

## Trace elements composition of some mineral waters from Transylvania

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**Abstract:** The content of some microelements (manganese, copper, zinc and lead) in mineral waters from Transylvania was determined using two analytical techniques: ICP-AES and CSV/ASV. The results are comparable and explain the reliability of both methods.

**Key words:** mineral waters, trace elements, ICP-AES, ASV/CSV

### INTRODUCTION

This paper presents the characterization of twelve samples of mineral water from Transylvania region from the point of view of some microelements content. These microelements were determined by two analytical techniques with different principles, but with similar operational analytical parameters: Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) and Anodic/Cathodic Stripping Voltammetry (ASV/CSV).

This region was chosen, being the richest zone in mineral waters from Romania. These mineral waters are carbonated and the presence of CO<sub>2</sub> is due to post volcanic activity of Gutâi-Calimani-Harghita mountains.

J. Bányai<sup>[1]</sup> is the first who explained the importance of microelements from mineral waters. Together with Straub, they determined the presence of Hg, Zn, Pb, Au and V in mineral waters from Harghita region.

Lithium and manganese ions were determined in mineral waters from Transylvania using atomic absorption spectrometry<sup>[2]</sup>. Also, copper and chromium were determined in mineral water samples by graphite furnace atomic absorption spectrometry<sup>[3]</sup>. Manganese and zinc were determined from various samples, including mineral water, by differential pulse polarography<sup>[4]</sup>, DPASV<sup>[5]</sup>, DPCSV<sup>[6, 7]</sup>.

### RESULTS AND DISCUSSION

ICP-AES determinations were carried out by an atomic emission spectrometer with inductively coupled plasma, SPECTROFLAME-P (SPECTRO – Analytical Instruments, Germany).

For CSV/ASV determinations an electrochemical system polarographic and voltammetric ensemble Trace Master 5 and POL 150 Polarographic Analyzer (Radiometer, Copenhagen) was used. The electrochemical cell contained a working electrode: hanging mercury drop electrode (HMDE), a reference electrode: Ag/AgCl and as auxiliary electrode: platinum wire. Temperature, pH and conductivity were measured at the sampling site with Multi 340i/set (Wissenschaftlich Technische Werksstatter-Germany) pH analyzer.

All experiments were performed at a constant temperature of 25°C.

At sampling site were measured the characteristics of mineral water samples that are presented in Table 1. The analysis of the samples was made in due time to assure the reliability of analytical results, because the samples are carbonated waters and the loose of CO<sub>2</sub> enable the formation of a precipitate which collect microelements and in these conditions the analytical results are not correct.

For manganese determination by DPCSV and copper, lead and zinc determination by SWASV, different physical-chemical parameters were studied in the view to establish the best conditions. For manganese the peak potential is -1.470 V vs. Ag/AgCl, and the calibration curve is linear up to 50 ng/mL, for copper is -0.09 V, the calibration curve is linear up to 10 ng/mL, for lead the peak potential is -0.350 V vs. Ag/AgCl, the calibration curve is linear up to 10 ng/mL and for zinc the peak potential is -0.960 V vs. Ag/AgCl, the calibration curve is linear up to 10 ng/mL.

**Table 1.** Physical-chemical characteristics of mineral water samples

Sample	Location	Water Temperature °C	pH	Conductibility mS
1	Vâlcele	9.80	6.34	3.50
2	Bodoc	10.00	6.48	5.00
3	Malnas Bai	10.80	5.92	1.24
4	Bixad	12.20	5.99	2.41
5	Tusnad Bai	15.20	5.59	2.00
6	Tusnad Sat	13.70	6.18	2.38
7	Sâncraieni	13.60	5.99	1.00
8	Miercurea Ciuc (Sumuleu Ciuc)	13.80	6.17	2.27
9	Harghita Bai	6.10	5.38	0.29
10	Szeltersz	12.20	6.28	4.20
11	Homorod Bai 1	9.90	5.98	1.94
12	Homorod Bai 2	8.60	5.96	1.66

The correlation coefficients, which are between 0.9966 and 0.9998, indicate a good linearity for all studied microelements.

In Table 2 are presented, comparatively, the results obtained by both techniques for manganese, zinc and lead.

**Table 2.** Results of analysis of mineral water samples by ICP-AES and CSV/ASV

Sample	Mn (ng/mL)		Pb (ng/mL)		Zn (ng/mL)	
	ICP-AES	DPCSV	ICP-AES	SWASV	ICP-AES	SWASV
1	120.70±4.56	101.78±3.88	8.30±1.01	5.60±0.77	<LOD	<LOD
2	578.00±7.88	446.93±6.34	60.40±4.14	49.60±3.34	<LOD	<LOD
3	461.50±6.21	420.22±7.87	76.00±5.22	55.90±4.87	25.70±2.76	19.60±2.65
4	692.00±8.05	565.95±6.97	38.70±3.12	24.27±3.05	10.00±0.78	7.66±0.86
5	2096.00±27.70	1841.36±20.43	31.20±3.78	23.52±2.00	17.30±0.89	12.23±1.54
6	652.00±10.15	579.33±7.03	<LOD	<LOD	18.40±1.02	15.30±2.44
7	772.00±11.75	688.26±7.14	21.60±2.57	17.39±1.76	<LOD	<LOD
8	604.00±8.05	562.95±6.95	45.50±4.01	36.33±3.12	8.80±0.90	6.40±0.50
9	582.00±9.28	573.40±7.22	19.70±1.95	12.33±1.11	24.12±2.90	14.06±2.88
10	556.00±10.23	445.38±6.43	<LOD	<LOD	18.40±2.21	17.77±3.21
11	563.00±8.33	457.91±7.11	<LOD	<LOD	18.64±2.98	16.30±1.77
12	613.00±12.56	592.61±10.21	32.90±3.00	29.76±2.45	18.39±3.03	13.87±1.85

Means of five determinations ±standard deviation

Copper was also determined by these techniques and the values were under the detection limit, which is, for both techniques, 0.1 ng/mL.

Due to the fact that these two techniques are different in principle, the results are included in the normal limits of analysis from microelements and trace elements.

For all microelements studied, the highest values were obtained for Mn. It is due to rhodocrosite and rhodonite present abundantly in the underground. High values were also determined in some samples for Al, kaolin being also found in high amounts in this area.

The standard addition method was applied for voltammetric determination, by adding stock solution of  $Mn^{2+}$ ,  $Pb^{2+}$  and  $Zn^{2+}$  to the previously analyzed samples, to check the validity of the proposed methods. For the determination of the repeatability of the methods, manganese, lead and zinc were analyzed five times in the same sample.

## CONCLUSIONS

The results obtained enable to conclude that the concentration of these microelements is situated in normal range, only with some exceptions, depending on the underground composition.

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