ISSN: 1224-7626

ANALELE
UNIVERSITĂŢII DIN ORADEA

Fascicula CHIMIE
XXIV
2017

EDITURA UNIVERSITĂŢII DIN ORADEA

- 2017-

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General Information

ISSN: 1224-7626
Place of publishing: Oradea, Romania
Year of the first issue: 1995
Releasing frequency: 1 issue / year
Language: English
Abstracting/Indexing: **Chemical Abstracts Service-CAS Source Index (CASSI)**

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APPLICATION OF GEOTHERMOMETERS IN THERMAL RESERVOIRS

Oana STĂNĂŞEL, Georgeta GAVRIŞ, Anda PETREHELE, Alina COZMA
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Abstract: *Geothermometers are based on the assumption that specific temperature dependent mineral/solute equilibria are attained in geothermal reservoirs. For a particular geothermometer this involves specific chemical components analysed in geothermal water. In this paper is presented a classification of geothermometers. According to different types of geothermometers it was possible to estimate the subsurface temperature of Romanian thermal reservoirs in western part of the country.*

Key words: *cation geothermometers, silica geothermometers*

1. INTRODUCTION

Chemical geothermometry is a basic tool used to determine subsurface temperatures of geothermal reservoirs. The input parameters are the chemical analysis of the water samples. The accuracy of the obtained subsurface temperatures calculated by chemical geothermometers depends on the accuracy of the chemical analyses. When different geothermometers are applied to the same fluid, different temperatures are obtained. This could be due to a lack of equilibrium between respective solutes and hydrothermal minerals or due to reactions or mixing with water during upflow, causing modification of geothermal fluid chemical composition.

The best way to estimate reservoir temperature is to consider simultaneously the state of equilibrium between a specific solution and many hydrothermal minerals as a function of time. The equilibrium constant is affected more by temperature and less by pressure. In a geothermal system the pressure is in the range 0-200 bar. For this reason pressure has little effect on the equilibrium constant. Equilibrium constant vary widely with minerals.

For a reaction, the free energy is:

$$\Delta G = \Delta G^0 + RT\log\frac{Q}{K} \qquad (1)$$

where:

ΔG - free energy;

ΔG^0 - free standard energy;

Q – activity coefficient;

K – equilibrium constant.

The temperature of convergence for a group of minerals in a log (Q/K) versus temperature plot likely be the temperature of the geothermal reservoir.

2.CATION GEOTHERMOMETERS

Cation geothermometers depend on ion exchange reactions which are temperature dependent. These are: Na-K geothermometer, Na-K-Ca geothermometer and K-Mg geothermometer. They are based on the temperature dependence of the following reactions:

$$K - feldspar + Na^+ = Na - feldspar + K^+ \quad (2)$$

$$\begin{aligned} &2.8K - feldspar + 1.6water + Mg^{2+} = \\ &0.8K - mica + 0.2chlorite + 5.4silica + 2K^+ \end{aligned} \quad (3)$$

The Na-K geothermometer uses a reaction that involves simultaneous equilibrium between Na^+ and K^+ in solution and pure albite and K-feldspar that is expressed by equation:

$$NaAlSi_3O_3 + K^+ = KAlSi_3O_3 + Na^+ \qquad (4)$$

Because feldspar and albite are almost pure minerals with activity approximating one, the equilibrium constant of reaction (4) is:

$$K_{eq} = \frac{[Na^+]}{[K^+]} \qquad (5)$$

In this paper the deep reservoir temperature based on Na-K geothermometer was calculated by the following equation:

$$t^{o}C=\frac{1390}{1.750-\log\left(\frac{Na}{K}\right)}-273.15 \qquad (6)$$

The Na-K-Ca geothermometer is based on the exchange reaction between Na^{+}, K^{+} and Ca^{2+} with mineral solids. It was proposed the following equation:

$$t^{o}K=\frac{1647}{\log\left(\frac{Na}{K}\right)+\beta\log\left(\frac{Ca^{0.5}}{Na}\right)+2.24} \qquad (7)$$

Concentrations are in mol/kg. The value β =1/3 should be used when the temperature of the water is less than $100^{0}C$, when $\log Ca^{2+}/Na$ is negative with concentrations expressed in molality units. When the geothermometer is applied to waters in which the partial pressure of CO_2 in the aquifer is above 10^{-4} atm, a correction factor is substracted from the right hand side of equation (7), where:

$$I=-1.36-0.253\log P_{CO_2} \qquad (8)$$

For K-Mg geothermometer was proposed the equation:

$$t^{o}C=\frac{4410}{14.0+\log\left(\frac{K^{2}}{Mg}\right)}-273.15 \qquad (9)$$

3. SILICA GEOTHERMOMETERS

Silica exists in different forms: quartz, cristobalite, chalcedony, amorphous silica. The surrounding rocks of most geothermal reservoirs contain quartz, which will disolve in the hot water. At temperatures above 230°C it is generally considered that quartz is in equilibrium between the solid and dissolved species:

$$SiO_2\,(s) + 2\,H_2O = H_4SiO_4\,(aq) \qquad (10)$$

The solubility of silica minerals depends on temperature and pH. Water rock interactions fix the pH of reservoir fluids at pH values between 5 and 7.5. Temperature reservoir in the range of $20^{0}C$ to 250°C can be calculated using the concentration of silica, in mg/kg (S), by the following equations:

Quartz without boiling:

$$t^{o}C=\frac{1309}{5.19-\log S}-273.15 \qquad (11)$$

Quartz after adiabatic boiling:

$$t^{o}C=\frac{1552}{5.75-\log S}-273.15 \qquad (12)$$

Chalcedony:

$$t^{o}C=\frac{1032}{4.69-\log S}-273.15 \qquad (13)$$

α - cristobalite:

$$t^{o}C=\frac{1000}{4.78-\log S}-273.15 \qquad (14)$$

β - cristobalite:

$$t^{o}C=\frac{781}{4.51-\log S}-273.15 \qquad (15)$$

Amorphous silica:

$$t^{o}C=\frac{731}{4.52-\log S}-273.15 \qquad (16)$$

The results discussed in this paper were calculated using chalcedony and quartz silica geothermometers.

4.ESTIMATING RESERVOIR TEMPERATURES

The results of the chemical analyses of the water samples[6,7,8], were used to calculate temperatures (table 1) based on these geothermometers[2,3,4,5] using the WATCH aqueous speciation program[1].

Table 1. Geothermometry calculations

Well no.	Wellhead temp, °C	Chemical geothermometers, °C		
		Quartz	Chalcedony	Na/K
4003	45	54.3	22.2	312.2
4012	43	66.8	34.6	313.0
4011	45	69.5	37.2	316.0
529	90	148.5	122.9	189.4
4058	84	108.3	78.5	52.9
4668	84	161.6	137.5	57.1
4797	71	97.7	67.0	172.5

Taking into account the results presented in table 1, the reservoirs temperatures indicated by the calculated chalcedony geothermometer are closer to the production temperatures of the waters than the values given by the other geothermometers. For wells 4058 and 4797 the calculated temperature based on the chalcedony geothermometer almost correspond to the wellhead temperature. The Na/K geothermometer yields higher values compared to the silica geothermometers for all the cases, except for wells 4058 and 4668, where were recorded lower values than wellhead temperatures. For this reason, for these two wells was applied also silica-enthalpy mixing model[9] (figure 1).

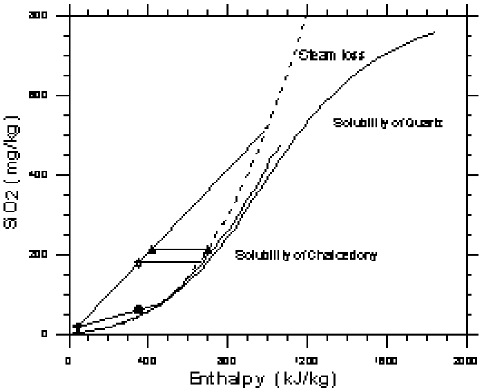

Figure 1. Silica-enthalpy diagram for wells 4058 and 4668

The temperature of the geothermal reservoir which supplies well 4668 (figure 1) was found to be 160ºC if there is no steam loss and about 170ºC assuming a steam loss before mixing. The wellhead temperature is lower probably due to mixing with cold water during infiltration.

The temperature calculated for the hot water from well 4058 by mixing model was 106ºC. The plot was very close to the solubility curve of chalcedony. The difference is assumed to be due to the contact of the hot water with the rocks.

For these two wells the source temperature of the hot water component calculated by mixing model is higher than the measured wellhead temperature. The temperatures 106ºC, respectively 160ºC are like those obtained by quartz geothermometers calculation.

The temperatures of the reservoirs indicated by the calculated silica geothermometers are close to the production temperatures of the waters from wells 4012, 4011 and 4003, but Na/K geothermometer yields higher values compared to the silica geothermometers for all these cases. This geothermometer does not give good results for low-temperature geothermal waters due to specific minerals which control the mineral-fluid equilibration. By applying silica-enthalpy model (figure 2) it was obtained a temperature of 46ºC for the deep geothermal water from well 4003, 63ºC for well 4011, respectively 59ºC for well 4012. These temperatures are close to the results of silica geothermometers calculated by Watch programme and indicate a shallow feed reservoir, according to the fact that the depths of the wells are low.

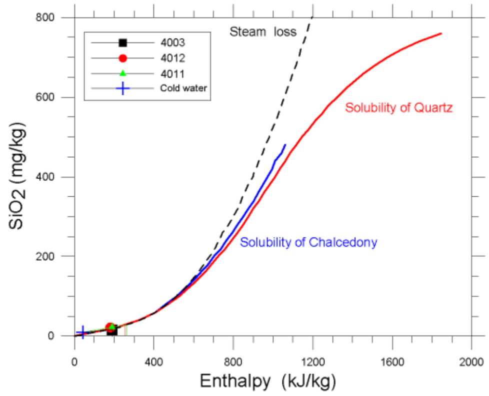

Figure 2. Silica-enthalpy diagram for wells 4003, 4011 and 4012

Based on silica-enthalpy model it results the temperature 144ºC for the deep geothermal water from well 529 (figure 3), like the temperature resulted by quartz geothermometer.

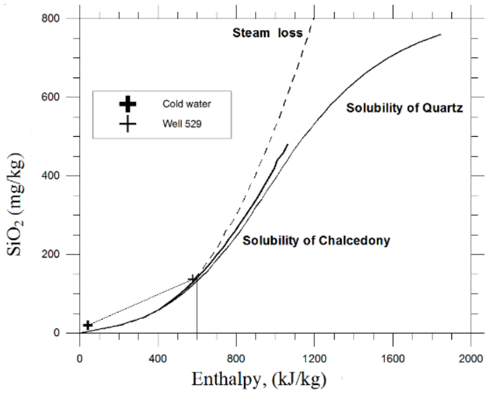

Figure 3. Silica-enthalpy diagram for well 529

The temperature of the reservoir indicated by the calculated chalcedony geothermometer (table 1) is close to the production temperature of the water from well 4797. The silica-enthalpy mixing model was also used in order to estimate the reservoir temperature. Based on this model, a temperature of 92ºC was obtained for the deep geothermal water from well 4797 (Figure 4).

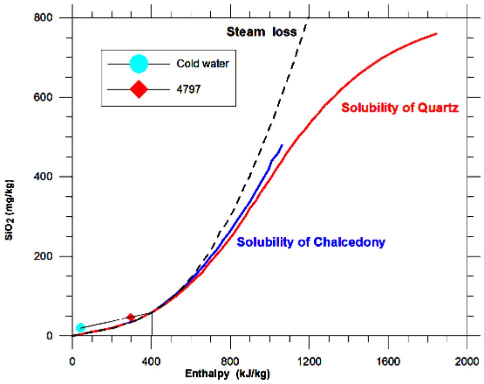

Figure 4. Silica-enthalpy diagram for well 4797

5. CONCLUSIONS

The deep water temperature is controlled for low-temperature geothermal wells by silica geothermometers.

The difference in temperature at wellhead and in the reservoir might be due to mixing with cold water in the upper layers or only due to contact by the cold rocks.

The silica-enthalpy mixing model was applied in order to estimate the temperature of the hot water component into the reservoir feeding the wells.

The temperatures obtained using this method are higher than both those calculated from the chalcedony geothermometer and those measured at the wellhead.

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SYNTHESIS STUDY OF THE MONOLACUNARY KEGGIN $K_7PMo_{11}O_{39}$

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Abstract: *The synthesis of monolacunary Keggin* $K_7PMo_{11}O_{39}$ *was effectuated in this article using three different methods and were found arguments for one by one. A direct combination of simple oxoanions in water solution, under rigorous pH control in HCl medium was used in first method. The second method started from complete Keggin structure,* $H_3PMo_{12}O_{40}\cdot 12H_2O$*, when a unity of molybdate was put out and the third technique was based a combination reaction between trilacunary* $Na_3H_6PMo_9O_{34}$ *and two molybdate unities at optimal pH.* $K_7PMo_{11}O_{39}$ *resulted from all synthesis methods was analysed with UV-VIS, thermogravimetry, conductometry, potentiomery and AAS methods for determination of the chemical composition and structure.*

Key words: *Keggin, polyoxometalate, synthesis, UV-VIS*

INTRODUCTION

In this paper, we proposed to study the synthesis of monolacunary Keggin structure, $K_7PMo_{11}O_{39}$, in aqua solution, using three different synthesis methods. Synthesis were impeded by the low stability in water medium of monolacunary species, characterized by a high ability to transform in another polyoxometalates species more stable. Despite of the fact that the ammonium salt of monolacunary would be easier to separate from solution, we decided to prepare the potassium salt, motivated by wider possibility to use it a lot of other experiments and applications [1-5].

Those three methods applying to the synthesis of $K_7PMo_{11}O_{39}$ were the next [1-5]:

1) The direct synthesis from oxoanions of components;
2) The elimination of someone molybdate unity from polyoxoanionic acid with completely Keggin structure, $H_3PMo_{12}O_{40}$, under slowly alkalinisation with rigorous pH control;
3) The addition of two molybdate unities at a trilacunary specia, $Na_3H_6PMo_9O_{34}\cdot 13H_2O$ to an optimal pH.

The composition and structure of synthesis produces were analysed using UV-VIS, thermogravimetry, FT-IR, AAS, flamephotometry and conductometry methods [1-5].

MATERIALS AND METHODS

All reagents used were a high chemical purity. Both conductometric and pH measurments were driven with an A multimeter Multi 720 Inolab series WTW equipment. A derivatograph type Paulik Erdely 1500 C MOM Budapest, with a heating speed by 5°C min^{-1}, in the range 20-500 °C in the presence of α-Al_2O_3 as reference material into a static air stream was used for thermogravimetry analysis. UV-VIS curves and photocolorimeter determinations were effectuated with a spectrophotometer T60.

Metod 1. Synthesis of $K_7PMo_{11}O_{39}\cdot 17H_2O$ *from oxoanions of components*

The chemical reaction characteristic for this method was the next (1):

$$NaH_2PO_4 + 11Na_2MoO_4 + 16HCl + 7KCl \rightarrow K_7PMo_{11}O_{39} + 23NaCl + 9H_2O \qquad (1)$$

The synthesis was realised like in the speciality literature [6, 7]. 0.55 g (3.7 mmoles) $NaH_2PO_4 \cdot H_2O$ were dissolved under vigorous stirring in 30 ml distilled water and HCl was added to arrive to pH 3.5. In this solution 9.65 g $Na_2MoO_4 \cdot 2H_2O$ (37 mmoles) were added and the final solution was clear and yellow for a pH 2.5-3.5. After 15 minutes, 2 g KCl powder were added under stirring in the clear yellow solution and $K_7PMo_{11}O_{39} \cdot 17H_2O$ started to precipitate and was separated from solution. 4.44 g $K_7PMo_{11}O_{39} \cdot 17H_2O$ were obtained with a yield by 52.73%. This notes sample **1.**

Method 2. Synthesis of $K_7PMo_{11}O_{39} \cdot 17H_2O$ from $H_3PMo_{12}O_{40}$

In this method the synthesis was occurred in two steps. In the first step, *$H_3PMo_{12}O_{40} \cdot 12H_2O$* was synthesised in conformity with literature data and in the second a molybdate unity was eliminated from complete Keggin framework adding in drops $KHCO_3$ solution just to pH 2.5-3.5 finishing with the formation of monolacunary $K_7PMo_{11}O_{39}$ [3, 6, 7].
The chemical reactions for this method were:

$$12Na_2MoO_4 + Na_2HPO_4 + 26HCl \rightarrow H_3PMo_{12}O_{40} + 26NaCl + 12H_2O \qquad (2)$$

$$H_3PMo_{12}O_{40} + 9KHCO_3 \rightarrow K_7PMo_{11}O_{39} + K_2MoO_4 + 6H_2O + 9CO_2 \qquad (3)$$

5% $KHCO_3$ solution was added in drops to 11.23 g (5.5 mmoles) $H_3PMo_{12}O_{40} \cdot 12H_2O$ solved in minimum quantity of distilled water into a baker, solved at room temperature at pH 2.5-3.5. Monolacunary compound started precipitating and after ten minutes was separated. The yield of synthesis was 70% corresponding to 7.85 g $K_7PMo_{11}O_{39} \cdot 17H_2O$. This was noted sample **2**

Method 3. Synthesis of $K_7PMo_{11}O_{39} \cdot 17H_2O$ from $Na_3H_6PMo_9O_{34} \cdot 13H_2O$

In this method at the trilacunary Keggin $Na_3H_6PMo_9O_{34} \cdot 13H_2O$ were attached two molybdate units in conformity with reactions (4) and (5):

$$9Na_2MoO_4 + NaH_2PO_4 + 16HClO_4 \xrightarrow{5°C} Na_3H_6PMo_9O_{34} + 16NaClO_4 + 6H_2O \qquad (4)$$

$$Na_3H_6PMo_9O_{34} + 2Na_2MoO_4 + 7KCl \rightarrow K_7PMo_{11}O_{39} + 7NaCl + 3H_2O \qquad (5)$$

$Na_3H_6PMo_9O_{34}$ was prepared from oxoanions to pH 7.0-7.5, at 5°C in perchloric acid solution [6, 7]. In a baker, 2.35 g (9.72 mmoles) $Na_2MoO_4 \cdot 2H_2O$ were solved in distilled water and pH 3.5 was adjusted with $HClO_4$. 8.5 g (4.86 mmoles) de $Na_3H_6PMo_9O_{34} \cdot 13H_2O$ were added in solution under vigorous stirring and rigorous pH control using $HClO_4$. Finally, the yellow mixture reacted for ten minutes at pH 2.5-3.5. 2 g KCl were added and started to form the yellow crystals of

$Na_3H_6PMo_9O_{34}\cdot 13H_2O$. After filtration and drying of crystals, $K_7PMo_{11}O_{39}\cdot 17H_2O$ weighed 7.88 g (yield 71.33%). This was noted sample **3.**

RESULTS AND DISCUSSIONS

Water molecules were determined with thermogravimetry method for all samples. For chemical composition, $K_7PMo_{11}O_{39}\cdot 17H_2O$ crystals were degraded with a 6N NaOH solution to pH 12 at boiling for 30 minutes. Molybdate was separated after precipitation with hydroxichinoline. From filtrate were determined phosphate with photocolorimeter method and potassium with flamephotometer technique. Results of experimental analysis were recorded in Table 1.

Basicity of $K_7PMo_{11}O_{39}\cdot 17H_2O$ was determined with both conductometric and potentiometric methods. The variation of conductometry was followed for three different samples containing 10 ml 0.001 M $K_7PMo_{11}O_{39}\cdot 17H_2O$ in pH 3 buffer solution, providing from **1**, **2** and **3** reaction produces under titration with 0.1M NH_4Cl (Fig. 1). In all situations the rate combination between ammonium cations and polyoxoanion was 7 to 1, corresponding to basicity seven of monolacunary $PMo_{11}O_{39}^{7-}$

.

Table1. Elemental analysis of $K_7PMo_{11}O_{39}\cdot 17H_2O$ samples

	Sample mass	Components	Quantitative data		Molar rate
Sample	(g)		(g)	(%)	
Teoretical data	2273.1	K	273.0	12.01	7
		P	30.97	1.52	1
		Mo	1055.34	46.43	11
		H_2O	306	13.46	17
1	2.1805	K	0.26	11.92	7
		P	0.03	1.38	0.97
		Mo	1.010	46.32	10.98
		H_2O	0.285	13.07	16.5
2	2.2661	K	0.27	11.91	7
		P	0.035	1.54	1.09
		Mo	1.050	46.44	11
		H_2O	0.300	13.24	16.76
3	2.2489	K	0.27	12.0	7
		P	0.032	1.42	1.04
		Mo	1.040	46.24	10.96
		H_2O	0.297	13.21	16.68

Other method using for basicity determination was the potentiometric titration with 0.1 M NaOH of 0.01 M $K_7PMo_{11}O_{39}\cdot 17H_2O$ solution. In Fig. 2 is recorded the plot resulted from variation of potential at adding of different volumes of 0.1M NaOH. The plot from Fig. 2 presented two potential slopes, first corresponded at using of seven cations for a single $PMo_{11}O_{39}^{7-}$ unity, while the second was more significantly and was attributed to decomposition of polyoxoanion in oxoanions of components under alkaline medium.

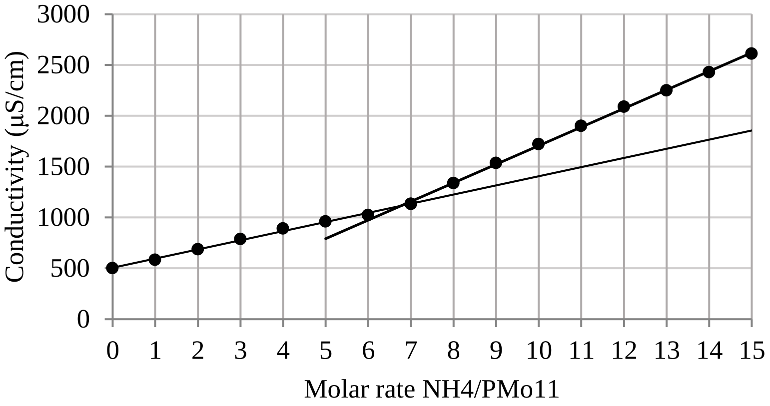

Fig. 1. The variation of conductivity at titration of 0.001M $K_7PMo_{11}O_{39}$ with 0.1 M NH_4Cl

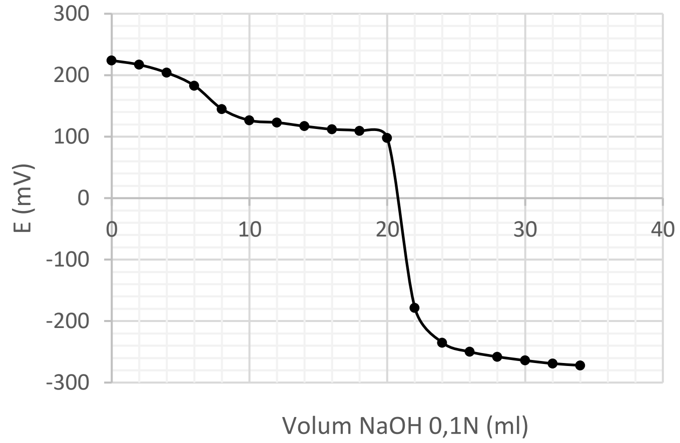

Fig. 2. The plot recorded after potentiometric titration of 0.01 M$K_7PMo_{11}O_{39}\cdot17H_2O$ with 0.1 M NaOH to pH 2.5 – 9

In Fig. 3, the multimeter was used for following the variation of conductivity in pH range from 2.5 to 11.5. pH modifications were realised using a 0.1M NaOH solution. Quickly changes of conductivity were recorded from pH 2.5 to 5.0, caused by a lot of the equilibrium reaction between polyoxoanionic species stables in this pH range. In Fig. 4 it was evidenced the exhibit of two slope changes points, first at pH 3.3 and the second at pH 4.3, corresponding to transformation of our compound in other with different structure and composition. Interesting, the increase of conductivity was insignificantly in a large pH range, from 4.7 to 9.6. The sudden increase of the plot slope after pH 9.6, respectively of the conductivity, was due to polyoxoanion decomposition and obtaining the oxoanions of components with a higher ionic mobility [1-5].

UV-VIS curves were recorded in Fig. 5 for $K_7PMo_{11}O_{39}\cdot17H_2O$. The study was effectuated for 10^{-6}-10^{-5} M solutions of all monolacunary produces from these three synthesis methods. The first maximum peak from 213 nm was assigned to an electronic transition from terminal length M=O of each MO_6 unity. The second maximum appeared faded like a shadow to 234 nm and corresponding to M-O-M electronic transitions from polyoxoanionic frameworks. From literature it was known the electronic transitions for $H_3PMo_{12}O_{40}$ and these were recorded at 208 nm for M=O and 229 nm for M-O-M and the last appeared better defined, characteristically for complete framework. The shift of both peaks in the UV-VIS spectrum of monolacunary to higher wave length indicated a decreasing of stability after damage of MO_6 unity from the complete polyoxoanionic framework [8, 9].

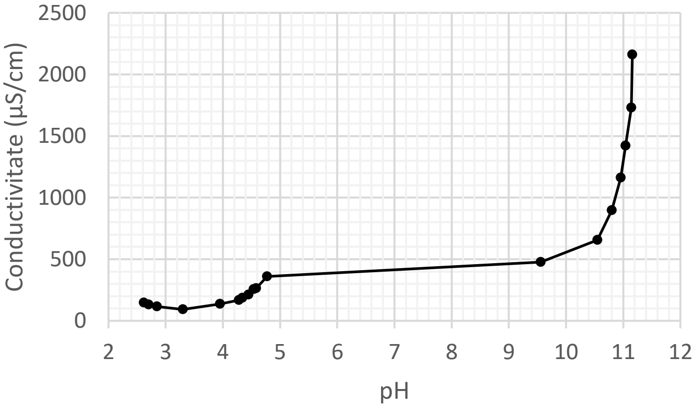

Fig. 3 Conductivity variation of 0.01 M $K_7PMo_{11}O_{39}\cdot17H_2O$ with pH from 2.5 to 11.5

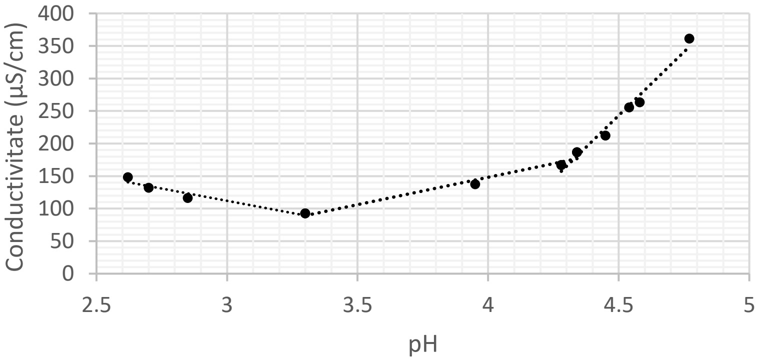

Fig. 4. Conductivity variation of 0.01M $K_7PMo_{11}O_{39}\cdot17H_2O$ in pH range 2.5-4.5

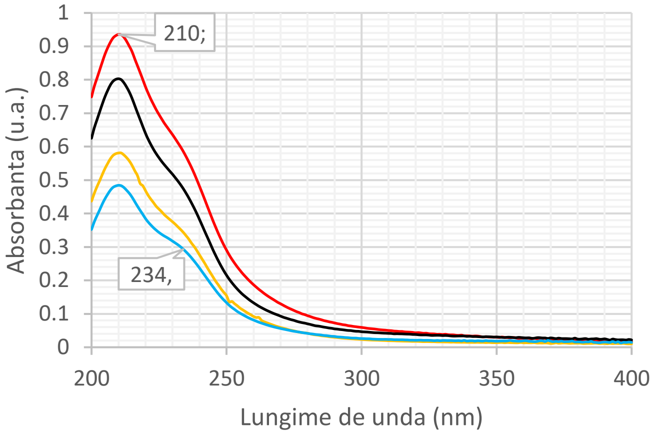

Fig. 5. UV-VIS curves of $K_7PMo_{11}O_{39}\cdot 17H_2O$ from all synthesis methods

CONCLUSIONS

The synthesis of $K_7PMo_{11}O_{39}\cdot 17H_2O$ was effectuated efficiently at pH 2.5-3.0, more conductometric study revealed the transformation in another compound over pH 3.3. Perchloric acid proved to be better than HCl in synthesis of $PMo_{11}O_{39}^{7-}$, it was noticed an increase of yield in this. Both, analytical and conductometric methods confirmed basicity seven of our synthesis produces, characteristic for monlacunary anion, $PMo_{11}O_{39}^{7-}$. Spectrum UV-VIS of all our synthesis compounds were similar, exposing two maximum so other Keggin polyoxometalates studied before and showed allure specific for monolacunary species.

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Analele Universităţii din Oradea-Fascicula Chimie, Vol. XXIV, 2017

STANDARD PHYSICO-CHEMICAL EVALUATION OF SOME COSMETIC PRODUCTS

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***Abstract**.*
A case study was conducted in this paper: a comparative study of the physico-chemical properties of two cosmetic products from Cosmetic Plant : a cream with honey and royal jelly, for dry and dehydrated skin and a cream with argan and aloe vera for normal-dry skin, based on argan oil For these cosmetical products, the main physico-chemical characteristics have been determined by specific methods: appearance, color, odor, solubility, melting point, pH, acidity index, iodine index, saponification index

***Key words**: cosmetic products, physico-chemical characteristics*

INTRODUCTION

Cosmetic creams are semisolid preparations designed to supply the necessary fat for the skin and to restore the optimal acid environment, as well as to remove the secretory substances, the most important factor in their diversification being raw and auxiliary materials. Dermatocosmetics have a special formula and contain high quality ingredients and preservatives chosen to avoid allergic reactions, ensure good tolerance, and be specific to each individual [1-8].

The main purpose of cosmetic creams refers to their action on the deep layers of the skin and not just to the action that has it on the surface of the skin. To achieve its goal, cosmetic creams must exhibit certain physico-chemical characteristics that support both the qualities required of such a product and the safety of their use in terms of chemical properties.

In this paper a case study eas performed, namely a comparative study of several physico-chemical properties, of two cosmetic creams from Plant Cosmetic, by determining the main physical and chemical characteristics: appearance, color, odor, solubility, melting point, pH, acidity index, iodine index, saponification index by specific methods.

MATERIALS AND METHODS

All chemicals used are p.a purity . The temperature at which the determinations were made is the standard at 25 ^oC. The main parameters of quality or physical-chemical properties that characterize cosmetic products are: smell, color, appearance, solubility, pH, acidity index, iodine index, saponification index, melting point.

Laboratory determinations were made with laboratory equipment and chemical reagents prepared according to specific methods [1,2,7].

RESULTS AND DISCUSSIONS

The two cosmetic creams studied are:
1) - a face cream, Cosmetic Plant with honey and royal jelly. for dry and dehydrated skin, (CP1)
2) a face cream, Cosmetic Plant with argan and aloe vera for normal-dry skin, based on argan oil, (CP2)

Physical properties of creams:

Determination of odor

To determine the smell of a cosmetic product, in our case a cream for hydrating the skin, the sample is spread on a thin glass plate, then the organoleptic odor can be perceived, which may vary according to the ingredients of the product (Table 1).

Determining the appearance

The appearance of the cosmetic product consists in pressing about 1 g of the product between two glass plates until a uniform layer of 0.5 mm is obtained. The sample to be analyzed is then examined by light transparency, [7] - Table 1.

Determining the color

We spread a sample of the cosmetic product to be analyzed on a thin layer on a white paper and compare the color with the standard sample [7], - Table 1

Determination of solubility

The substance is considered to be dissolved when the examined solution with the naked eye has no longer suspended particles. The traces of mechanical impurities are not taken into account if the solution, without being filtered, meets the transparency standard and if after a 1 hour rest, these impurities are not visible. (Table 1)

Determination of emulsion type

Creams can only be diluted in their continuous phase. When applying the dissolution method, if the cream is diluted in water it means that its continuous phase is aqueous. It turned out that the two creams analyzed are oil-in-water type.
When applying the staining method, the analyzing cream on a watch bottle extends to 1 mm thick. In a few places, one drop of 1% methyl blue to the pipette was added. After 10 minutes, we examined the surface of the sample. The reagent diffused in blue stains on both samples, which confirmed that the samples were of the oil-in-water type.

Determination of melting point

The melting point is the temperature at which the sample to be analyzed melts completely.
The sample to be analyzed is injected into a two-end open glass tube, 10 cm in length and 2 mm in internal diameter, to obtain a compact 10 mm sample of the sample to be analyzed. The sample tubes were kept at 7 ° C for 24 hours. Adding a thermometer to the tube, then placing it in an Erlenmeyer flask with water, we warmed to 5 degrees lower than the expected melting point of the sample, aprox. 35 ^{o}C. The assumed melting point is the temperature at which the sample moves to the top of the tube [8] – Table 1

Table 1 .The physical properties of studied cosmetic creams

Sample	Odor	Color/ Appearance	Solubility	Emulsion type	Melting Point ºC
CP1	Intens smell of honey	White/ Opaque	in water, without residue	Oil in water	40
CP2	Smell of argan oil	White/ translucid	in water, without residue	Oil in water	37

Chemical properties of cosmetic creams

Determination of pH

Cosmetics should have a pH of between 5 and 7, with the exception of intimate hygiene products or acid-based treatments for skin exfoliation. Eye care products are important to maintain a pH value of 7 (neutral) in order not to cause stomach ache when used. Both acidic and alkaline products are aggressive to skin contact, so if they have a pH between 4-5 and 7-10 they can cause small irritations, and those with pH below 4 or over 10 cause severe and permanent burns to the skin .

Adjusting the cosmetic pH is of great importance in the cosmetic product completion. If the pH is above 7, it should be lowered using an acid (usually lactic or citric acid), and if the pH is below 5 then it is raised using a base (using a solution soda).

Measurement was done with pH indicator paper. Both samples indicated pH values within the allowable range (Table 2).

Determination of acidity index

Analytical weighted samples were dissolved in 50 ml solution of equal volume alcohol and ether, neutralizing with a few drops of phenolphthalein. We titrated the solution with 0.1 N KOH in water until the pink color is stained [8]. We also titrated a blank test. The acidity index is higher for argan cream, CP2 (Table 2).

Determination of saponification index

Fatty substances are saponified with KOH, and excess KOH is titrated with HCl. In a flask, the sample of cream is analitical weighted and 25 ml of KOH and 50 ml of alcohol were added. The balloon is covered with a plug, through which an ice-cooled refrigerant passes, then it is heated in the water bath for 30-40 min. After this time the solution is titrated with 0.1 N HCl, after adding 4-5 drops of phenolphthalein. In another flask a blank sample is prepared, so the difference between the titration of the control sample and that of the creamer solution will give the number of ml of KOH used for saponification. From this result, the number of KOH mg needed to saponify a gram of cream [8] is calculated. The CP2 argan cream has a higher saponification index (Table 2).

3.1.9.1 Determination of iodine index

The iodine value is the degree of unsaturation of a fat. It is the value that expresses the amount of iodine added to 100 g of the sample to be analyzed. The sample to be analyzed is weighed, then dissolved in 4 ml of chloroform and 5 ml of 0.1 N iodine alcohol solution were added to a 300 ml round bottom flask. The closed bottle is kept in the dark for 30 minutes, shaking from time to time. To the solution in the flask is added 3 ml of KI and 2 ml of water and then titrated with 0.1 N sodium thiosulphate until the light yellow color appears. After the yellow-colored appearance, 4 ml of starch is added to the solution and titration is continued until discoloration. A blank test will also be titrated. The iodine index is calculated according to the standard method [8]. Obviously the sample with argan oil (liquid, unsaturated), CP2 has a higher iodine index (Table 2).

Table 2 .The chemical properties of studied cosmetic creams

Sample	pH	Acidity index mg KOH/g cream	*Saponification index* mg KOH/g cream	Iodine index (g I/100 g sol)
CP1	7	2.85	95.96	0.893
CP2	5,5	8.63	136.66	3.06
Blank sample	-	2.24	-	1.26 g

CONCLUSIONS

In conclusion, the two studied cosmetical products, (face creams), have properties consistent with those recommended for skin care products as follows:

- ➢ pH values range from 5 to 7. Skin pH is a measure of the acid layer on the skin and helps to maintain skin health, playing an important role in protecting the skin from pollution, food and hormone factors. pH determines the quality of the creams and influences the stability of the emulsion, the degree of dispersion and the viscosity of the creams.
- ➢ The cream layers do not contain crystalline particles or agglomerates (grunts) and no drops of oil, water or fat to indicate lack of stability.
- ➢ The smell of the studied creams is characteristic of the standard, with no odor or rancid odor.
- ➢ The water content and volatile substances depend on the type of emulsion, the cream with argan oil being fatter as the honey cream.
- ➢ The total fat content of the creams varies depending on their type between 1-33%, and we can characterize the honey-semigrass cream and the cream with argan-fat oil.
- ➢ The saponification index, ie the amount of NaOH (in mg) required to neutralize free acids and those resulting from the saponification of one gram of product for the two creams corresponds to the recommended standard values.
- ➢ The stability of the creams is appreciated by the amount of time expressed in hours in which creams retain their homogeneity. Creams

retained their appearance over the 6-hour study period, with melting points of 37 ° C (CP2) and 40 ° C (CP1) respectively - values clearly higher than 34 ° C, where the stability of the cosmetics studied is appreciated.

➢ The iodine or peroxide index shows the degree of oxidative grease grazing and indicates that the CP2 cosmetic product is more susceptible to oxidation than CP1.

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Cosmetic products to be used, other than enrollment in the standard quality parameters, must also fulfill additional conditions established by the European policies, namely the requirements for hazard characterization and exposure to chemicals [9-17]

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SURVEY OF IRON CONTENT IN SOME VEGETARIAN DIETARY SOURCES

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Abstract: *The deficiency of iron, an essential micro mineral, in the human body, is very common, especially for the vegetarians. Vegetarians are more susceptible to the deficiency of iron because they consume non-heme iron therefore they need to use a large amount of food rich in iron. In the present study some vegetarian food samples, acquired from local (Oradea Romania) sources, belonging to different food categories (vegetable, seeds, cereals, beans and fruits) were analysed. The iron content was determined using the thiocyanate spectrophotometry technique. The results showed that from the analysed food the sesame seeds and chickpeas beans had the maximum contribution towards the dietary iron content followed by parsley leaves and oat. The analysed fruits had the minimum iron content.*

Key words: *vegetarian food iron content, UV-VIS spectrophotometric technique*

Introduction

Iron is an essential nutrient that plays an important role in many bodily functions. A diet lacking in iron can lead to symptoms as: low energy levels, shortness of breath, headaches, irritability; dizziness or anemia [1]. Iron can be found in two forms in foods: heme and non-heme bounded [2]. The primary dietary sources of heme iron are hemoglobin and myoglobin from meat whilst nonheme iron is took over from cereals, seeds, legumes, fruits, and vegetables [3]. Heme iron is highly bioavailable (15%-35%) and there are little effect of dietary conditions on its absorption. Nonheme iron absorption is much lower (2%-20%) and it is strongly influenced by the presence of other food components [3]. Nonheme iron, despite its lower bioavailability, generally contributes more to iron nutrition than heme-iron because the quantity of nonheme iron in the diet is usually greater than that of heme-iron in most meals [4].

The recommended daily intake (RDI) for iron is based on an average intake of 18 mg per day. Individual requirements depend on the person's gender and life stage. The fraction of iron absorbed from the amount ingested is typically low (5% to 35%) depending on circumstances and type of iron [5]. The average adult stores about 1-3 g of iron in the body outcome the balance between dietary uptake and loss. About 1 mg of iron is lost each day through scaling of cells from the skin and mucosal surfaces [6]. Menstruation increases the average daily iron loss to about 2 mg per day in female adult’s cases [7]. These basal losses represent approximately 0.9 mg of iron for an adult male and 0.8 mg for an adult female [9]. The rise during childhood period requires a higher dietary iron intake [8]. All those aspects must be taken in consideration for a balanced daily iron dietary.

Consequently, there is a need to survey the amount of iron in the local vegetarian food products to establish a correct dietary for the vegetarians. In the present study some vegetarian food samples belonging to different local purchased food categories (vegetable, seeds, fruits, grains and cereals) were analysed.

MATERIALS AND METHODS

Food samples

Twenty vegetarian food samples belonging to different food groups: vegetables, seeds, fruits, grains and cereals were bought from the local supermarkets of Oradea-Romania (table 1).

Samples processing:

1-15 g of the edible portion of the food samples was weighed and dried at 200-240ºC, to constant weight, in an oven with air flow. After the drying process the samples were dissolved in 10 mL-30 mL of 2 M HCl. The obtained samples solutions were stirred for about 5 minutes and then filtered [1].

Analysis of the samples:

Thiocyanate spectrophotometry was carried out in the visible range of the spectrum [10]. The absorbance values were measured using a Spectrophotometer UV-VIS T60, at 480 nm, for all twenty samples and then the concentration of iron were determinate using the previous calibration curve recorded using standard solutions of $FeCl_3$ and on the principle of the Beer-Lambert law. The absorbance was measured immediately after adding KSCN because the colour of the solution fades within 15-20 minutes and the absorbance value can be affected [1].

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Table 1. The iron content in different food samples

No.	**Vegetarian Food Category**	**Items taken in survey**	**Iron content** **(mg Fe^{3+}/100 g food sample)**
1.	Seeds	Sesame raw	14,6
2.		Linen raw	5,7
3.		Nut raw	2,6
4.		Sunflower raw	1,45
5.	Beans	Chickpeas dried	6,2
6.		Yellow lentils dried	5,98
7.		Kidney bean dried	2,19
8.		Pease dried	1,5
9.	Cereals	Oat whole grain	4,65
10.		White rice, long grain	4,4
11.		Wheat whole grain	3,35
12.		White Quinoa whole grain	1,4
13.	Vegetables	Parsley leaves	6,2
14.		Spinach	2,7
15.		Broccoli	0,7
16.		Eggplant	0,456
17.	Fruits	Strawberries	0,35
18.		Peaches	0,30
19.		Red grapes	0,24
20.		Plum	0,17

RESULTS AND DISCUSSIONS

The absorbance values were determined and the concentration was found out by interpolation or extrapolation using the calibration graph prepared earlier. The iron determined in the different food samples is presented, by categories and in decreasing orders in Table 1

Among the five food groups, the seeds (sesame seeds-14,6 mg/ 100 g of food sample) were observed to contain the maximum iron content followed by beans, cereals, vegetables and fruits. Parsley leaves and chickpeas (6,2 mg/ 100 g of food sample) and sesame seeds (14,6 mg/ 100 g of food sample) were found to contain exceptionally high quantities of iron. Through the cereals oat and white rice have the highest iron content with a value of 4,65 respectively 4.4 mg/ 100 g of sample. The fruits were seen to have the lowest iron content (plum 0,17 mg/ 100 g of food sample). Amidst fruits the peaches and strawberries had a good iron content of 0,30-0,35 mg/ 100 g of sample.

CONCLUSIONS

The main aim of this survey was to determine the iron content in 16 local (Oradea-Romania) purchased vegetarian food samples using the thiocyanate spectrophotometric technique.

The results showed a good quantity of iron in the seeds and vegetables followed by grains, cereals and fruits.

The poorest source of iron was found within the local fruits (plums). An extremely high quantity of iron was observed in sesame seeds and parsley leaves.

Vegetarians, being usually susceptible to low iron intake, as they are dependent on non-heme sources of iron which are not readily absorbed and are not very rich in iron as are the heme sources, may improve their dietary iron intake (according to RDI of iron) by following a diet containing iron-rich vegetarian food sources like green leafy vegetables (spinach), seeds (sesame), grains (lentils and kidney beans).

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THE INTERPRETATION OF SOME PARTICULAR PHYSICO-CHEMICAL PARAMETERS OF THE "BIG EYE" WATER OF PEȚA RIVULET

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Abstract: *The present study aims at interpreting several physico-chemical parameters of the Peța Rivulet water in the Big Eye area - where the Peţea Nature Reserve - Natura 2000 site was delineated, compared to the values of the same parameters of the different samples of water taken from points – considered as relevant for the study - of Peţa downstream. The experimental data were reported for the 3rd class quality of water, by the monitoring institution, the Crişuri Basin Water Administration Oradea. Most of the analyses were made in the laboratories of Oradea Water Company and their interpretation revealed vulnerabilities in the sense of eutrophication and lack of thermal water of the Big Eye water of Peței Reservation.*

Key words: *ecosystem, biotope, biocenosis, eutrophy, Nymphaea Lotus L. Var. Thermalis, Melanopsis parreysii, Scardinius erythrophthalmus racovitzai, thermal aquifer.*

1. INTRODUCTION

Peța Rivulet Nature Reserve from Băile 1 Mai, Bihor County, is declared by Law no. 5 of the 2000 a protected area, part of the Nature 2000 European Ecological Network, belonging to IV IUCN category. The Nature 2000 form specifies the following features of the site: "An aquatic ecosystem with a well-defined physiognomy, representing the only natural thermal ecosystem in Romania. The reservation is of great scientific significance for the European genofond due to relict species that survived the quaternary glaciations: the termal pond-lily - Nymphaea Lotus L. Var. Thermalis, is the only case where a species of tropical plant lives spontaneously in a temperate climate; Melanopsis parreysii, after Muhlfeld - is an endemic relict species of snail, and Scardinius erythrophtalmus racovitzai – the rudd is an endemic species of fish[4,5].

At the time of its declaration as a nature reserve, its territory included the Peței water upper course, with a length of about 1500 m, including the Eye of Gypsies - with the first thermal spring – the Eye of Pump and the current Eye, with an arm having the witdth of approximately 10-20 m and the length of about 800-1000 m. These three waterholes had (the Gypsies' Eyes and the Eye of Pump are clogged) or still have (the Big Eye, which dwelt the relict fauna, as well as the main thermal sublacustrine spring) a series of sublacustrine springs as sources of thermal water supply and a few streams as surface tributaries. On the upper course of Peţa Rivulet, in this geothermal area, the 1 Mai balneoclimatic resort is situated. After a distance of about 12 km, Peţa flows, crossing a part of Oradea city, in Crişul Repede[4].

The Big Eye feature is similar to the eutrophic lakes. The favorable environmental factors are: richness of nutrients, temperature, light, CO_2 coupled with a contribution of allogene or intrinsic organic substances, where the biogenic elements N and P are triggering factors. In the first phase, the biological productivity of the habitat populations increased, favoured by the thermal regime of the thermal water. By increasing the biomass of macrophytes, planktonic algae, they led to the thickening of the bottom of the lake with organic suspensions, which, decomposing themselves, consume oxygen, and from some point on the decomposition becoming anaerobic (in the lower areas of the lake and of the sludge due to lack of oxygen), toxic gas generator (methane, hydrogen sulphide, ammonia etc.), unsuitable for biocenoses and also for biogenic elements that strengthen the cycle of biomass generation. Due to the decrease in the amount of the oxygen dissolved in the lower part of the lake, the fish fauna has also reduced. The increase of the amount of the sapropelic sludge deriving from the decomposition of the biomass leads to the decrease of the depth of the lake (unfavorable to the growth of the water lily rhizome) and its clogging. At the same time, the sludge being rich in salts and with a slightly acidic pH promotes the absorption of biogenic elements (N and P) by the submerged and floating flora that have osmotic absorption, to the detriment of the water lily and of the plants with roots, which have radicular absorption[5].

The contribution of agricultural suspensions brought from the surrounding lands, during the spring floods, by the cold Betfia rivulet, but also duet o pollution, has overlapped the natural phenomen. Concurrently, a major factor in the ecological disaster of today's reservation, when all the three relict species are no longer present in their natural environment (the thermal snail is extinct and the water lily and the rudd are reproduced in captivity or in special pools) is the irrational and partly illegitimate use of geothermal water in Băile 1 Mai and Băile Felix resorts.

2. MATERIALS AND METHODS

As Peţa rivulet is a surface water which is not subject to industrial pollution, the list of indicators to be interpreted includes: temperature, pH, conductivity, total solids dissolved, total hardness, dissolved oxygen, chemical oxygen consumption, nitrates, nitrites, sulphates, phosphates, chlorides, ammonium. During the elaboration of this list, there were taken into consideration the quality elements necessary for the assessment of the ecological state of the rivers and lakes, as provided by the Law regarding Water from 25.09.1996, updated on 15.02.2017, indicated by physico-chemical parameters: temperature conditions, oxygenation, mineralization, acidification, nutrients, transparency, pollution[6].

The analyses were partly carried out at the Oradea Water Company, and the interpretation of the data was performed in cooperation with institutions specialized in water monitoring in Bihor County: Crişuri Basin Water Administration Oradea, Custody of Peţea Rivulet Nature Reserve, University of Oradea, Public Health Directorate Bihor.

The water sampling map to be analyzed was correlated with their relevance for the "ecosystem diagnosis". Thus, the following points were selected:

1. The Big Eye - km 0, as here there is the sublacustrian spring deriving from a funnel with a diameter of about 5-10 m and a depth of 4.3-5 m, which feeds the lake of geothermal interest and which housed at the greatest extent the relict flora and fauna of Peţea Nature Reserve – and then downstream[4];

2. Rontău bridge - km 1, because Peţa passed through Venus Pool, but still has not reached the confluence with its cold tributary, Hidişel, possibly a domestic water supply.

3. Ion Bradu Bridge - km 5. Combined with Hidisel rivulet and entering Oradea, Peţa rivulet also passed the agricultural land and the industrial area of the former C.E.T. 2, with a decommissioned waste dump. These are the major potential pollutants, the rivulet being a collector of zonal rainwater.

4. Ronald Reagan Bridge - km 8 - is the second collecting point in Oradea. At Reagan Bridge, Peta has a 3 km route in the city and also has made its confluence with Adona brook.

5. Traian Blajovici Bridge - km 10, is the last point of collecting in the city, other downstream points being hardly accessible and irrelevant for the research.

The water samples have been collected in plastic containers because of their mechanical strength and because of this, ions exchange between the water and the container is thus avoided. Water samples were analyzed within 1-3 hours since the moment of collecting so that water did not change its chemical composition due to oxidation-reduction processes, microorganism activity, and ions exchange between vessel walls and water[3] .

The measurements were carried out over two years, namely: June-July 2016, March-June 2017, at relatively stable hydrodynamic and warm intervals, in areas where the currents are more stable

.

Also, the obtained values were compared with the standard admissible values of the indicators for different classes of surface water quality, according to the updated 107/1996 law and compared with the quality status class referring to different indicators, class established by the Crişuri Basin Water Administration Oradea, which monitors this creek[6].

The methods used are illustrated in Tables 1-7 of the "Results and Discussion" section.

3. RESULTS AND DISCUSSIONS

For the first session of collecting the water samples, performed on 29.06.2016, the data obtained from the analysis of the parameters measured at the Drinking Water Laboratory of the Water Company Oradea for samples taken from the Big Eye, compared to the other locations, are included in Table 1 .

The second series of determinations, following the incursion on the Peţa Rivulet from 01.07.2016, was carried out at the Laboratory of Hygiene of Ionizing Radiation within the Bihor Public Health Directorate. The results are contained in Table 2.

The third series of determinations were carried out at the Waste Water Laboratory of Oradea Water Company on 05.07.2016. The results are shown in Table 3.

Table 4 shows the results of temperature, pH and conductivity measurements performed by using the HQ30D.99.103203 digital multimeter Kit manufactured by Hach Lange Germany, in the spring of 2017, in relatively stable hydrodynamic periods, in clear days with temperatures of the air between 18-240C, within the time interval 9-12. Repeated samples were taken from the lake over several days, due to the particular importance regarding thermality.

Table 1. Values of physical and chemical indicators obtained at the Drinking Water Laboratory, Oradea - June, 2016

Indicator	Unit	The value obtained at the Big Eye	Range of values obtained	Analysis method
Turbidity	NTU	3.47	1.82 ÷ 15.1	SR EN ISO 7027/01
Conductivity	µS/cm	710	688 ÷ 817	SR EN 27888/97
Total dissolved solids	mg/l	341	330 ÷ 393	SR EN 27888/97
Hardness (Ca+Mg)	°germane	12.20	6.83 ÷ 21.61	SR ISO 6059/08
Ca^{2+}	mg/l	49.60	26.4 ÷ 100.1	SR ISO 6058/08
Mg^{2+}	mg/l	22.84	13.6 ÷33.04	SR ISO 6058/08
Fe_{total}	mg/l	0.289	0.112 ÷ 0.532	SR ISO 6332/96
Permanganate index	mgO_2/l	4.51	2.61 ÷ 3.80	SR EN ISO 8467/01

Table 2. Results of Radiochemical Analysis - July, 2016

MS analysis method		Radionuclide standard	Valid values Law 458/2002	Result with standard extended uncertainty (k = 2)
Global Alpha	SR ISO 9696/2013 PS-LIRI-06 Ed.3.Rev.0/2014	americium 241	0.1 Bq/l	0.027±0.011Bq/l
			0.1 Bq/l	0.078±0.026 Bq/l
Global Beta	SR ISO 9697/2013 PS-LIRI-07 Ed.3.Rev.0/2014	Potassium chloride	1 Bq/l	0.077±0.051 Bq/l
			1 Bq/l	0.243±0.098Bq/l

Table 3. Values of physical-chemical indicators obtained at the Waste Water Laboratory, Oradea - July, 2016

Indicator	Unit	The value obtained at Big Eye	Range of values obtained	Analysis method
pH	unit. pH/temp	7.47 at 25.1 ^{0}C	7.47 at 25.1^{0}C ÷ 8.01 at 24.8^0	SR EN ISO 10523/2012
Total Suspensions	mg/l	<4.0	<4.0	SR EN 872/2005
O_2 dissolved	mgO_2/l	3.61	3.61 ÷ 10.6	SR EN 25813/2000
Ammonium	mg/l	0.495	<0.02 ÷ 0.495	SR ISO 7150-1/2001
Nitrates	mg/l	1.85	1,85 ÷ 6,81	HACH LCK 339
Nitrites	mg/l	0.105	0.024 ÷ 0.242	HACH NitriVer 3
Phosphates	mg/l	0.227	0.227 ÷ 1.09	HACH LCK 349
Chlorides	mg/l	10.1	3.72 ÷ 22.3	SR ISO 9297/2001
Sulphates	mg/l	74.0	60 ÷ 123	HACH SulfaVer 4

Table 4. Results obtained by immediate analysis with the digital flexiparameter

Sample	Data	Air temperature (^{0}C)	Sample temperature (^{0}C)	pH (unit.)	Conductivity (µS/cm)
1	31.03	18.2	25	7.205	595
1	31.03	18	24.7	7.228	630
1	20.06.2017	23.1	22.9	7.302	566
1	20.06.2017	23	22.8	7.304	539

The characterization of the ecological status according to the requirements of the Water Framework Directive (transposed into the Romanian legislation by Law 310/2004 which amends and completes the Water Law 107/1996) is based on a system of classification in 5 classes, namely: very good, good, moderate, weak and low.

The institutional correspondence with ABA Crişuri revealed that this institution deduced, following the monitoring of both the natural reserve and the whole course of Peţa Rivulet, that the final ecological state of the rivulet, both on Peţa-Sânmartin/the Big Eye - middle section and on the section Peța - downstream Oradea per 2016 is moderate (3rd quality class), that is, according to the definition of this state in the Law of Water, "the values of the biological elements for surface waters deviate moderately from the values characteristic of the unaltered areas (of reference) or with minor anthropogenic alterations"[6].

The analysis and the discussion on the values of the indicators obtained reveal:

1) As reflected in Table 4, the air temperature is close to that of the water, depending mainly on the solar radiation. The collections were made closer to the banks, which explains the relatively high thermal values; indeed, it is known that the bank's temperature is higher than in the middle of the stream due to the faster heating of the shore than of the water. At the same time, the days of collecting were hot days when, due to water evaporation, there may occur increases in the concentrations of salts in the upper layers which, becoming denser, come down. Seasonal thermal variations lead to variations in the density of water layers, the stratification being direct in summer when the temperature of the layers decreases from top to bottom; in spring and autumn, due to the mixing of the layers with the horizontal currents and winds, there is a thermal uniformization. This is even more pronounced in the small lake and in the brook[2,4].

The interesting hypothesis we issue is that it is possible that the water temperatures in the Big Eye may be higher on a day of March with lower air temperature than on a day of June with high temperature, as it can be seen in table 4, because the climatic season had not yet begun, when the consumption of geothermal water led to a decrease in the water level in the lake and its temperature. Also, a few meters from the lake, the water temperature of the creek leaving the Big Eye area under the concrete bridge was less than about 10^0C. However, the water temperature values in the lake denote a low thermality - if we can speak of thermality - compared to the values obtained in the previous years (in 2003 - about 30^0C at the spring). The values in the lake have been measured in the area of the funnel below which the sublacustrian spring originates[4].

2) The pH values cover a normal range for non-alkaline surface water with values between 7.205 at 25^0C and 8.01 7.7 at 24.9^0 C.

3) The total water nitrogen in the water consists of organic nitrogen, derived from biological compounds, i.e. aminoacids, peptides, proteins and the anorganic, the mineral one (ammonium, nitrites, nitrates). The large amount of plankton and suspended organic matter, as it appears in Peța Rivulet in many places, is an important source of nitrogen[4].

The ammonium ion showed low concentration values at all collecting points in both successive years of determinations, with only one exception: the value of at least 10 times higher, on the average, of the ammonium ion concentration at point 1 in the Big Eye area, as shown in Table 3. The value in the point 1 area is in the third quality grade class attributed in 2016 to the brook in that area, for the ammonium, the maximum status being identified by the ABA Crişuri, the monitoring institution at that point. This high ammonium ion concentration can correlate with lake eutrophication. The large amount of biomass was aerobically oxidized, then the decomposition became anaerobic. Biogenetic elements (ammonium, for example), as well as toxic gases (methane, ammonia, hydrogen sulfide), which have affected the Big Eye's biocenosis, have a negative effect on the lake habitat. The high ammonium ion value can also be due to organic pollution in the area, to the supply of agricultural suspensions deriving from the spring floods of Betfia stream[4].

The nitrites result from the incomplete oxidation of ammonia in the presence of nitrifying bacteria. They represent a more advanced stage of the decomposition of organic substances with N (the first stage being the appearance of ammonia). The presence or increase of the normal nitrite concentration indicates an older, less dangerous pollution. The concomitant presence of ammonia and nitrates indicates continuous pollution. Sometimes, nitrites can also come from reducing the nitrate in the presence of a reducing flora and an increase in the temperature of the environment[1]. The values of nitrate ion concentration, determined in the two years and recorded in Table 3, corresponded, on average, to classification in the third grade class of quality of the brook water. The relatively high value of this ion concentration in the Big Eye is highlighted, the causes being similar to those revealed at the previous point (eutrophication of the lake).

4) The phosphates derives either by dissolving minerals and then they accompanied by the fluoride anion or by pollution with waste water, pesticides, fertilizers, alkaline detergents, leakage from sanitary facilities, and their excess favours the eutrophication of basins, through their role in algae development. High phosphate contents may indicate pollution of animal origin, especially if correlated with the development of microbial fauna, as algae consume phosphorus[1,3].

The phosphate ion showed high values of its concentration, exceeding the moderate values, the maximum value being about 5 times higher at the collection point 4, compared to the point 1 – Big Eye, where the value of the phosphate ion concentration was within the maximum value of this indicator, corresponding to class 3 of water quality. These data can be seen in Table 3.

5) Turbidity, global mineralization, calcium and magnesium ions, total iron, radioactivity, nitrogen and chlorine in the water of the Big Eye - were within normal limits.

6) Oxygen favors the destruction of anaerobic bacteria and contributes to the oxidation of organic matter. Oxygen consumption takes place within the process of biochemical transformation and degradation of organic and mineral substances (iron, manganese etc.). In waters with high organic concentration, processes of anaerobic degradation of organic

matter are installed. Large organic load may also be due to the phenomenon of self-pollution, a natural phenomenon of massive destruction of flora and fauna, especially after periods of intensive proliferation of vegetation of the water - a phenomenon present in eutrophication - followed by the increase of organic substances in decomposition, rotting and degrading[1].

If in the case of oligotrophic lakes, the distribution of oxygen follows the temperature dependence of the gas solubility, in the case of lakes or waters with less turbulent flows, such as the Peța Rivulet, where the eutrophic phenomenon is present, the oxygen is over-saturated and deficient in the bottom water due to the decomposition of benthic water deposits. In the case of Peţa Rivulet, both at the lake from Big Eye and along the course, one can observe the substantial development of phytoplankton and submersible and floating vegetation, indicating eutrophication. The biomass productivity is disproportionately high compared to its decomposition and aerobic mineralization, so that accumulation of partially mineralized organic matter and concomitant decrease of dissolved oxygen in water occur[4].

Table 3 shows that the dissolved oxygen concentration in the Big Eye area is very small, characteristic of a 5-grade water quality, even if the collection was performed on a warm day when the solubility of the oxygen decreases in water. At all the other collecting sites, the dissolved oxygen values were high, reported at peak on water quality classes. This is an indicator which, along with the high value of the ammonium and phosphate indicator, leads to the assertion of the eutrophication of the lake from the Big Eye. The amount of oxygen dissolved in the water can qualitatively correlate with those of chemical oxygen consumption by organic matter, because large amounts of organic matter in water involve germs pollution - which causes oxygen consumption for the oxidation of organic matter.

Oxygen consumption values were determined by the "permanganate index" method and are presented in Table 1. It should be noted that the values of the two indicators are determined for different water samples taken on different days but close chronologically and integrated into the same meteorological, hydrological chart. It is noted that the highest oxygen consumption is also recorded for the sample from the Big Eye, which demonstrates the validity of the above-mentioned conclusion.

4. CONCLUSIONS

By analyzing and interpreting some physical-chemical parameters of the water in the Big Eye area of Peţa Nature Reserve, it was aimed at establishing a "diagnosis" of the ecosystem of this rivulet which shelters, at its origins, a nature reserve site Natura 2000 and whose biocenosis is affected by irrational exploitation of geothermal water in the area of spa resorts Băile Felix and Băile 1 Mai. The Big Eye clogging - the lake underlying the thermal water that provided the tertiary survival of endemic relict species Nymphaea Lotus L. Var. Thermalis, Melanopsis parreysii and Scardinius erythrophtalmus racovitzai, - the erosion of its sublacustrian source, the phenomena of spontaneous and pollution-induced eutrophication are factors that endanger the reservation itself.

Taking into account the quality elements necessary for the assessment of the ecological status of the rivers and lakes provided for in the Law of Water of 25.09.1996, updated on February 15, 2017, we analyzed the values of some physical-chemical parameters of the water of the rivulet, taking samples of water from five places relevant to research, starting with Big Eye, located at the origin of the Pețea Rivulet Nature Reserve - which dwelt relict fauna as well as the main thermal sublacustrian spring - during June-July 2016 and March-June 2017, in relatively hydrodynamically stable and warm ranges.

The obtained values were compared with the standard values admitted for different classes of surface water quality, according to the updated Law 107/1996 and compared with the quality status report related to different indicators for the near sampling areas obtained by the Crişuri Basin Water Administration Oradea which monitors this rivulet.

The results indicated the average framing of these indicators in the quality class 3 of Peța Rivulet water, as established by the monitoring of ABA Crişuri. But there have been highlighted values that exceed the admitted values for this class and which contribute to shaping an ecological "diagnosis" or "strengthening" one already developed.

Thus, the ammonia ion has a quantitative peak at point 1 of collection - Big Eye, which is in the 3rd class of water quality but is about 10 times higher than the most measured values along the the course of Peța Rivulet water. Probably this peak correlates with the eutrophication phenomenon of the lake from Big Eye.

The nitrate ion has higher concentrations of water in the Big Eye - probably due to the eutrophication of the lake - but also in the 4th and 5th collecting points, probably due to pollution with substances that supply biogenic elements: detergents, domestic waters, organic pollution. The phosphates have high concentration values exceeding the quality class 3 admissible values at collection points 3, 4 and 5. These high values can come either by the dissolution of minerals or, especially, or by pollution generated by waste water, pesticides, fertilizers, detergents, animals. The result of the increasing of the phosphorus content, a biogenic element, could be to stimulate eutrophication. In the Big Eye water the values of phosphates correspond to the classification in the 3rd class of quality.

The values of dissolved oxygen and of chemical oxygen consumption are correlated with a deficiency of oxygen in the Big Eye, which again leads to the eutrophication phenomenon of the Big Eye.

In conclusion, there are four vulnerabilities that have been identified as a result of this research:

a) Increased concentrations of ammonia and nitrate ions, the relatively high concentration of phosphate ion, and the small amount of oxygen dissolved in the Water of the Big Eye, illustrate the current state of eutrophication; the substantial presence of phosphates in this site indicates a favorable eutrophication factor.

b) The water temperature in the Big Eye is improper to thermal water, the sublacustrian source being affected by the irrational use of geothermal water in the area. The vulnerabilities described have irreversibly damaged the habitat of Peţa Nature Reserve.

It is advisable that the researches be continued by an interdisciplinary team of experts from chemistry, biology, geography, hydrology, geology so that whole sets of experimental data are gathered through analysis that are repeated at the same points over several days and seasons, in order to validate a representative conclusion on the state of this ecosystem.

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Analele Universităţii din Oradea-Fascicula Chimie, Vol. XXIV, 2017

DETERMINATION OF STABILITY CONSTANTS AND OPTIMAL SYNTHESIS CONDITIONS FOR THIOCYANATE COMPLEX OF FE (III)

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Abstract:
In this paper the formation of thiocyanate complex of Fe(III) was studied. We proposed to determine the optimal formation condition into a synthesis from $FeCl_3$ and KSCN mixture. Achieving of thiocyanate complex was favored by room temperature, pH 2 and a reaction time by minimum 50 minutes. It was recommended using of HCl for acidulation of reaction medium and it was indicated to avoid sulfuric acid and acetate acid. Stability constant recorded the highest value to pH 2 and decreasing at pH growth. The study was accomplished in 1-4 pH range.

***Key words**: thiocyanate, iron, stability constant, spectrophotometry*

INTRODUCTION

Substitution reaction (1) between iron (III) aquacomplex and thiocyanate took place just to an equilibrium point, defined by a stability constant, noted in equation (2) [1-5]. Equilibrium concentrations of both iron and thiocyanate were characterized by equations (3) and (4):

$$[Fe(H_2O)_6]^{+3} + SCN^- \overset{K_S}{\Leftrightarrow} [Fe(H_2O)_5(SCN)]^{+2} + H_2O \qquad (1)$$

$$K_S = \frac{[\,Fe(H_2O)_5(SCN)^{+2}\,]_{eq}}{[\,Fe^{+3}\,]_{eq} \cdot [\,SCN^-]_{eq}} \qquad (2)$$

$$[Fe^{+3}]_{eq} = [Fe^{+3}]_{initial} - [Fe(H_2O)_5(SCN)^{+2}]_{eq} \qquad (3)$$

$$[SCN^-]_{eq} = [SCN^-]_{initial} - [Fe(H_2O)_5(SCN)^{+2}]_{eq} \qquad (4)$$

External factors like pH, temperature, reaction time, reaction medium (counterions, solvent) may involve in the reaction evolution. Such as we proposed to determine the optimal synthesis conditions of complex $[Fe(H_2O)_5(SCN)]^{2+}$ from $FeCl_3$ and KSCN: pH, type of acid from reaction medium, reaction time and work temperature. More we calculated the stability constant for this reaction conditions [6,7].

Materials and methods

All substances used in our experiments were analytical purity and the solutions were prepared with distilled water. All determinations were effectuated with a spectrophotometer T60.

pH influence in $[Fe(H_2O)_5(SCN)]^{2+}$ synthesis

The study was realised for pH values from 1 to 4. In four tubes 0.25 mL 0.02 M $FeCl_3$ and 0.25 mL 0.02 M KSCN were added. The pH control from 1 to 4 was realized with HCl solution by different concentration and distilled water just a final volume by 5 mL in all four samples prepared. Absorbances of solutions were measured with spectrophotometer at 470 nm, after 30 minutes reaction at room temperature beside a blank (0.25 mL 0.02 M $FeCl_3$ solution raised with distilled water to 5 mL). Results were recorded in Fig. 1. The higher absorbance was determined for reaction mixture prepared to pH 2. More, in range pH 1-4, the absorbance values of $[Fe(H_2O)_5(SCN)]^{2+}$ decreased from pH 2 to pH 4 [8].

In this experiment, we prepared four samples mixture reaction like in previous study at pH 2, with the difference that the acid added was not the same in all sample tubes (Table 1). Absorbances were measured after 30 minutes reaction at room temperature at 470 nm using the blank solution from Table 1.

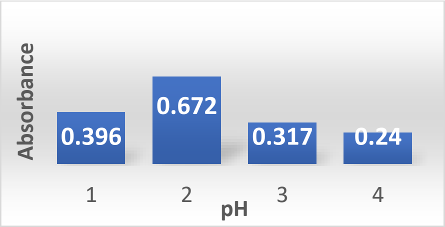

Fig. 1. pH influence in $[Fe(H_2O)_5(SCN)]^{2+}$ synthesis

The influence of the acid nature in $Fe(H_2O)_5(SCN)]^{2+}$ synthesis

At pH=2, the highest value of absorbance was recorded for reaction mixture prepared in acetic acid solution, but in this case the increasing of absorbance may be due to suppose of absorbance value of red solution from very stable complex $[Fe_3(\mu_3\text{-}O)(OAc)_6(H_2O)_3]^+$. In these conditions, the synthesis of $[Fe(H_2O)_5(SCN)]^{2+}$ was favorized by HCl presence and was the worst in H_2SO_4.

Table 1. The reaction mixtures prepared in different acid medium at pH 2 for $[Fe(H_2O)_5(SCN)]^{2+}$ synthesis

Reaction medium	0.02 M $FeCl_3$ (mL)	0.02 M KSCN (mL)	Vacid/Vwater (mL)	Absorbance
HCl	0.25	0.25	4.5	0.405
H_2SO_4	0.25	0.25	4.5	0.05
HNO_3	0.25	0.25	4.5	0.286
$H_3C\text{-}COOH$	0.25	0.25	4.5	0.415
Distilled water	0.25	0	4.75	0

Influence of temperature in $[Fe(H_2O)_5(SCN)]^{2+}$ synthesis

In five samples tube were added reaction mixtures between 0.02 M $FeCl_3$ and 0.02 M KSCN prepared like in Table 1 in HCl solution to pH 2. Each samples was put to react for 30 minute at 20 °C, 40 °C, 60 °C, 80 °C and 100°C. After reaction time, samples were could and the absorbance were determined at 470 nm related to the same blank. The highest values of absorbance were recorded at 20-40 °C and the absorbance decrease to increasing of temperature, so it was seen in Fig. 2 [9].

Influence of the reaction time in $[Fe(H_2O)_5(SCN)]^{2+}$ synthesis

A reaction mixture was prepared exactly in previous experiment and was stated measured the absorbance values at 470 nm between 5-120 minutes, every five minutes. The absorbance started to be constant from 50 minutes by reaction and kept unmodified after 24 hours (Fig. 3) [10].

Determination of the stability constant for $[Fe(H_2O)_5(SCN)]^{2+}$ at different pH

Values of absorbance for different complex concentrations resulted from reaction mixtures between 0.002 M KSCN and 0.2 M $FeCl_3$ were recorded in Table 2. Measurements of absorbances were effectuated after 30 minutes at room temperature at 470 nm to blank [11-13].

In Fig. 4, the equation from the linear variation of absorbance with complex concentration was determined and was used for calculated of $[Fe(H_2O)_5(SCN)]^{2+}$ concentration to equilibrium for reaction mixtures mentioned before in Table 3.

In Table 4, the values of stability constant (K_s) for each reaction mixture studied were determined with the help of equation (1), (2) and (3). For the median value of constant stability was calculated $\log K_s$.

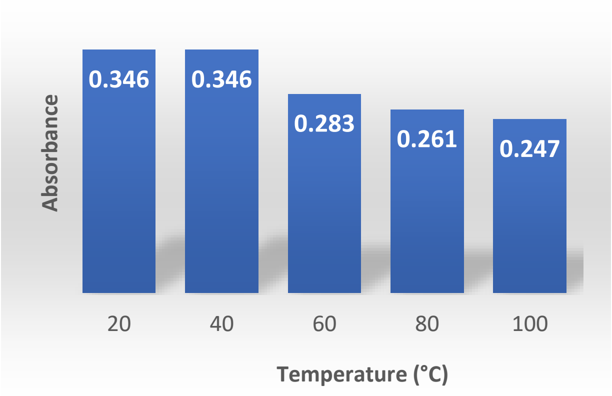

Fig. 2 Influence of the temperature in $[Fe(H_2O)_5(SCN)]^{2+}$ synthesis

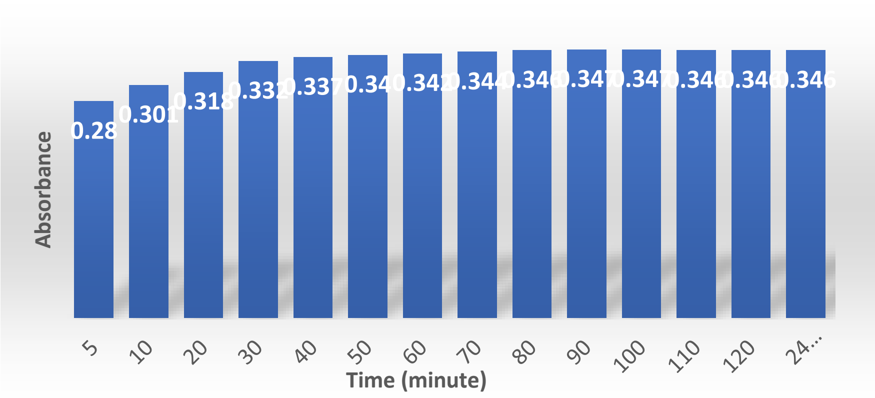

Fig. 3. Variation in time of $[Fe(H_2O)_5(SCN)]^{2+}$ absorbance

Table 2. Determination of absorbance for different $[Fe(H_2O)_5(SCN)]^{2+}$ concentrations to pH 1

0.002M KSCN (mL)	0.2M $FeCl_3$ (mL)	HCl (mL)	$[Fe(H_2O)_5(SCN)]^{2+}]$ (mmol/L)	Absorbance
0	1,25	3,75	0	0
0,05	1,25	3,7	0,02	0,078
0,1	1,25	3,65	0,04	0,146
0,2	1,25	3,55	0,08	0,296
0,3	1,25	3,45	0.12	0,432
0,4	1,25	3,35	0.16	0,574
0,5	1,25	3,25	0.2	0,735

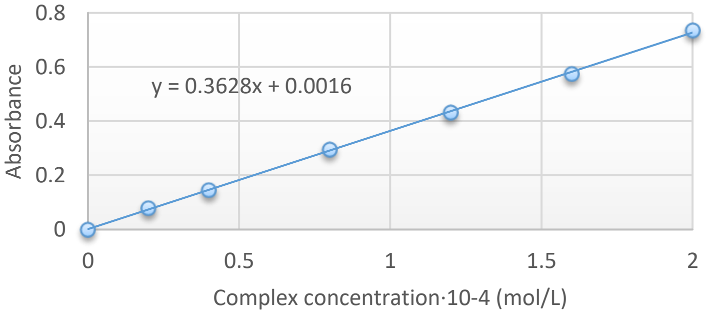

Fig. 4. Determination of equation from linear variation of absorbance with $[Fe(H_2O)_5(SCN)]^{2+}$ concentration to equilibrium at pH=1

Table 3. Determination of $[Fe(H_2O)_5(SCN)]^{2+}$ concentration at equilibrium to pH 1

KSCN 0,02M (mL)	$FeCl_3$ 0,02M (mL)	HCl (mL)	Absorbance	$[Fe(H_2O)_5(SCN)]^{2+}\cdot 10^{-4}$ (mol/L)
0,05	0,25	4,7	0,195	0,537
0,1	0,25	4,65	0,387	1,177
0,15	0,25	4,6	0,598	1,648
0,2	0,25	4,55	0,815	2,246
0,25	0,25	4,5	1,027	2,831
0,5	0	4,5	0,05	

Table 4. Determination of stability constant of $[Fe(H_2O)_5(SCN)]^{2+}$ to pH 1

Initial		Equilibrium			
$[SCN^-]$ (mmol/L)	$[Fe^{3+}]$ (mmol/L)	$[Fe(H_2O)_5(SCN)]^{2+}$ (mmol/L)	$[SCN^-]$ (mmol/L)	$[Fe^{3+}]$ (mmol/L)	K_s
0.2	1.0	0.0537	0.1435	0.9435	396.63
0.4	1.0	0.1177	02795	0.8795	478.8
0.6	1.0	0.1648	0.4214	0.8214	486.5
0.8	1.0	0.2246	0.5616	0.7616	525.12
1.0	1.0	0.2831	0.7169	0.7169	547.33
					486.876
				$\log K_s = 2.687$	

Stability constants were calculated for similar reaction mixtures in HCl solution prepared at room temperature but at different pH values. Absorbance of all these solutions were found at 470 nm after 30 minutes.

The values of stability constants and log K_s from these conditions were noted in Table 5. The highest stability constant was recorded at pH 2, in concordance with data resulted from influence pH study.

Table 5. The values of stability constant of $[Fe(H_2O)_5(SCN)]^{2+}$ at different pH

pH	K_s	$\log K_s$
1	486.876	2.687
2	917.52	2.963
3	403.183	2.606
4	202.66	2.307

CONCLUSION

The synthesis of $[Fe(H_2O)_5(SCN)]^{2+}$ from a mixture between $FeCl_3$ and KSCN took place better in HCl solution, to pH 2, at room temperature after 50 minutes of reaction.

Following the variation of $[Fe(H_2O)_5(SCN)]^{2+}$ stability in time indicated touching of the equilibrium after 50 minutes and preservation of this for 24 hours surely.

The synthesis of $[Fe(H_2O)_5(SCN)]^{2+}$ from $FeCl_3$ and KSCN is recommended to be effectuated in HCl solution and avoided using of sulfuric acid or acetate acid.

Determination of stability constant to different pH values indicated a highest value at pH 2 and a decreasing at pH growing.

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(12pt)

INSTRUCTIONS FOR AUTHORS (TIMES 14 PT BOLD, CAPITAL LETTERS, CENTRED)

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Abstract: *Abstract of 50-120 words (10 pt italic). It contains concise information about: objectives of the work, the results obtained, conclusions*

Key words: List 2-6 keywords. (l0 pt, italic).

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The paper has to be written in English. Each paper should be concise including text, figures and tables. Authors are kindly requested to submit a paper a hard copy or in electronic format in Microsoft Word file form. Acceptable versions are MS-Word 2003, 2007, 2010. The suggested structure of the main text: Introduction; Methods, techniques, materials, Study area; Results and Discussions; Conclusions; References. (10pt)

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- Use A4 format (210 x 297 mm),
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(Report)

[2] Carter, B., and Connell, C. (1980). Moa Point Wastewater Treatment Plant and Outfall Study, Report for the Wellington City Council, Wellington, pp. 31.

(Book)

[3] Grady, C.P.L., and Lim, H.(1980). Biological Wastewater Treatment Theory and Application, Marcel Dekker, New York, pp. 375.