu-

ally only 9 variables were needed to reach the same classification success: calcium, ammonium, fluoride, chloride, iodide, hydrogen carbonate, and carbon dioxide mass concentrations, temperature and conductivity. As shown in Figure 3, Slovenian water sample (number 5) was misclassified; it does not belong into the group of Slovenian springs but to the samples from the Western Balkans territory.

The header of Table 3 shows cumulative percentage of all four discriminant functions. Since they are hierarchical, the first two discriminant functions (DF1 and DF2 used in Figure 3) contain almost 90% of total information and are well representing the sample categorization, which, in fact, is fully described by a four-dimensional space (DF1 to DF4).

The importance of original variables with respect to individual DF's is expressed by the standardized discriminant function coefficients, collected in Table 3. Another way how to express it is constructing an LDA biplot, which is more instructive but less quantitative. For a detailed interpretation of the achieved results we will use therefore Table 3 together with Figure 3. As shown in Figure 3, DF1 is used for discrimination of all classes except class 3, which is separated from others by DF2. The most influencing variables for a particular DF are represented by the underlined coefficients in Table 3. Therefore Cl, Na, HCO3, and Cond are most important for DF1.

As can be seen, almost the same variables are very important for DF2 as for DF1. Temp is most important for DF3 and Cond for DF4, however, their impact on the discrimination of mineral water classes is pretty low (10% altogether) since it is given by a combination of two factors: relative percentage valid for the given DF (e.g. 14.5% for DF2) and the value of the standardized discriminant function coefficient (SDFC).

Taking into account the previously described way of interpretation, it is possible to characterize the studied classes of mineral water samples more in detail. Class 3, situated at lowest DF2, is characterized by high Cl, HCO3 and SO4 values (with negative SDFC's) and also high Na,
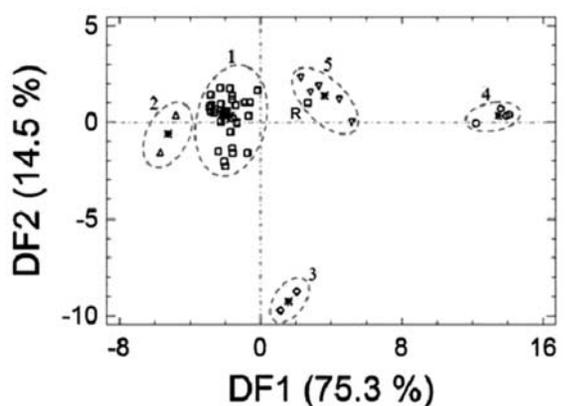
Figure 3. Linear discriminant analysis of mineral water samples using the plane of discrimination functions DF 2 vs. DF 1. Selected nine best variables are indicated in the text. The sampling territory is given by numbers used in legend to Figure 1. The object "R" belongs to class 1 but was classified into class 5. Class centroids are marked by the * symbol.

Classes
- 1 - Slovenia
- 2 - Czechia
- 3 - Hungary
- 4 - Germany
- 5 - W. Balkan

typical for class 2 but with regard to low SFDC's they have a minor effect on its position along the DF1. Class 4, situated on the negative side of the DF1, has an exceptionally high CO_2 values. Class 5, closest and left to the "reference" class 1, has typical high values of HCO_3 and F (negative SDFC's). Class 1 has an exceptionally high median value of pH, however, it is of minor importance with respect to the DF's.

The sample number 37, taken in Ljutomer in Slovenia, differs very much from all other samples by extra large values of Temp, Na, Cl, NH_4 and Cond. It might be caused by a large borehole depth, which is related to high spring temperature, conductivity and total mineral content.

4. Conclusions

The goal of the presented work was to discover relationships among chemical composition, physical properties and the water sampling area. Sample characteristics, typical for the given territory, were discovered and described. Qualitative pictorial representations were made by principal component analysis and cluster analysis, which showed natural grouping of the samples. On the other hand, quantitative interpretation is based mainly on the results of linear discriminant analysis. Slovenian natural mineral water samples differ mostly from the German ones. The samples from the Western Balkan territory and the Czech samples are most similar to Slovenian ones. Hungarian mineral water samples are less similar to the Slovenian samples, even though they are more similar to mineral waters sampled in the eastern part of Slovenia, where the Pannonian sea used to be located.

Cond and Mg (positive SDFC's). According to the median values, which we calculated for all variables and all classes, high Temp, K, NH_4 and I values, found for class 3, were not reflected in the class position with respect to the DF2 due to low SDFC's. The spread of four remaining classes along the DF1 axis can be explained by the differences of class 4, class 5 and class 2 with respect to the most populated class 1 (Slovenian springs). Class 2 is characterized by high Mg and Ca values (positive SDFC's) as well as SO_4 (negative SDFC), which has an opposite effect. High median values of Mn and Fe are also

Table 3: Standardized discriminant function coefficients.

Variable	DF1 (75.3%)	DF2 (89.7%)	DF3 (96.6%)	DF4 (100.0%)
pH	0.01	0.26	0.12	–0.38
Temp	–1.14	–0.67	1.79	–0.08
Ca	3.66	0.43	1.06	1.11
Mg	5.28	3.69	–0.70	–0.52
Na	32.49	17.68	–1.25	–1.74
K	0.27	0.86	–0.22	–0.48
NH_4	0.93	–0.77	–0.34	0.08
Fe	–0.31	0.46	0.68	–0.17
Mn	0.35	0.01	0.33	–0.12
F	–1.12	–0.14	–0.48	0.65
Cl	–33.17	–18.77	0.24	–1.72
I	0.39	–0.47	–0.61	0.35
SO_4	–3.10	–1.76	0.51	–0.64
HCO_3	–16.18	–9.98	–0.63	0.16
NO_3	0.30	0.04	–0.04	–0.09
CO_2	–2.38	–0.04	0.53	–0.10
Cond	6.19	5.11	0.45	3.35

Note: Relative percentages, corresponding to discriminant functions, are: 75.3, 14.4, 6.9, and 3.4%.
The variables most important for discriminating classes are marked by bold faces.

6. References

1. P. Kralj, *Slovene mineral and thermal waters in economy and science*. IIIrd conf. Geološki zavod Ljubljana, Ljubljana, **1992**.
2. M. Penič, *J. Haz. Mat.* **1994**, *37*, 101–105.
3. EEC Council Directive 80/777/EEC on the approximation of the laws relating to the exploitation and marketing of natural mineral waters. *Official J. Europ. Commun.* 229/10, **1980**.
4. L. A. Hütter, *Laborbücher Chemie, Wasser und Wasserunter-suchung*. 2nd Ed. Verlag Moritz Diesterweg, Aarau, **1984**.
5. V. Čoh, *Sodobno kmetijstvo* **1995**, *28*, 487–491.
6. M. Simonič, *Contribution to the Hydrochemistry and the Application of Thermal Waters in Pomurje*. Ph.D. Thesis, Department of Analytical Chemistry, University of Maribor, **1998**.
7. P. Glavič, *International unit and symbol system* / Mednarodni sistem merskih enot in znakov (in Slovenian). Tiskarna tehniških fakultet, Maribor, **1997**.
8. *Pregled prirodnih mineralnih voda Jugoslavije*. Zbornik radova, Letopapir Čačak, Beograd, **1985**, pp. 36–53.
9. M. Sigmund, *Wasser – Trinkwasser – Mineralwasser – Wassergesundheit*, Web page: (Sept. **1998**).
10. *ISO 5667-11 Water quality – Sampling Part 11: Guidance on Sampling of Ground Waters* **1992** (E), International organization for standardization / Technical Committee ISO/TC 147 / Switzerland.
11. *ISO 10304-1 Water quality, Determination of Dissolved Anions by Liquid Chromatography* **1996** (E), International organization for standardization / Technical Committee ISO/TC 147 / Switzerland.
12. *ISO 7150/1 Water quality, Determination of Ammonium* **1984** (E), International organization for standardization / Technical Committee ISO/TC 147 / Switzerland.
13. *ISO 7890/1 Water quality, Determination of Nitrate* **1986** (E), International organization for standardization / Technical Committee ISO/TC 147 / Switzerland.
14. *SIST ISO 6332 Water quality, Determination of Iron – Spectrometric method using 1,10-phenanthroline* **1996**, International organization for standardization / Technical Committee ISO/TC 147 / Switzerland.
15. *DIN 38406 E2 Water quality, Determination of Manganese – Formaldoxime spectrometric method* **1983**, International organization for standardization / Technical Committee ISO/TC 147/Switzerland.
16. *ISO 9964-3 Water quality, Determination of Sodium and Potassium,* **1993** (E), International organization for standardization / Technical Committee ISO/TC 147 / Switzerland.
17. *ISO 6058 Water quality, Determination of Calcium content – EDTA titrimetric method* **1984** (E), International organization for standardization / Technical Committee ISO/TC 147 / Switzerland.
18. *ISO 6059 Water quality, Determination of the sum of Calcium and Magnesium – titrimetric method* **1984** (E), International organization for standardization / Technical Committee ISO/TC 147 / Switzerland.
19. *SIST ISO 9280 Water quality, Determination of Sulphate* **1996**, International organization for standardization / Technical Committee ISO/TC 147 / Switzerland.
20. *SIST DIN 38409-7 Water quality, Determination of Hydrogen carbonate* **1996**, International organization for standardization / Technical Committee ISO/TC 147 / Switzerland.
21. *ISO 7888 Water quality, Determination of Electro Conductivity* **1985**, International organization for standardization / Technical Committee ISO/TC 147 / Switzerland.
22. *ISO 10523 Water quality, Determination of pH* **1994** (E), International organization for standardization / Technical Committee ISO/TC 147 / Switzerland.
23. *Teach/Me*. SDL-Software Development Lohninger; Teach/Me Data Lab 2.002, Springer, Berlin, **1999**.
24. *STATGRAPHICS Plus*. Manugistics Inc., Rockville, MD, U.S.A, **2001**.
25. I. T. Joliffe, *Principal Component Analysis*. Springer, New York, **1986**.
26. B. Flury, H. Riedwyl, *Multivariate Statistics, a Practical Approach*. Chapman and Hall, London, **1988**.
27. F. J. Manly, *Multivariate Statistical Methods*. Chapman and Hall, London, **1990**.
28. M. P. Derde, D. L. Massart, *Anal. Chim. Acta* **1986**, *191*, 1–16.

Povzetek

Analizirali smo petdeset vzorcev naravne mineralne vode iz izvirov v Sloveniji, na Madžarskem, v Nemčiji, Češki republiki in državah bivše Jugoslavije. Masne koncentracije kationov (Na$^+$, K$^+$, Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, NH$_4^+$) in anionov (F$^-$, Cl$^-$, I$^-$, NO$_3^-$, SO$_4^{2-}$, HCO$_3^-$), temperaturo izvira, pH, prevodnost in masno koncentracijo ogljikovega dioksida smo določili z uporabo standardnih analiznih metod.

Uporabili smo primerne statistične in kemometrijske metode za evalvacijo podatkov: (i) opisno statistiko, (ii) analizo glavnih komponent (PCA), (iii) analizo klastrov in (iv) linearno diskriminantno analizo (LDA). Potrdili smo, da se slovenske mineralne vode razlikujejo predvsem od nemških in da so sorazmerno podobne češkim in madžarskim. Vzorci vode iz Madžarske so podobni tistim iz vzhodne Slovenije.