Chemical Composition Assessment of Sulphurous Waters

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The study aims to assess the chemical composition of sulphurous spring waters collected from Pucioasa – Vulcana Bai balneotherapeutical area, Dambovita County. The sampling were achieved from active and preserved sulphurous sources (i.e. five springs), during the summer period of the year 2016. The content of nine metals (i.e. Cr, Mn, Fe, Co, Ni, Cu, Cd, Zn, and Pb) in water samples was determined by Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS). The relationships between physicochemical parameters (i.e. pH, conductivity, TDS, salinity, total hardness and dissolved oxygen) and metal concentrations were investigated, as well.

Keywords: sulphurous waters, ICP-MS, chemical composition

Sulphurous spring waters are used as therapeutic and preventive remedies for a various disorders such as those of the locomotor system (e.g. rheumatism [1-2], arthritis [3-4], post-traumatic [2]), respiratory tract [5-6], gynecological apparatus [7-8] and peripheral neurological system (e.g. paresis, paraesthesia, polyneuropathies) [9-10]. In skin disorders, they are indicated in psoriasis [11-12], parapsoriazis [13], and other skin thickened disorders, which have a keratolytic effect [1, 14], which helps to remove thick and excess of skin [1]. Today, the major dermatologic diseases (i.e. psoriasis and atopic dermatitis) are frequently treated by balneotherapy or spa therapy. Other medical studies [15-17] shown that these mineral waters have antioxidant properties in oral treatment. The mechanisms through which sulphurous waters exert beneficial effects on the human body, in therapeutic rheumatic treatment [16] are: the warmth of the bath activates circulation at the level of diseased tissues and helps to their resorption and skin exciting, which producing the antibodies needed to combat the infectious disorder for certain types of rheumatism; the sulphur assimilated in body increases the basal metabolism with 40%, causes vasodilatation in the central cutaneous tissue, induces a decrease of tension values, and increases the number of red blood cell and hemoglobin quantity. Among the physico-dynamic components is also mentioned the production of abundant sweating, the decrease of the muscles excitability, the acceleration of the exudation resorption and the provocation of a sedative action that explains the relieving of the pain. The resorbed sulphur occurs in the general metabolism of the human body, which explains the sugar decrease at diabetics [18], the remaking of the reserves in chondroitin sulphuric acid at articular cartilage level of the rheumatics.

Mineral waters were classiûed in many ways according to their physical and chemical elements, such as temperature, chemical composition, molecular concentration, and mechanisms of therapeutic action.

In Romania, one of the most well-known balneal resorts is Pucioasa -Vulcana Bai area from Dambovita County. In Pucioasa Resort, the sulphurous cold waters are originated in sedimentary rocks (rich in sulphates such as gypsum, and sulphides) of the hillsides behind the mineral springs. The first data on the chemical composition of sulphurous waters in this area are dated from the 1800s. For the first time, it was mentioned about therapeutic effect of these waters on several diseases, such as: pulmonary congestion, dermatitis, hemorrhoids, and rheumatic disorders. Today, the Pucioasa Resort has five springs: the spring 1, which feeds the treatment area, has sulphurous, chlorinated, calcic, sodic, and hypotonic water with a total mineralization 3.4 g/L; springs 2, 3 and 4 have sulphurous, sulphated, chlorinated, calcic, sodic, hypotonic, and carbonated waters, with total mineralization of 2.20 g/L, being preserved; spring 5 contains a highly concentrated mineral water with a total mineralization of 122.3 g/L which was preserved, as well. Also, the *p*H of sulphurous mineral waters is essential and responsible for its therapeutic effects.

In the same therapeutic area is found other four springs (Vulcana Bai, Dambovita County) which have reach a higher content in sulphur and iodine. The most known springs are Carol Spring and Ovesa Spring. First source has iodinated water and is mainly recommended for external rheumatism, gynecological and scrophalosis. The Ovesa Spring contains non-thermal water used in the gastric treatment, biliary and renal lithiasis, and chronic bronchitis.

The aim of this study was to investigate the chemical composition and several physicochemical indicators of sulphurous waters collected from five springs of Pucioasa - Vulcana Bai area in order to obtain information about the therapeutically properties of active and preserved sources, used in treatment of different diseases. The content of nine metals (i.e. Cr, Mn, Fe, Co, Ni, Cu, Cd, Zn, and Pb) from spring water samples, collected in the summer of 2016 was determined by Inductively Coupled Plasma - Mass Spectroscopy (ICP-MS). The physicochemical indicators (i.e. *p*H, conductivity, TDS, salinity, dissolved oxygen, hardness, and several ions) were analyzed as well.

Experimental part

Site description and sampling

The sampling was carried out between June and August 2016, in five mineral springs of Pucioasa-Vulcana Bai therapeutic area from Dambovita County, Romania (table 1).

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Table 1
MINERAL SPRING'S DESCRIPTION

Sample point	Sampling source	Description
S1	Mineral spring **1** which supply Pucioasa Spa Resort	calcic-natric-sulphate-sulphurous-chlorinated and hypotonic spring mineral water
S2	Mineral spring **2** preserved from Pucioasa area	calcic-natric-sulphate-sulphurous-carbonated and hypotonic spring water
S3	Mineral spring **5** preserved from Pucioasa area	natric, concentrated spring mineral water
S4	**Carol** Mineral spring from Vulcana Bai area	calcic-sulphate-sulphurous-chlorinated spring mineral water
S5	**Ovesa** Mineral spring from Vulcana Bai area	calcic-sulphate-sulphurous-chlorinated spring mineral water

Forty-five samples were collected during June-August 2016 period (e.g. three samples / month) according with [19].

Reagents

All chemical reagents were in high-purity grade. Distilled deionized water (Milli-Q Water System Millipore, USA) was used throughout the experiments. All glass beakers and containers were kept and stored in 1.0mol/L HNO_3 to eliminate any possible contamination. Also, nitric acid (high purity, Merck) was used for the blank preparation (1 % nitric acid) and digestion process. Standard Reference Material (SRM NIST Trace Element in Water, 1643e) was used for evaluating methods used in the determination of Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb in sulphurous water samples.

Analytical techniques

The analysis and quantification of elements (i.e. Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb) were performed by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) by using iCAP™ Qc device [20-24]. For ICP-MS analysis, the samples (about 15 mL) were digested [25-29] with aqua regia on a hot plate by using a TOPwave Microwave-assisted pressure system. After digestion process, the PTFE-TFM vessels with samples were cooled for 1 hour, and then the solutions were transferred with distilled water to 25 mL volumetric flasks. Finally, the clear solution samples were analyzed by ICP-MS. The quantification of this technique was performed by a standard curve procedure. Metals calibration curves showed good linearity over the concentration range (0.1 to 10.0 mg L^{-1}), with R^2 correlation coefficients in the range of 0.997 to 0.999. Calibration was performed using aqueous standard solutions (Merck). The measurements were performed in triplicate mode. The relative standard deviation (RSD) was less than 5%.

Results and discussions

It is well-known that chemical composition of sulphurous mineral waters is very important in treatment of different diseases for optimal therapeutic results. In these waters the main chemical element is sulphur, which may be present as a free or combined ion. Thus, the sulphur activity on the skin is related to its interaction with cysteine and its catabolites. Also, sulphur in different ionic forms interact with oxygen radicals in the deeper layers of epidermis when is produced sulphur or disulphur hydrogen, which then resulted pentathionic acid ($H_2S_5O_6$). This transformation represents a good source of antibacterial and antifungal activity of sulphurous water for treatment of dermatologic practice, psoriasis, ulcers, and gynecological disorders. Finally, in the therapeutic treatment of rheumatism, the resorbed sulphur occurs in the metabolism of the human body remaking the reserves in chondroitin sulphuric acid at articular cartilage level of the rheumatics. Therefore, the obtained concentration of sulphur as both ionic forms, SO_4^{2-} and S^{2-} (table 2 and fig. 1), ranged from 130.20±1.07to 139.80±1.21mg/L and 181.30±2.44 to 188.80±2.56 mg/L, respectively. The beneficial effects of sulphurous waters have been attributed to the presence of sulphur mainly in the form of hydrogen sulphide. This form is usually available in acidic *p*H conditions and low oxygen concentration. In this study the *p*H of the mineral water ranged from 7.43 to 7.64, that means lower alkaline *p*H (table 3 and fig. 2). Therefore, it can conclude that mainly anions S^{2-} was available in all water samples with a lower amount of HS^-. Also, the presence of oxygen (table 2) could diminish the reduction force and in this case amount of S^{2-} was significant in spring water. High concentration of bicarbonate (table 2 and fig. 1) was obtained in sample S2, preserved source. A high concentration of magnesium (table 2), through its competition with calcium concentration, in human body, may causes vasodilation, thereby lowering blood pressure, a very good indicator for different disorders. The mean concentration of chlorine ranged from 74.00±0.77 mg/L (i.e. S1 spring used in balneal treatment) to 122.10±1.15 (i.e. S3 preserved source).

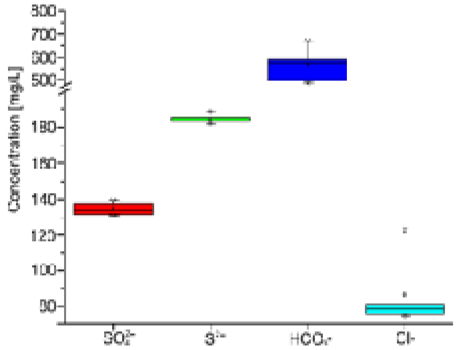


Fig. 1. Average of anions concentration (i.e. SO_4^{2-}, S^{2-}, HCO_3^-, and Cl^-) in sulphurous water samples

Table 2
CONCENTRATION (MEAN VALUES) OF SEVERAL IONS IN SPRING WATER SAMPLES

Sample point	SO_4^{2-}	S^{2-}	HCO_3^-	NO_3^-	Ca^{2+}	Mg^{2+}	Cl^-
	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]	[mg/L]
S1	139.80±1.21	188.80±2.56	480.00±6.24	5.59±0.05	136.27±1.32	70.30±0.88	74.00±0.77
S2	130.20±1.07	181.30±2.44	612.00±8.99	10.78±0.09	158.80±1.48	90.20±0.93	75.20±0.73
S3	133.60±1.09	183.20±2.51	501.00±7.71	7.64±0.08	193.20±1.83	81.40±0.83	122.10±1.15
S4	131.50±0.99	183.80±2.49	481.00±6.14	7.31±0.07	149.22±1.15	72.90±0.73	118.20±1.18
S5	137.10±1.18	185.40±2.52	497.00±1.21	8.42±0.08	151.04±1.16	79.80±0.81	101.10±0.92

Table 3
PHYSICOCHEMICAL PARAMETERS (MEAN VALUES) OF MINERAL WATER SAMPLES COLLECTED FROM FIVE SPRINGS OF PUCIOASA-VULCANA BAI AREA

Sample point	pH	Conductivity	TDS	Salinity	Dissolved oxygen	Hardness
		[µS/cm]	[mg/L]	[‰]	[mg/L]	[°D]
S1	7.43±0.05	2062.10±25.31	1154.78±8.31	0.20±0.01	7.89±0.06	21.30±0.42
S2	7.52±0.06	1719.20±19.84	962.04±7.03	0.20±0.01	8.01±0.07	22.60±0.53
S3	7.64±0.07	2369.40±23.69	1326.20±9.06	0.30±0.01	8.21±0.07	26.80±0.71
S4	7.47±0.05	1812.10±18.20	1014.19±9.54	0.20±0.01	7.78±0.05	21.90±0.46
S5	7.44±0.05	1852.10±19.02	1036.52±9.77	0.20±0.01	7.42±0.06	22.10±0.50

Tabel 4
MEAN CONCENTRATION OF METALS IN ANALYZED SAMPLES

Sample point	Mean concentration of metal [µg/L]								
	Cr	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Cd**	**Pb**
S1	20.07±0.18	34.35±0.37	5897.11±10.91	0.82±0.01	10.03±0.05	36.38±0.22	47.83±0.30	1.46±0.02	14.44±0.02
S2	73.63±0.94	46.62±0.42	7993.43±11.47	2.04±0.03	26.08±0.11	97.41±0.65	27.53±0.22	0.31±0.01	50.10±0.08
S3	53.19±0.44	27.06±0.31	3735.68±9.43	1.94±0.02	19.51±0.09	114.78±0.94	20.17±0.18	0.08±0.01	53.99±0.09
S4	22.44±0.20	43.65±0.45	10474.39±12.62	1.68±0.02	15.45±0.07	126.26±0.96	24.43±0.19	0.26±0.01	40.04±0.07
S5	67.74±0.57	66.83±0.70	13650.07±12.94	2.10±0.02	26.38±0.12	116.76±0.95	26.30±0.23	0.29±0.02	35.14±0.06

The results (table 3 and fig. 2) showed that conductivity level ranged from 1719.20.1±19.84 to 2369.40±23.69 µS/cm, the Total Dissolved Solid (TDS) varied between 962.04±7.03 and 1326.20±9.06 mg/L with a total hardness values contained in the range 21.30±0.42 till 26.80±0.71 °D. It is well-established that the acidity of water increases the mobility and bio-availability of cations that total dissolved solids concentration. But in this case the metal ions decrease their solubility at week alkaline *p*H (table 3).

According to table 4 the mean concentration of Fe recorded in samples S4 and S5 was higher than the other analyzed samples, means that the hillsides behind the mineral springs from Vulcana Bai area are very rich in Fe. From table 4 it was observed that concentration of Cr, Mn, Fe, Co, Ni, Cu, and Pb in the mineral springs used in balneal treatment was lower than in the other water samples. In the preserved springs (i.e. S2, S3, S4, and S5), as well as expected, the metals concentration was higher, probably

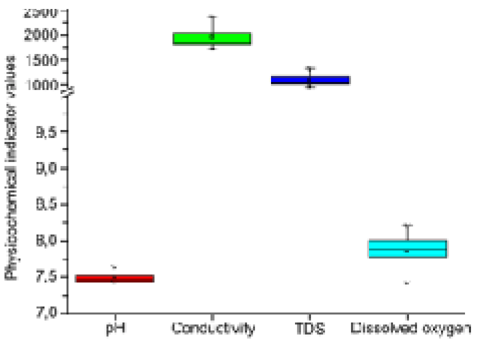
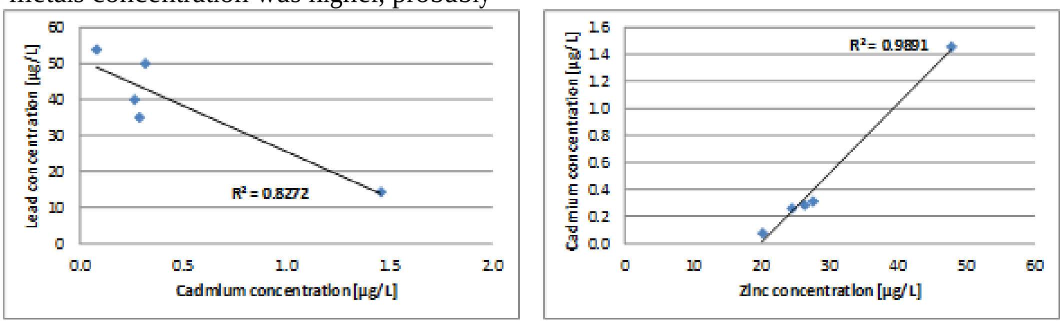


Fig. 2. Average of physicochemical parameters (i.e. *p*H, conductivity, TDS, and dissolved oxygen) in collected sulphurous water samples

due to the atmospheric depositions or disuse of these mineral waters. From the above results, the Cd, Cu, Mn, Ni, Co, Pb, metal concentrations in analyzed samples were

a



b

Fig. 3. The relationship between concentration of: (a) cadmium and lead; (b) zinc and cadmium;

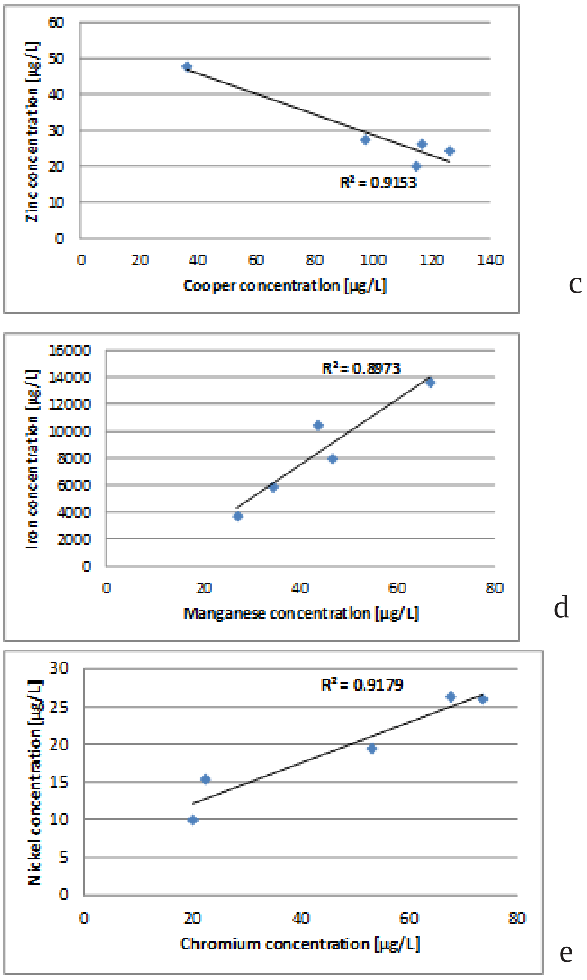


Fig. 3. The relationship between concentration of: (c) cooper and zinc; (d) manganese and iron; (e) chromium and nickel.

lower than the values provided in Surface Water Quality Standards [30].

Correlation analysis results

Studies (fig. 3) have shown an interesting dependence between metals from spring water samples. Direct correlation with a high coefficient ($R^2 > 0.80$) was recorded between cadmium and lead ($R^2=0.8272$), zinc and cadmium ($R^2=0.9891$), cooper and zinc ($R^2=0.9153$), manganese and iron ($R^2=0.8973$), and chromium and nickel ($R^2=0.9179$). This indicates the presence of a synergistic interaction between these metals, as a result of existing salts in sulphurous water.

Conclusions

In conclusion, the metal concentrations of the spring water samples were below the reference values provided in [30] excepting iron and cooper. In order to verify the accuracy of the ICP-MS method, the certified reference of Trace Element in Water, 1643e was analyzed and the results obtained were in good agreement with the certified values of the analytes. The results obtained in this study proved that physicochemical parameters and chemical composition of all mineral springs not exceeded the limit values and thus, sulphurous waters of these springs are indeed recommended for therapeutic treatments. In the further investigations different other type of mineral springs will be assessed in order to obtain a larger image of the chemical composition of sulphurous waters used in balneal resort.

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