JAP&T
TPA-Timişoara

Available online at http://journal-of-agroalimentary.ro

Journal of Agroalimentary Processes and Technologies 2015, 21(1), 88-94

Journal of Agroalimentary Processes and Technologies

PCA multivariate analysis for concentration in macro and micro elements in mineral water samples collected from the western, central and northern Romania

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Received: 15 February 2015; Accepted: 25 February 2015

Abstract

In the present paper were statistically analyzed by PCA method the concentration values of macro and microelements from nine mineral water samples collected in western, central and northern Romania. In case of macro elements multivariate analysis PCA of data from atomic spectroscopy for mineral water samples showed a good classification of samples B and C, data variance is explained 100% of the first three principal components (47% PC_1, 49% PC_2 şi 4% PC_3). For microelements this analysis led to the good group of samples A and B, samples C are irregularly distributed. The variance explained is of almost 100% for the first principal component.

Keywords: mineral water, macro elements, microelements, Principal Component Analysis – PCA

1. Introduction

Certain quantities of dissolved inorganic salts are present in all natural waters, therefore the waters found in nature are mineralized. Drinking water could be considered as natural mineral water but in most cases drinking water is technologically processed and does not fulfill 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. [1]

Atomic absorption spectroscopy (AAS) is a spectroanalytical procedure for the quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state. In analytical chemistry the technique is used for determining the concentration of a particular element (the analyte) in a sample to be analyzed. AAS can be used to determine over 70 different elements in solution or directly in solid samples employed in pharmacology, biophysics and toxicology research. [2, 3]

For the determination of trace metals in natural and mineral waters different spectrochemical methods are used. However, flame atomic absorption spectrometry (FAAS) is one of the most extensively used techniques for determining various elements with significant precision and accuracy. This analytical technique is remarkable for its selectivity, speed and fairly low operational cost.9 However, in some cases there are many difficulties in determining traces of heavy metals in environmental samples due

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to insufficient sensitivity or matrix interferences. [4, 5]

Principal components analysis (PCA - Principal Component Analysis) forms the basis for the analysis of multivariate data. [6]

Generally the output of a PCA package is a graph which are called ‘‘scores” (equivalent to the variables) that are estimated in bilinear modelling methods where information carried by several variables is concentrated onto a few underlying variables. Each sample has a score along each model component. The scores show the locations of the samples along each model component, and can be used to detect sample patterns, groupings, similarities or differences. One of the other graphs produced using PCA are called ‘‘loadings” that are estimated in bilinear modeling methods where information carried by several variables is concentrated onto a few components. Each variable has a loading along each model component. The loadings show how well a variable is taken into account by the model components. They can be used to understand how much each variable contributes to the meaningful variation in the data, and to interpret variable relationships. They are also useful for interpreting the meaning of each model component. [7, 8]

Principal component analysis (PCA). Principal component analysis was used to provide a new set of variables (the least possible number) that were calculated in such way as to keep most of the present information in the original data set. Principal components (PCs) derived from the original data set with the eigenvalues >1.0 were used for further analysis with linear discriminant analysis. [9]

2. Material and methods

For principal component analysis (PCA) was used program “The Unscrambler 9”, trial version.
Principal components analysis (PCA) was performed in three steps:

- in the first stage have been used as input data the macro elements concentrations of sodium, potassium, calcium and magnesium and trace elements concentrations for lead, nickel, manganese, iron, copper, chromium, cadmium, obtained by atomic absorption spectrometry.
- in the second stage were used as input data the value of macro elements concentrations of sodium, potassium, calcium and magnesium obtained by the same method;
- in the third stage are used as input values of concentrations of lead, nickel, manganese, iron, copper, chromium and cadmium, obtained by the same method. [6, 7]

3. Results and discussion

Statistical results obtained behind principal component analysis (PCA).

PCA multivariate data analysis representing the concentration of macro and trace elements from mineral water samples showed a good classification for samples B and C (except B3) grouping samples into the bottom left of the graph scores (Figure 1), data variance being explained in 100% of the first three principal components (47% PC_1, 49% PC_2 and 4% PC_3).

The same group is observed better for three dimensional representation of dependence PC_3 *versus* PC_1, PC_2 (Figure 2).

It can be seen that in PC_3 representation *versus* PC_1, this group of samples is not evident (Figure 3).

For this classification are responsible the independent variables of Na and Ca concentrations in the main, the first for PC_1 and the second in specially for the PC_2 (Figure 4).

In Figure 5 is represented variance residual concentration data (macro and trace elements) for PCA analysis by atomic absorption spectrometry obtained for samples of mineral water. [6, 7]

Table. 1. The input data for the multivariate analysis PCA for macro elements concentration Na, K, Ca, Mg. (mg / L) [6]

Sample	Na	K	Ca	Mg
A1	294	9,2	133	40,5
B1	121	5,1	98	33,5
C1	1,1	0,29	76	2,7
A2	93	12,9	274	85
B2	27,4	1,1	76	32
C2	88	8,9	84	38,5
A3	19,2	3,4	330	5,4
B3	223	47,4	184	76
C3	25,1	4,7	141	45

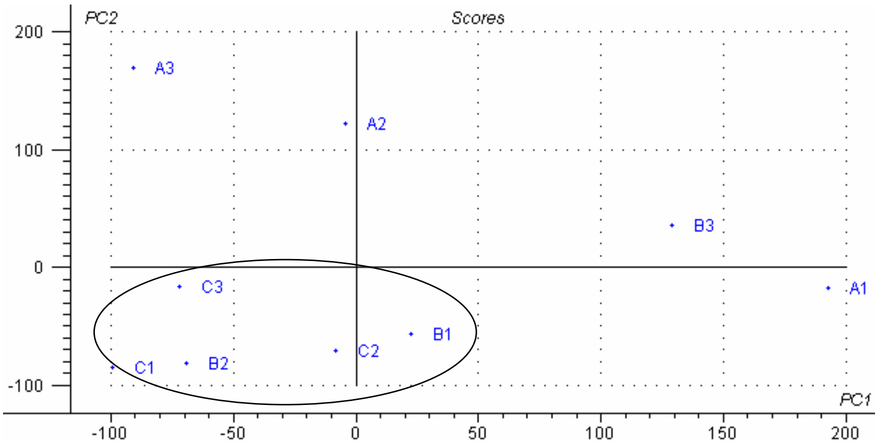

Figure 1. PC_2 vs. PC_1 scores graphic for PCA analysis using all data obtained from analysis by atomic absorption spectrometry for mineral water samples studied

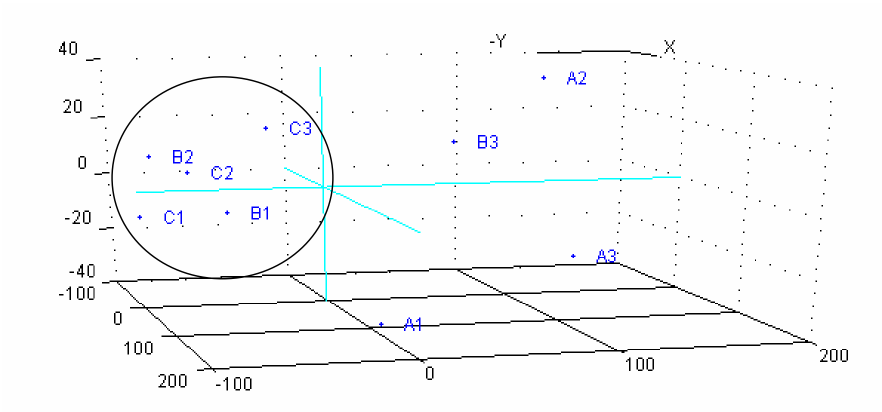

Figure 2. PC_3 vs. PC_1, PC_2 scores graphic for PCA analysis using all data obtained from analysis by atomic absorption spectrometry for mineral water samples studied

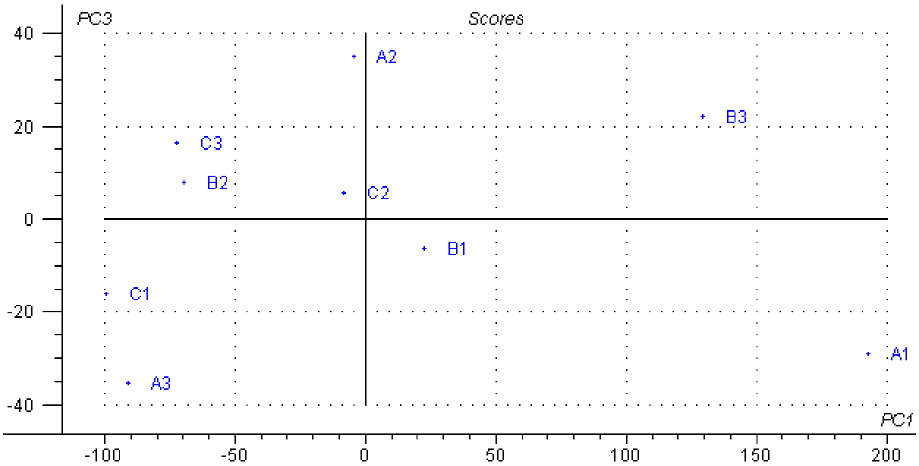

Figure 3. PC_3 vs. PC_1, scores graphic for PCA analysis using all data obtained from analysis by atomic absorption spectrometry for mineral water samples studied

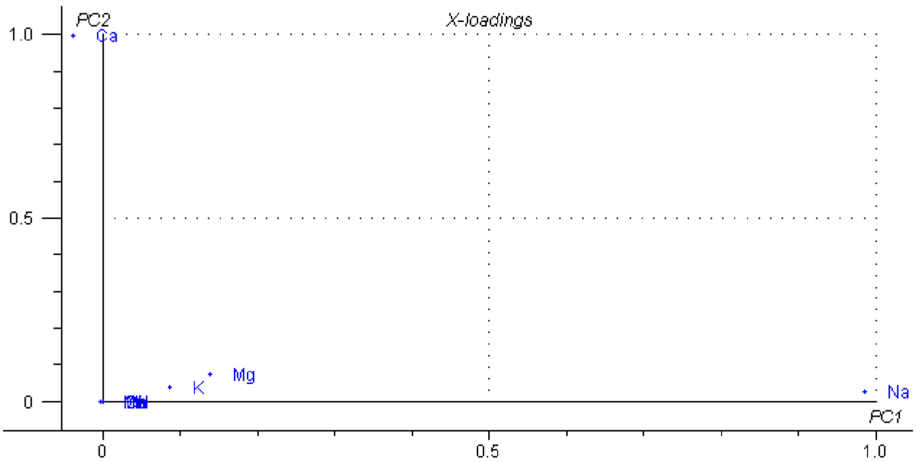

Figure 4. PC_2 vs. PC_1 records graphic for PCA analysis using all data obtained from analysis by atomic absorption spectrometry for mineral water samples studied

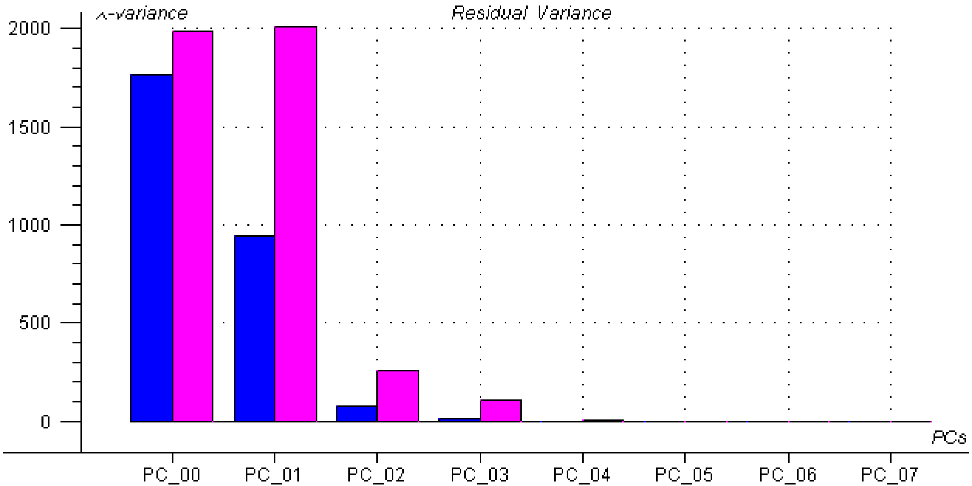

Figure 5. Residual variance for PCA analysis using all data obtained from analysis by atomic absorption spectrometry for mineral water samples studied

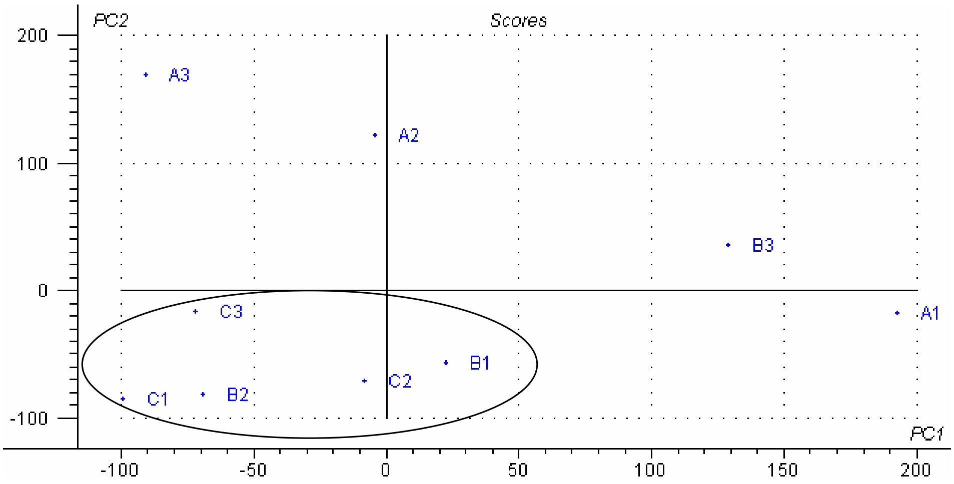

Figure 6. PC_2 vs. PC_1, scores graphic for PCA analysis using as input the macro elements concentration (Na, K, Ca, Mg) content in mineral water samples analyzed

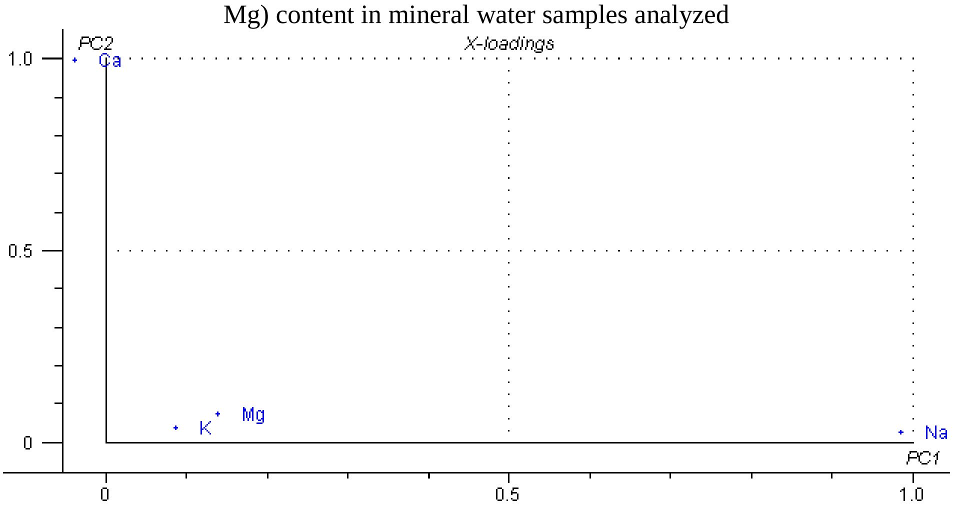

Figure 7. PC_2 vs. PC_1 scores graphic for PCA analysis using as input the macro elements concentration (Na, K, Ca, Mg) content in mineral water samples analyzed

Table. 2. The input data for the multivariate analysis PCA for trace elements concentration Pb, Ni, Mn, Fe, Cu, Cr, Cd (µg/L) [6]

Sample	Pb	Ni	Mn	Fe	Cu	Cr	Cd
A1	18,60	31,74	360	4,84	0,000	4,10	8,18
B1	5,40	12,66	327	6,00	0,000	0,000	6,05
C1	1,70	4,89	0,81	1,67	0,000	0,000	3,07
A2	6,90	21,04	144	5,07	0,000	1,35	0,000
B2	1,45	9,81	241	2,36	0,000	0,000	0,000
C2	4,27	54,15	260	1,96	0,000	1,55	0,000
A3	2,43	12,61	352	4,40	0,000	0,000	1,91
B3	9,11	14,16	334	6,25	0,000	6,13	1,13
C3	5,51	4,78	4,395	0,34	0,000	0,000	0,000

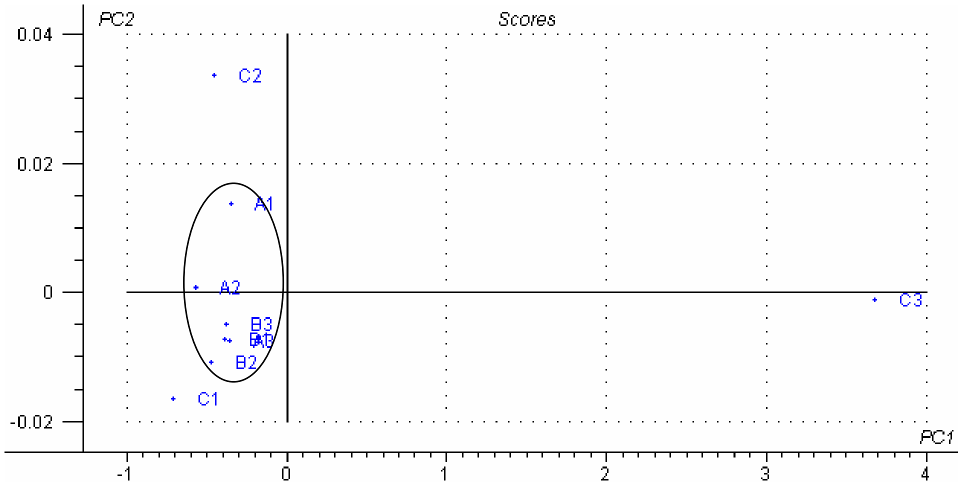

Figure 8. PC_2 vs. PC_1, scores graphic for PCA analysis using as input the trace elements concentration (Pb, Ni, Mn, Fe, Cu, Cr, Cd) content in mineral water samples analyzed

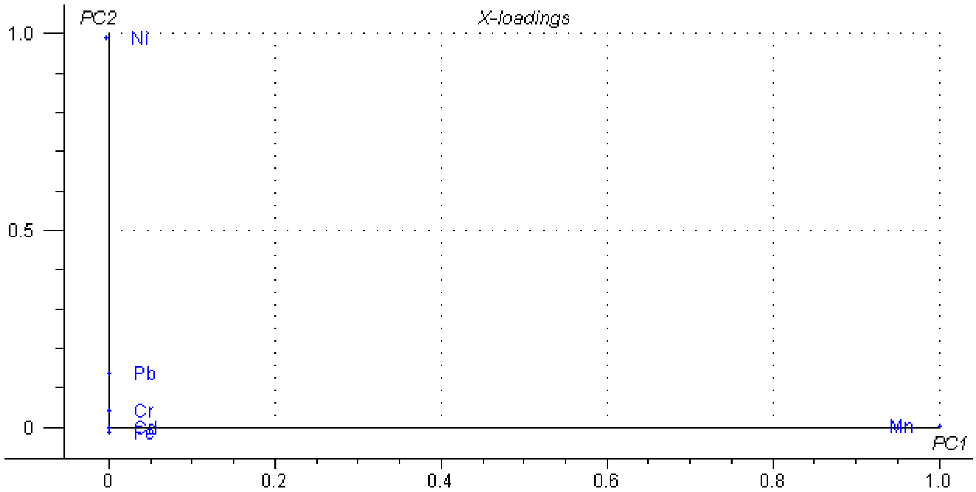

Figure 9. PC_2 vs. PC_1 records graphic for PCA analysis using as input the trace elements concentration (Pb, Ni, Mn, Fe, Cu, Cr, Cd) content in mineral water samples analyzed

Tried using concentration data for macro (Na, K, Ca, Mg) in multivariate analysis and obtained a sample group B and C similar previous case, here variances are explained in order: 38%, 56% şi 5% (Figure 6.), the grouping was mainly due to the Na and Ca concentrations (Figure 7).

Not the same thing happens if we take into consideration the corresponding variables concentrations of trace elements (Pb, Ni, Mn, Fe, Cu, Cr, Cd). This analysis resulted in a very good group (on the left-center of the graph scores) of samples A and B, the C samples being scattered irregularly (Figure 8). The variance explained is almost 100% for the first principal component and are primarily responsible for classification concentrations of Mn, Ni and even Pb. (Figure 9). [6, 7]

4.Conclusions

Principal components analysis (PCA) using as input the macro elements concentrations: sodium, potassium, calcium and magnesium obtained by atomic absorption spectrometry allowed a better classification of samples B and C except B3 sample from the north zone. Responsible for this classification were the elements sodium and calcium.

Principal components analysis (PCA) using as input the concentrations of trace elements: lead, nickel, manganese, iron, copper, chromium and cadmium, obtained by atomic absorption spectrometry allowed a very good classification of samples A and B, the C samples being spread unevenly. Responsible for this classification are the elements manganese, nickel and lead.

Compliance with Ethics Requirements. Authors declare that they respect the journal's ethics requirements. Authors declare that they have no conflict of interest and all procedures involving human / or animal subjects (if exist) respect the specific regulation and standards.

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