

## PHYSICO-CHEMICAL CHARACTERIZATION OF SPRING AND SALT LAKES FROM SOMESENI TURENI (CLUJ COUNTY)

ANDREEA BRAȘOVAN<sup>a</sup>, RAMONA FLAVIA CÂMPEAN<sup>b</sup>,  
NELI KINGA OLAH<sup>c,b</sup>, CLAUDIU MORGOVAN<sup>c</sup>,  
CARMEN POPESCU<sup>c</sup>, PAUL ATYIM<sup>c</sup>

**ABSTRACT.** The study refers to the analysis of the chemical composition of water samples from Pata Rât salt lake and salty spring from Micești. The physical and mineralogical characteristics of water and sludge specific of Pata Rât lake are suitable to be used in alternative treatments for rheumatism, skin peeling treatments and skin SPA therapy. The difference in salt crystallization in homogeneous and heterogeneous conditions was evaluated by using a model of salt crystallization in homogeneous conditions. The optical mineralogical micro-photographs in polarized light of the water samples are providing information about heterogeneous crystallization of salt. The mineralogical composition of the water sample was determined by X-ray diffraction and the following minerals were determined: quartz, calcite, lepidolite and kaolinite. By colorimetry were determined the physico-chemical properties of salty water. It was determined also the pH and the conductivity.

**Keywords:** salty natural water, pH, conductivity, microscopy, X ray diffraction.

### INTRODUCTION

The salt deposits from Transylvania are the purest in the world, they are made by massive blocks of sodium chloride, crystallized in simple cubic system in the form of halite [1]. They were formed by lowering the water level

---

<sup>a</sup> Babeș-Bolyai University, 1, Kogălniceanu Street, 400084, Cluj-Napoca

<sup>b</sup> SC PlantExtrakt SRL, 407059 Rădaia.

<sup>c</sup> "Vasile Goldis" Western University of Arad, Faculty of Medicine, Pharmacy and Dental Medicine, 86 Rebreanu Street, Arad, Romania

\* Correspondent authors: olahdr@aol.com, ramona\_c@yahoo.com, claudiuorgovan@yahoo.com, carmen\_popescu@yahoo.com

of the Paratethys Sea in the Badenian, from the Middle Miocene era [2]. The sediments cover the thick layer of salt, which sometimes permeate the earth's surface in the form of mushrooms, which were later exploited (mines), or in the form of salty springs due to water sources which dissolve the salt [4]. The most representatives deposits are located along the Sovata-Praid and Cojocna-Turda line [3]. The presence of salt deposits influences considerably the topography and the stability of the targeted areas. They reported significant ground movements due to rapid change of salt deposits conformation affecting the railway embankment Apahida-Câmpia Turzii, Cluj County [4].

In Micești area, to Deleni and Tureni, the deep waters dissolved the salt and permeated the limestone, bringing at the surface layer of salty springs, the place being actually called "Valea Mărtoare".

The sodium chloride is a salt soluble in water. So the presence of fresh water springs in the proximity of a massive salt underground will lead to its gradual dissolution and in the formation of salty springs, such as those at Micești. Considering that specifically Badenian formations which cover the salt deposits are from limestone rock mixed with sandy quartz conglomerate and with a soil layer of clay structure [5], the dissolution of the salt appears as a cavity, proportional to the volume that causes the crumbling of this friable formations. In such cases, salt lakes have varied diameters and depths, depending on the areas conformation and on the water's flow rate.

This paper presents the evaluation of the mineralogical and the chemical composition of two natural water sources: salty spring from Micești respectively the Pata Rât salt lake.

## RESULTS AND DISCUSSION

After performing the physico-chemical determinations on salt water samples were obtained the results shown in Table 1.

**Table 1.** The chemical composition and some physical properties of water samples from Pata Rât salt lake and salty spring from Micești

The property	Pata Rât salt lake*			Salty spring from Micești*
	Surface	10 cm	20 cm	
pH	7,04	7,06	7,21	6,05
Conductivity mS/cm	225,5	221,1	217,4	236
Chlorine, mg/L	<LOD	<LOD	<LOD	<LOD
Nitrites, mg/L	<LOD	<LOD	<LOD	<LOD
Sulphates, mg/L	101,2	100,8	100,5	200
Nitrates, mg/L	<LOD	<LOD	<LOD	<LOD
Iron, mg/L	<LOD	<LOD	<LOD	<LOD

PHYSICO-CHEMICAL CHARACTERIZATION OF SPRING AND SALT LAKES FROM SOMESENI TURENI

Chlorides , mg/L	601,7	600,4	600,1	300
Hardness, German degrees mg/L CaCO <sub>3</sub>	25,8	25,5	25,3	450
Ammonium, mg/L	<LOD	<LOD	<LOD	<LOD
Lead, µg/L	<LOD	<LOD	<LOD	<LOD

\* All determined values are the mean of 3 determinations.

The presence of suspensions in water can significantly affect its properties. One of the most important physical property is the conductivity, which is very high because of the huge quantities of dissolved sodium chloride. On the surface it is around 225,5 mS/cm at Pata Rât and 235,9 mS/cm at Miceşti. Not at least, the pH is a very important for the water characterization.

The salty water contains dissolved salts, ions: hardness due by Ca and Mg carbonates, chlorine, chlorides, sulphates, nitrates, ammonium, iron and lead. The hardness is a summ of the dissolved salts in the water, particularly slowly soluble such as carbonates. In this way both the adjacent soil and mineral particles in direct contact with salty water can affect in some ways the water hardness.

The increased hardness value obtained in the sample from Miceşti, proves that it has a higher hardness than the salt water from the lake. This can be explained by the structure of the adjacent soil.

An important physico-chemical property for water is the residual chlorine. These waters are natural and untreated in processing stations of water, so it is normal to be free of residual chlorine.

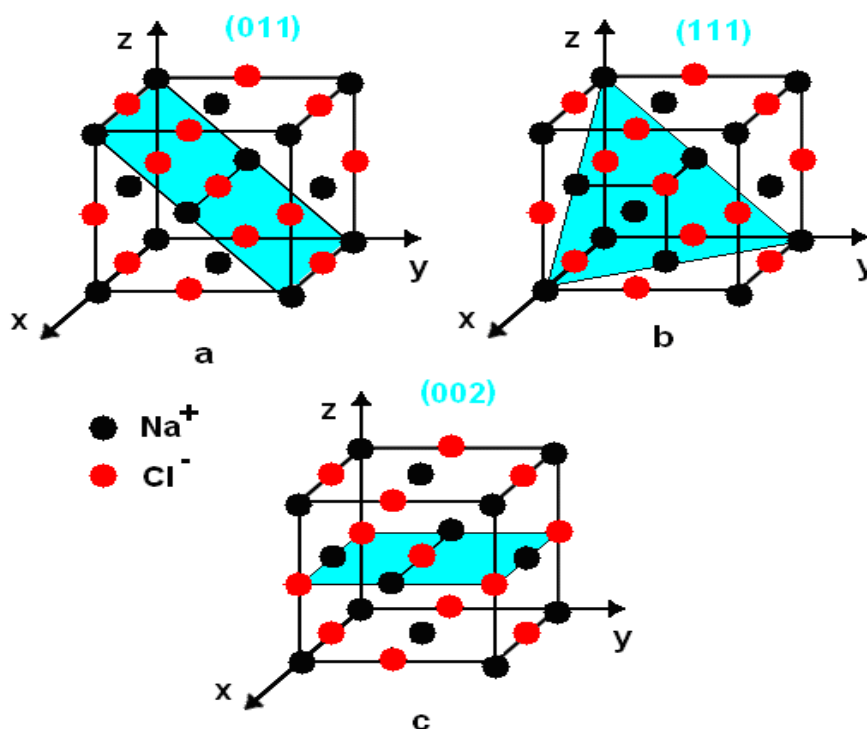
The content of chloride is given mainly by the dissolved halite. The presence of other ions is given by the minerals found in rocks structures adjacent to salts deposits. The chlorides content of the water samples shows values between 300 and 600 mg/l, given by the very rich content of sodium chloride. The obtained values show that the brine was formed in depth in the salt deposit and its concentration is not affected by the presence or the absence of mineral particles from the soil surface.

The sulphates content of water samples investigated presents a variation of 100-200 mg/l for each sample.

The nitrites content, ammonium, iron and lead is below to the detection limit of the used tests kits. You can say that they are missing from the salted water from Pata Rât lake and salty spring from Miceşti. That is likely to confirm the special origin of salted water from the investigated area.

By comparing the physico-chemical parameters of the Mierlei lake at different depths, more precisely at 10, 20, 40, 80 cm, with those of Pata Rât lake and the salty spring of Miceşti, the values are almost the same but with small variations. The pH value varies between 8,14 and 7,26. The conductivity value varies between 33,9 and 215,8 mS/cm.[10]

In order to see the difference of salt crystallization in homogeneous and heterogeneous conditions, it was performed a model of salt crystallization in homogeneous conditions [3]. Based on the FCC cell unit, in Figure 1 are shown the most important directions and their corresponding crystallographic planes, that are able to help the ideal salt crystal growth.



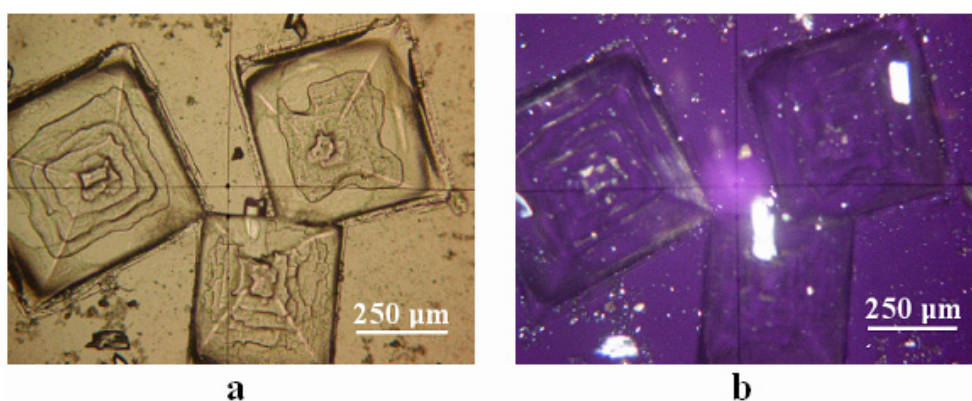
**Figure 1.** The evidence of crystallographic planes on the halite elementary cells. The crystallographic planes: a) {110}, b) {111}, and c) {200}.

The halite crystals have a complex cubic centered face (FCC) consisting of two cubic faces of Na<sup>+</sup> and Cl<sup>-</sup> ions overlaid, centering each the other face [6,3]. Considering the side of halite crystal FCC, here they are the following crystallographic planes, described by Miller indices [6]: {111}, {200}, {220}, {311}, {222}, {400}, {331}, {420}, și {422} [2].

Figure 2 presents the microstructure of water sample taken from the surface of Pata Rât salt lake. It is observed the well-developed salt crystals after the crystallographic directions {110} and {200} accompanied by material particles of mineral origin [9].

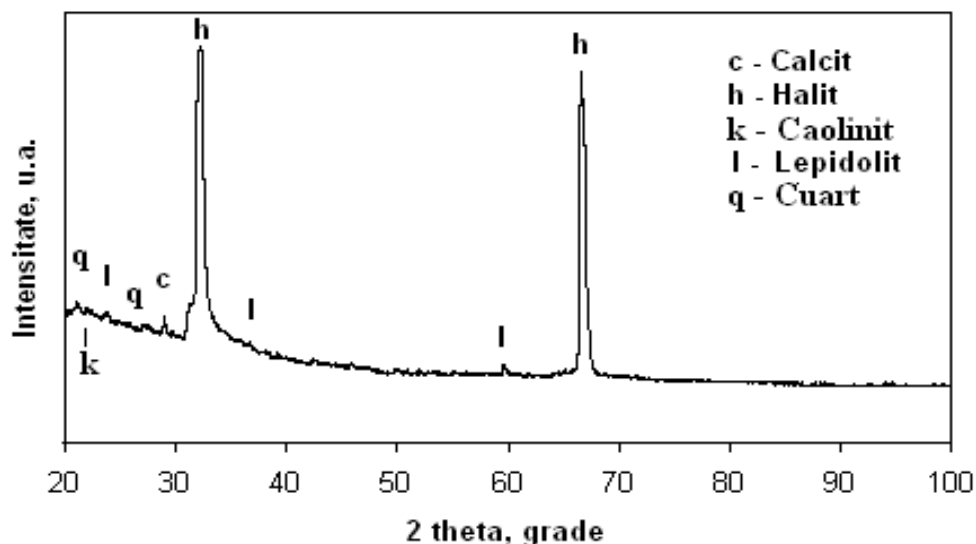
The optical mineralogical micrographs were not revealed significant differences for Pata Rât salt lake and the salty spring from Micești.

The mode of their crystallization is approaching ideal conditions, defects of packing of formed crystals not being visible. In polarized light, in Figure 4b, the salt crystals appear blue translucent on the dark background. Small, interesting inclusions are appearing, intercrystalline tabulated in blue light, which are not distinct on the observation in transmitted light. The situation was not observed in water samples taken in „static” conditions. This leads to the conclusion of the possible inclusion of calcium sulphate, which have been reported in the scientific literature as the accompanying of the Badenian salt [7]. The calcium sulphate can crystallize in two allotropic forms [6] of gypsum, forming filiform prismatic crystals, with shiny white appearance in polarized light with crossed nicols, and the anhydrite which form blue-violet tabular-lamellar crystals in polarized light with crossed nicols. Therefore, those observed in Figure 4b, could be traces of the anhydrite as inclusions, inside the halite crystals.



**Figure 2.** The optical mineralogical microphotographs:  
a) in transmitted light and b) in polarized light with crossed nicols

The mineralogical composition of water samples were determined by X-ray diffraction. The resulting diffractograms are shown in Figure 3. It is observed very slender maximums and well developed for the halite, corresponding to planes {200} and {400}.

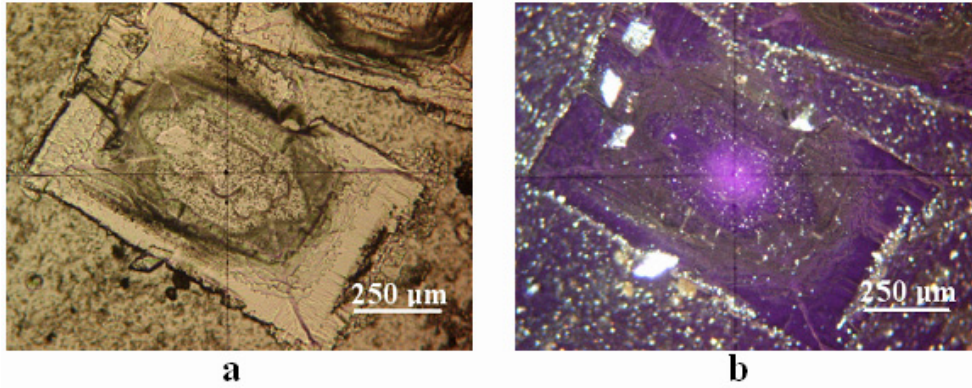


**Figure 3.** The salt water sample diffractogram.

The X-ray diffraction analysis of water samples have not revealed significant differences for the Pata Rât salt lake and salty spring from Micești.

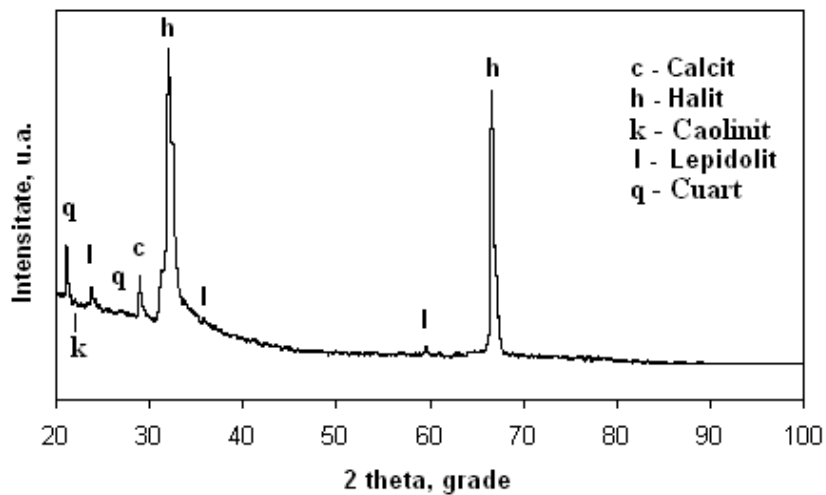
The minerals found as solid particles, dispersed in water sample, present relatively small maximums in relation to the intensity of those for halite, fact in full compliance with microscopic observations. It was identified a certain maximum for quartz, calcite, lepidolite and kaolinite. These are suitable with those observed in the composition of adjacent lake soil and certifies their origin from the surface layers. The presence of these minerals dispersed in water sample did not interfere much with the halite crystal formation, demonstrated clearly in the microscopic observation.

At 10 cm depth, the density of mineral particles dispersed in unit volume increases, as shown in Figure 4a. It shows a salt crystal formed after direction {200} almost visible with the eye (about 1 mm) surrounded by mineral particles from aqueous suspension (calcite, quartz, very fine particles of lepidolite, kaolinite). That corresponds to a heterogeneous germination promoted by solid inclusions dispersed in the saline solution. In figure 4b can be observed no less than three intercrystalline inclusions of anhydrite and an anhydrite crystal formed at the halite crystal limit.



**Figure 4.** The optical mineralogical microphotographs for water sample from 10 cm depth: a) in transmitted light and b) in polarized light with crossed nicols

The X-ray diffraction analysis (Figure 5) shows well-developed maximums of halite corresponding to the crystallographic planes {200} and {400} for the water sample from 10 cm depth. The situation is somewhat similar with that of the surface sample, but the specific maximums of minerals dispersed from the sample, are considerably more intense, which confirms their high proliferation in unit volume of water sample. There were identified quartz, calcite, lepidolite and kaolinite [8].



**Figure 5.** The sample diffractogram at 10 cm depth.

## CONCLUSIONS

From the investigation results that the interrelationship soil-water-salt deposits demonstrates the formation of salt lakes in the Transylvanian Basin. The performed analysis shows a high solubility of sodium chloride in water, forming rapidly a saturated solution in contact with the underground salt. It is noted that the evaporation of water from such a natural brine, leads to the formation of microscopic crystals of halite. That in itself has a relative importance when it is separately evaluated, extremely useful mining method „Solvay”, where the salt is extracted by means of a saturated brine.

In the case of Pata Rât salt lake and the salty spring from Micești, it is revealed the close relationship between salt massive and the sediments above them, mediated by the presence of springs and deep water layers. The performed analysis revealed in these salty water sources, significant amounts of calcite embankment and mixed with large clay deposits and sandy-loamy deposits (kaolinite, lepidolite mixed with quartz and/or calcite sand).

Because of the lack of information regarding to these natural water sources from Cluj county region the results presented in this paper could have relevance for the future exploitation of these natural resources of very high purity waters. The physical-mineralogical characteristics of water samples and sludge samples adjacent to the Pata Rât salt lake, could be suitable for the use in alternative treatments of rheumatism, skin exfoliation treatments, SPA therapy for skin and beneficial for the osteoarticular system.

## EXPERIMENTAL SECTION

In the current study there were collected 4 water samples, a sample from the salty spring from Micești and three samples from Pata Rât lake, from different depths (surface, 10 cm and 20 cm). The water samples were preserved at cold and the physico-chemical analysis were performed in the same day with the sampling.

The determination of the residual chlorine, chlorides, nitrites, nitrates, iron, lead, sulphates, ammonia, total hardness was performed by colorimetric methods using different reagents. The analyses were performed with Spectroquant ready to use reagents and the colorations were quantified with a Spectroquant photometer Nova60.

The nitrites in acidic solution react with sulfanilic acid to form a diazonium salt, which then reacts with N-(1-naphthyl) ethylenediamine dihydrochloride to form a red-violet azo dye, determined colorimetric.



The nitrates are reduced to nitrite ions that react in acidic solution with 2,6-dimethylphenol to form 4-nitro-2,6-dimethylphenol.

The lead in alkaline solution reacts with 4-(2'-pyridylazo)resorcinol to form a red complex.

The ammonium reacts with Neßler's reagent in order to form a yellow-brown compound.

The iron (III) ions are reduced to iron (II) ions that reacts with a triazine derivatives in order to form a red-violet complex.

The total hardness: in the presence of a green indicator the  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions react with Titriplex III in order to form a colorless, stable complex. The hardness ions that are present in excess relatively to Titriplex III react with the indicator in order to form a red complex.

The sulphates react with a red thorium-barium complex, releasing yellow thorium compound.

The chlorides react with silver ions, decolorizing the red-brown silver chromate.

The chlorine oxidizes the dipropyl-p-phenylenediamine to a red-violet dye.

The conductivity and pH were measured with HI 255 Combined Meter & EC/TDS/NaCl Hanna Instruments.

There were determined in the salty waters the mineralogical composition by X-ray diffraction and the salt crystallisation. For each water sample were prepared slides for microscopic investigation and X-ray diffraction analysis.

The X-ray diffraction analyses were performed using a DRON 3 diffractometer equipped with data acquisition module and Matmec VI.0 software. The mineral identification from the resulted X - ray diffraction patterns was done using MATCH 1.0 X – ray diffraction database powered by Crystal Impact Company.

The morphology outline was investigated by a dark field optical microscopy on a IOR 8 microscope. The quantitative measurement on the microphotographs was done using the Image J Processing soft.

The cross polarized light microphotographs were done on a mineralogical Laboval 2 Karl Zeiss Jena mineralogical microscope. The digital capture used for all microscopy investigation was done with a Samsung 8 MPx camera.

## REFERENCES

- [1]. N. Har, O. Rusz, V. Codrea, O. Barbu, *Carpathian Journal of Earth and Environmental Sciences, Baia Mare*, **2010**, 5, 2, 127-135.
- [2]. M. Peryt, *Sedimentary Geology*, **2006**, 188–189, 379–396.

- [3]. I. Chicinaș, N. Jumate, V. Pop, „Fizica materialelor metode experimentale”, Presa Universitară Clujeană, Cluj Napoca, **2001**, 325.
- [4]. E. Constantinescu, L. Matei, „Mineralogie determinativă”, Ed. Universitatii din Bucuresti, Bucuresti, **1996**.
- [5]. Cs. Krézsek, (PhD thesis), Babeș-Bolyai University, Cluj-Napoca, Romania, **2005**, 166.
- [6]. G. Arghir, L.M. Gherghari, „Cristalografie Mineralogie. Îndrumător de lucrări de laborator”, Litografia IPC – N, **1989**, 371.
- [7]. E. Gergely, „Tureni, studiu monographic”, Ed. Casa Cărții de Știință, Cluj-Napoca, **2002**, 220.
- [8]. N. Cianga, D. Costea, „Journal: Aerul și Apa: Componente ale Mediului”, Cluj University Press, **2011**, 185-191.
- [9]. I. Petean, G. Arghir, R.F. Câmpian, M. Bărăian, Al. Gertrud Hosu Prack, *Acta Technica Napocensis Series: Matematica Aplicata si Mecanica*, **2011**, 54 (I), 193 – 200.
- [10]. S. Crognale, I. Máthé, V. Cardone, S.R. Stazi, B. Ráduly, *Geomicrobiology Journal*, **2013**, 30, 9.