

The Use of Chemical and Cluster Analysis for Studying Spring Water Quality in Świętokrzyski National Park

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Abstract

The regional and local monitoring of underground waters as well as general water resource balance studies have encompassed only individual springs in some Polish national parks. This report presents the results of cluster analysis derived from the chemical analyses of spring waters collected in Świętokrzyski (Holy Cross Mountains) National Park in 2004 and 2006. The cluster analysis technique enabled me to obtain information about similarities or differences between sampling sites. This technique also indicated that the division of waters only on the basis of their quality and chemistry was not fully substantiated and required further study.

Keywords: springs, water quality, water chemistry, cluster analysis, Świętokrzyski National Park, south-central Poland

Introduction

Springs belong to very important abiotic elements of the environment, especially in legally protected areas [1]. Like bioindicators, they react to any changes that occur in natural ecosystems [2, 3]. A decrease in the number of springs or the drop in their discharge, as well as disadvantageous changes in chemistry and quality of spring waters, indicate degradation of the environment. The quality of groundwater is controlled by combined interactive natural (including lithologic, tectonic, topographic, climatic, edaphic) and anthropogenic factors [4, 5]. This is the main reason why the springs are assigned to the best environmental geoindicators now [6].

No complex spring mapping combined with chemical and isotopic studies of spring waters have been conducted in national parks of Poland. Regional and local under-

ground water monitoring as well as general hydrologic studies have encompassed only individual springs in some of these parks. A detailed study of springs in Świętokrzyski (Holy Cross Mountains) National Park was performed in the summer 2003 through the spring of 2006.

This study presents the application of statistical analysis to better understand the groundwater circulation system in Świętokrzyski National Park. Based on the results derived from detailed element determinations performed in 2004 and 2006, the cluster analysis technique used for the purpose of this study enabled me to trace similarities or differences between sampling sites [7].

Materials and Methods

Study Area Localization and Characterization

Świętokrzyski National Park is located in the north-eastern part of Kielce province and the northern part

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of the Świętokrzyski province (south-central Poland) (Fig. 1). Established in 1950 and then enlarged in 1996, Świętokrzyski National Park is the second oldest national park in Poland. In respect of geomorphology, it is situated in the northern part of the Holy Cross Mountains occupying an area of 7,626.45 ha [8]. The axis of the park encompasses the highest range (Łysogóry) including Łysica Mt. (612 m a.s.l.) in the western part and Holy Cross (or Bald) Mt. (595 m a.s.l.) in the eastern part. The Łysogóry range belongs to medium and low mountains with relative elevations, in places exceeding 300 m.

This range is made of middle and upper Cambrian quartzite, quartzitic sandstone and siltstone with clayey shale interbeds [9]. The central and northern area of the park consists of the easternmost part of Wilków Valley and the Dębno Valley abutted to the north by the eastern Klonów Range. The last-mentioned geomorphologic unit encompasses lofty Bukowa and Psary mountains. The park also includes three northeastern enclaves: Las Serwis (Forest Service) as well as Chełmowa Mt. and Zapusty Scarp belonging to the western Pokrzywiański Range. Chełmowa Mt., which is well known for larch stands, was the first nature preserve, established in 1920 and preceding the following nature preserves: Łysica Mt. (established in 1922), Holy Cross Mt. (1922) and Bukowa Mt. (1932). The basement of the Wilków and Dębno Valleys consists of Silurian clayey shales and

graywackes covered by Pleistocene sands and tills, whereas the Klonów and Pokrzywiański Ranges are composed of Lower Devonian quartzitic sandstones, siltstones and clayey shales with tuff interbeds, locally (Zapusty Mt.) of Middle Devonian limestones and dolomites. These ranges are blanketed by loesses that in places are a few meters thick [8].

The number of permanent springs and seeps in Świętokrzyski National Park is assessed at about 60. However, their exact number is not known due to:

- (1) very low yields of many springs and
- (2) the presence of appearing and disappearing streams within thick waste mantle.

An individual stream may form alternate outflows and inflows, merge below the surface with other streams, forming a network of underground channels. The springs and seeps are not evenly distributed.

The largest numbers of springs (60%) occur on northern slopes of the Łysogóry Range, primarily due to the presence of a thick waste mantle and the northward dip of rock beds. Six springs occur close to the top of Bukowa Mt., one spring is located on the northern slope of Psarska Mt., and two springs are situated on the southern and eastern slopes of Chełmowa Mt. [1]. All these springs can be assigned to the low-yield ones not exceeding 1 cubic meter of water per hour. The springs: "Dębno" (Zr-20), "Złoty Stok" ("Golden Slope") (Zr-13)

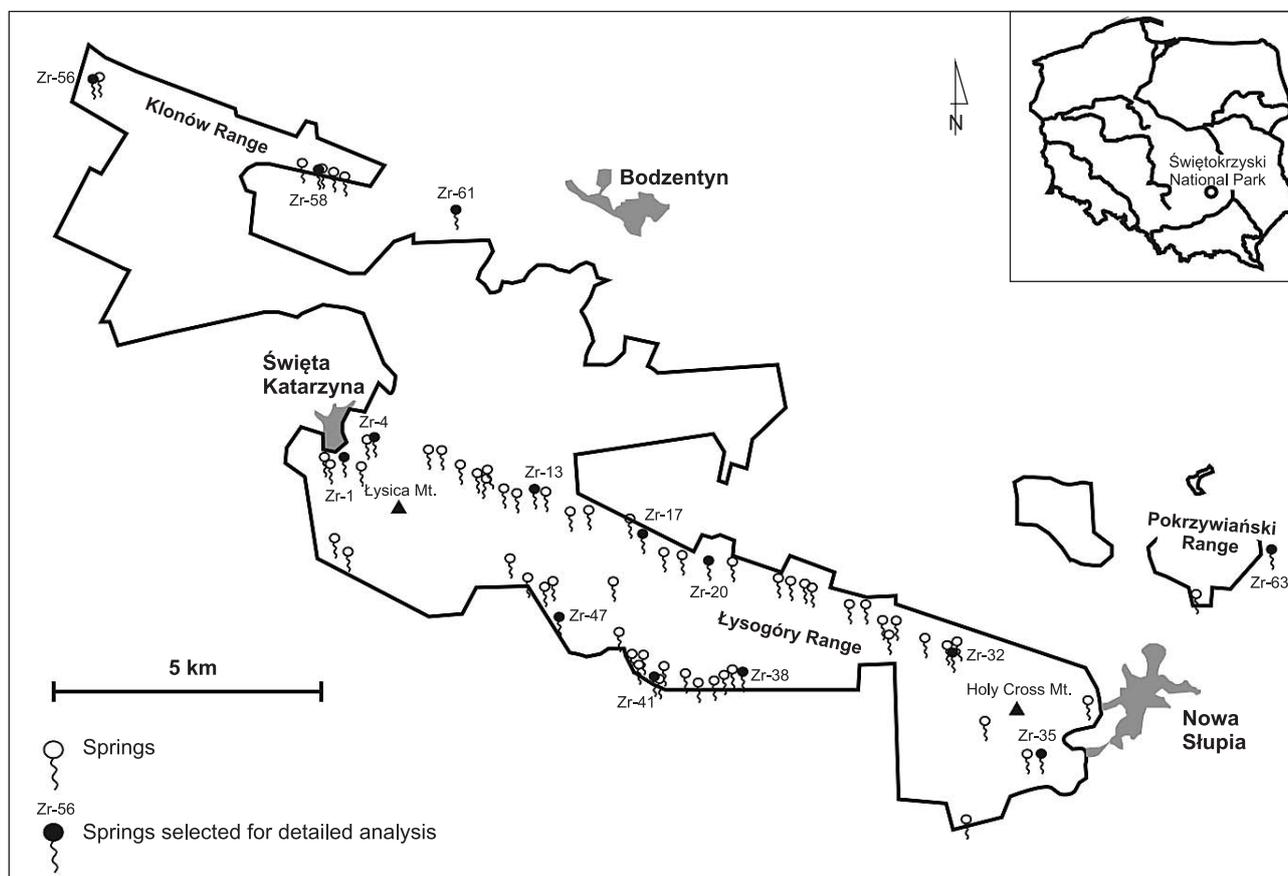


Fig. 1. Locations of permanent springs in Świętokrzyski National Park, with sampling points.

and “Saint Francis” (Zr-1) are highlighted by the highest water yields varying from 2 to 4 cubic meters per hour.

Sampling, Sample Preparation and Analysis

Water sampling for detailed element analyses was conducted in the summer of 2004 (14 springs) and the spring of 2006 (8 springs). The water samples were collected and placed in polyethylene bottles, according to recommendations made for the Geochemical Map of Europe [10]:

1. 500 mL unfiltered and unacidified water samples for major anion determinations. The analyses were made using a high-performance liquid chromatograph (Waters HPLC Ion Chrom) with a conductometric detector (Br^- , Cl^- , F^- , HPO_4^{2-} , SO_4^{2-}) and a UV detector (NO_2^- , NO_3^-). NH_4^+ was determined using a spectrophotometer UV-Vis (Varian – model Cary-1e). Besides, HCO_3^- was determined with an LF-205 spectrophotometer (Slandi, Poland).
2. The first phase of the investigation (in 2004) analyzed 30 mL filtered (membrane filter 0.45 μm) and acidified (1.5 mL HCl 1:1) water samples for determinations of 23 elements (Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, Pb, SiO_2 , Sr, Ti, V, Zn) using inductively coupled plasma-optical emission spectrometry (ICP-OES; multichannel spectrometer Jobin-Yvon – model PANORAMA with horizontal plasma). In contrast, during the second phase of investigation (in 2006) 30 mL filtered and acidified (1.5 mL HNO_3 1:4) water samples for determinations of 6 elements (Ca, Fe, K, Mg, Na, SiO_2) using an ICP-OES method and 25 elements (Ag, Al, As, B, Ba, Be, Cd, Co, Cr, Cu, Li, Mn, Mo, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, Tl, U, V, Zn) using inductively coupled plasma mass spectrometry (ICP-MS; spectrometer Elan DRC II with laser ablation attachment LSX-500). The total organic carbon (TOC) content of water was estimated using a spectrophotometer (SPF Pastel UV Secomam).
3. 100 mL unfiltered and acidified (1.5 mL HCl 1:1) for determinations of mercury using an atomic absorption spectroscopic method (AAS; Altec amalgam analyzer AMA 254).

The chemical analyses were done according to methods used for environmental samples in the Central Chemical Laboratory of the Polish Geological Institute in Warsaw. Four samples were randomly selected for routine replicate analyses, and international standards, i.e. SRM 1643e and TMDA-54.3, were inserted accordingly. Uncertainties at 0.05 probability level were about 3% for pH, 5% for EC, and 10% for the remaining species.

Statistical Analysis

Cluster analysis is the method used for finding different classes and groups within the obtained data. The clus-

ter analysis is a group of multivariate techniques whose primary purpose is to assemble objects based on the characteristics they possess [11]. The resulting clusters of objects should exhibit high internal homogeneity and high external heterogeneity. Hierarchical agglomerative clustering is the most common approach that provides intuitive similarity relationships between any sample and entire data sets typically illustrated by a dendrogram (Fig. 2) [12]. The dendrogram provides a visual summary of the clustering processes, presenting a picture of the groups and their proximity with a distinct reduction in dimensionality of the original data. The Euclidean distance usually gives the similarity between two samples, and the distance can be presented by the difference in analytical values from the samples [13]. The data derived from this study (Table 1) were originally centered by logarithmic transformation with all variables standardized later. In the case of the springs analyzed in 2004 and 2006, the arithmetic mean was used. The cluster analysis was done by means of Ward's method using squared Euclidean distances as a measure of similarity. Ward's method enables an analysis of variance approach to evaluate the distances between the clusters in order to minimize the sum of squares of any two clusters (that can be formed at each step). The spatial variability of water quality in all the examined springs was determined from the cluster analysis, using the linkage distance reported as $D_{\text{link}}/D_{\text{max}}$, which represents the quotient between the linkage distances for a particular case divided by the maximal linkage distance [14-16].

Results and Discussion

Water Chemistry

The field measurements (pH, electric conductivity, and locally redox potential) of spring waters were performed in 2003-05. They enabled identification of two seepage stream areas that differ in water chemistry and quality: (1) the Łysogóry Range and (2) the Klonów and

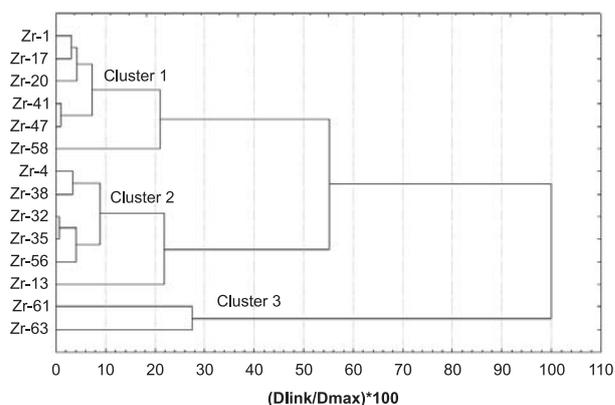


Fig. 2. Dendrogram showing clustering of springs based on chemical analyses of their waters.

Table 1. Selected water quality parameters used for water chemistry characterization and cluster analysis.

Spring	pH	EC $\mu\text{S}\cdot\text{cm}^{-1}$	T $^{\circ}\text{C}$	Total Alkalinity CaCO_3 $\text{mg}\cdot\text{L}^{-1}$	$\text{mg}\cdot\text{L}^{-1}$										$\mu\text{g}\cdot\text{L}^{-1}$							
					SO_4^{2-}	NH_4^+	NO_3^-	Cl^-	Ca	Fe	K	Mg	Na	SiO_2	Al	Ba	Cu	Li	Mn	Ni	Sr	Zn
2004																						
Zr-1	6.24	69	12.0	<0.1	5.25	<0.05	14.00	3.69	6.4	0.010	0.7	1.8	2.1	8.6	<10	12.00	7	<2	3.0	<5	16.0	29.0
Zr-4	6.01	88	12.5	<0.1	10.80	<0.05	11.90	5.58	8.6	0.010	0.7	2.4	3.0	8.5	10.0	18.00	7.00	4.00	5.0	<5	47.0	94.0
Zr-13	5.99	93	14.0	<0.1	13.20	0.05	7.68	4.23	8.2	<0.01	1.2	3.6	2.8	10.3	<10	13.00	7.00	6.00	<1	<5	36.0	84.0
Zr-17	5.95	78	14.0	3.5	7.53	<0.05	7.20	2.49	6.7	<0.01	0.7	3.4	1.9	9.8	10.0	5.00	5.00	4.00	1.0	<5	11.0	160.0
Zr-20a	5.78	67	12.5	<0.1	5.43	0.05	8.42	3.28	5.5	0.03	1.0	2.1	2.1	8.9	30.0	15.00	3.00	2.00	7.0	<5	11.0	135.0
Zr-20b	5.81	65	15.5	<0.1	6.11	<0.05	8.22	2.98	5.8	<0.01	0.9	2.3	2.1	9.3	20.0	15.00	<2	2.00	6.0	<5	11.0	136.0
Zr-32	5.25	83	13.5	<0.1	16.20	<0.05	10.10	3.56	7.7	<0.01	0.6	1.8	2.0	8.3	210.0	54.00	<2	<2	49.0	6.0	38.0	140.0
Zr-35	5.70	71	11.0	<0.1	3.18	<0.05	11.80	4.47	6.8	<0.01	0.6	1.3	2.5	11.4	40.0	14.00	<2	<2	2.0	<5	18.0	139.0
Zr-38	5.58	67	12.0	<0.1	14.00	<0.05	1.70	3.20	6.1	<0.01	0.4	1.7	2.1	9.5	280.0	29.00	<2	<2	115.0	<5	24.0	57.0
Zr-41	5.74	65	10.5	3.5	4.07	<0.05	5.33	1.94	6.4	<0.01	0.5	2.4	1.9	8.6	10.0	6.00	<2	<2	1.0	<5	14.0	16.0
Zr-47	6.59	107	12.0	<0.1	27.10	<0.05	5.38	3.91	11.0	0.02	1.3	2.8	2.9	14.6	60.0	37.00	3.00	2.00	18.0	7.0	42.0	22.0
Zr-56	6.38	132	13.0	49.0	5.17	<0.05	1.74	2.18	13.1	<0.01	2.4	7.1	1.7	10.4	30.0	11.00	<2	6.00	11.0	<5	30.0	8.0
Zr-58	5.17	192	14.5	<0.1	56.30	<0.05	11.50	6.28	19.0	<0.01	1.8	5.7	3.0	15.2	430.0	42.00	2.00	9.00	761.0	52.0	89.0	132.0
Zr-61	6.79	497	13.5	255.0	13.20	0.09	0.03	7.34	78.4	0.75	1.5	22.6	6.9	16.0	<10	83.00	<2	6.00	421.0	<5	142.0	<3
2006																						
Zr-1	5.23	33	11.5	3.5	5.60	<0.1	13.80	3.20	6.3	0.010	0.7	1.8	2.0	8.6	8.8	13.84	15.78	2.01	5.0	5.3	16.8	82.0
Zr-13	5.44	50	9.0	13.9	11.40	<0.1	8.30	<2.0	7.6	<0.01	0.8	3.4	2.5	10.2	6.7	14.27	1.17	5.61	0.9	2.2	37.5	86.0
Zr-20	5.15	50	9.5	6.9	5.50	0.10	9.40	<2.0	5.2	<0.01	0.7	2.0	1.7	8.8	23.2	14.97	1.52	2.18	2.2	2.5	10.5	140.0
Zr-32	5.10	52	9.0	<0.1	7.30	0.10	9.20	8.10	5.2	0.020	0.9	1.3	2.1	7.9	41.5	22.83	1.33	0.74	6.8	1.1	23.4	30.0
Zr-41	5.42	47	11.5	6.9	4.10	<0.1	6.40	<2.0	6.2	0.010	0.6	2.3	1.8	8.5	4.2	6.91	0.78	2.02	1.0	1.0	15.3	19.0
Zr-58	5.59	126	7.5	24.0	45.00	<0.1	12.20	7.30	19.4	0.020	1.7	6.9	5.0	12.8	12.9	26.96	2.01	8.50	19.1	25.4	55.4	26.0
Zr-61	6.74	413	10.0	288.0	11.40	0.30	<0.5	5.50	73.0	0.850	1.3	20.1	6.0	14.5	5.1	84.37	0.79	5.90	358.3	<0.5	128.5	11.0
Zr-63	6.47	589	11.0	407.0	24.00	0.10	9.10	9.10	108.1	0.050	2.7	24.7	9.1	11.9	2.5	77.34	2.49	14.78	1.9	1.4	277.0	16.0

Uncertainty at 0.05 probability level is about 3% for pH, 5% for EC, and 10% for the remaining species

partly Pokrzywiański Ranges. The spring waters of the Łysogóry Range show relatively low pH with a 3-year geometric mean of 5.69, very low conductivity (mean $73 \mu\text{S}\cdot\text{cm}^{-1}$), and relatively fixed redox potential (mean 302 mV). In contrast, the spring waters of Bukowa Mt., Psarska Mt. and Chełmowa Mt. show somewhat raised values of pH (mean 6.07) and a three times higher conductivity (mean $224 \mu\text{S}\cdot\text{cm}^{-1}$). A relatively small area of Świętokrzyski National Park excludes a considerable diversity in rainwater chemistry. This evidence suggests that the main reason for higher pH and conductivity values of spring waters is the specific geologic setting of the area examined. The bedrock of the northern ranges of the park consist of sandstones with clayey shale and tuffite interbeds, limonite and siderite inclusions, and intercalations, as well as dolomite and local limestone series, and loess covers [9]. Some of these rocks show buffering capacity and potential as a source of various ions.

The results derived from the detailed chemical analyses confirmed the diverse chemistry of spring waters in the Łysogóry Range versus the Klonów and Pokrzywiański Ranges. The spring waters of the Łysogóry Range show very low ion concentrations with the prevalent SO_4 -Ca-Cl-Mg and SO_4 -Ca-Mg-Cl water types (Altowski-Szwiec classification)[5]. Only two springs display higher concentrations of hydrocarbonates, exceeding 20% mval, but also in this case sulfate anions prevail over hydrocarbonate ones. In contrast, the spring waters of the remaining ranges of the park show some similarities to the neighboring areas of the Świętokrzyski province with hydrocarbonates prevailing over sulfates (HCO_3 -Ca-Mg) [17]; the SO_4 -Ca-Mg water types are scarce here.

Of the trace metals, only Ba, Cu, Mn and Zn occur in somewhat higher concentrations, both in the Łysogóry Range and the northern area of the park. The spring waters of the Klonów and Pokrzywiański Ranges are highlighted by raised levels of most metals. Spring Zr-63 showed the highest concentrations of Ca, Fe, Na, SiO_2 , Cd, Mg, Ba and Sr, but most of all Mn.

The sodium-chlorine coefficient ($r\text{Na}^+/r\text{Cl}^-$) of most of the spring waters exceeds 1. This coefficient, combined with very low conductivity, indicates a strong influence of meteoric waters and simultaneously young geologic age. The highest yield springs display lower values of the sodium-chlorine coefficient, which may suggest a longer circulation of waters. In contrast to the other anions, the higher concentrations of sulfates also enable assessment of the degree of water metamorphism and the origin of spring waters. The sulfate coefficient of the examined spring waters determined by equivalent ratio $r\text{SO}_4^{2-}\times 100/r\text{Cl}^-$, varies from 26.3 (spring Zr-35) to 331.1 (Zr-58). This indicates a distinct predominance of shallow waters in an active exchange zone. The sulfate coefficient of seawater is 10.3. The values obtained preclude mixing of underground water with relic seawater. The infiltration origin of the underground water is also supported by the subsequent hydrogeochemical coefficient ($r\text{Na}^++r\text{K}^++r\text{Mg}^{2+}/r\text{Cl}^-$). It does not exceed 1 in the zones of dynamic and

hydrochemical stagnation. In contrast, the value above 1 indicates the origin of waters from active exchange zones and their contact with meteoric water. This coefficient varies from 6.3 to 39.2, which points up to the meteoric origin of the waters examined [18].

Cluster Analysis

Cluster Analysis yields a dendrogram (Fig. 2), grouping 14 springs into three statistically significant clusters at $(D_{\text{link}} / D_{\text{max}})\times 100 < 50$. Cluster 3 contains two spring samples from outside the Łysogóry Range. Spring Zr-63 is located close to a Holocene calcareous sinter outcrop in the Pokrzywiański Range. The spring Zr-61 of the locality Psary Stara Wieś is within the extent of the Psary – Św. Katarzyna diabase intrusion. The influence of local geologic factors (especially the bedrock lithology) is the main cause of distinct differences in chemism of the spring water examined.

Cluster 1 encompasses two of out three springs showing the largest discharge, i.e. “Saint Francis” (Zr-1) and “Dębno” (Zr-20). The consecutive two springs Zr-41 and Zr-47 reveal a steady yield with very little fluctuations during the hydrological year. Spring Zr-17 is located near spring Zr-20. These two springs display similar chemistry affected by the same geogenic factors. The springs ascribed to this cluster are located in the center of the Łysogóry Range on its northern and southern slopes. The only exception is spring Zr-1 at Łysica Mt.

Cluster 2 encompasses most of the springs scattered around the park. A little variation in the chemistry of these waters is reflected by prevailing quartzites and quartzitic sandstones in the bedrock of the park. The water of springs Zr-32 and Zr-35 in northwestern and southeastern parts of Holy Cross Mt. show a close similarity.

Spring Zr-58 appears to be similar to the springs grouped in Cluster 1. This spring is located near the village of Psary Podlesie and used by the local community. Its different chemistry may be caused by stronger influence of anthropogenic factors. Spring Zr-13 shows the largest yield of the remaining park springs, and its chemistry ranks it among cluster 2.

Cluster 3 includes two separate springs in the northern part of the park. Their chemistry seems to be influenced by some carbonate rocks of undetermined geologic position.

Conclusions

The following is a list of some of the more important conclusions of this study:

1. The chemistry of spring waters is largely influenced by the specific geologic setting of the park, especially bedrock lithology and a few-meter-thick waste mantle covering the main range slopes.
2. The hydrogeochemical coefficients show that the examined waters are of meteoric origin; no mixing with

relic or juvenile waters was recorded. In addition, these waters are young in terms of geologic time.

3. The cluster analysis of obtained data reflects greater diversity in the chemistry of spring waters from the Łysogóry Range versus the northern ranges.
4. The cluster analysis turned out to be useful for finding homogeneity groups within the data from chemical spring water analysis.

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