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Tel. ++ 389 032 550 575	**Тел. 032 550 575**

E-mail: todor.serafimovski@ugd.edu.mk

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Original scientific paper

FLUORIDE CONTENT AND DEPENDENCE ON OTHER ELEMENTS IN SOME GEOTERMAL WATERS IN REPUBLIC OF MACEDONIA

Tena Šijakova-Ivanova[1], Vesna Ambarkova[2], Vassiliki Topitsogloy[3], Vesna Paneva-Zajkova[1]

[1]Faculty of Natural and Technical Sciences, "Goce Delčev" University, Goce Delčev 89, MK–2000, Štip, Republic of Macedonia
[2]Faculty of Dentistry, Department of preventive dentisivy, Ss. Cyril and Methodius" University in Skopje, Republic of Macedonia
[3]Faculty of Dentisty, Aristotle University of Thessaloniki, Greece
tena.ivanova@ugd.edu.mk

A b s t r a c t: The paper presents the results obtained for the fluoride content in some geothermal waters in Republic of Macedonia. The results made it possible to determine the dependence between fluoride and other chemical elements in the geothermal water. Fluoride content was determined with jon-analyser (EA 920 ORION) and Ion selective electrode for detection of trace fluoride. For chemical analysis was used 10% TISAB Alumina. Samples were collected in plastic bottles and kept in dark place not longer than two months. Examination on other chemical elements was carried out with AES-ICP. First, the samples were filtered and preserved with HNO_3.

Key words: fluoride; jon analyzer; AES-ICP

INTRODUCTION

Fluoride is an ion of the element fluorine, and is a natural component in most water resources.

Fluoride is an essential element notably for health (Frencken, J. E. 1992; USNRC 1993; USPHS 1991). Fluoride is present in surface, more in ground water and much more in geothermal and mineral water (Allmann, R. and Koritnig,1974; Deshmukh A. N. and Maple D. B. 1996; Gaciri S. J. and Davies 1993; Handa B. K. 1975). Fluorine content varies widely.

Fluoride content in water depends on several factories such as:

– geology of the terrain,
– porosity and alkali of soil,
– type of rocks,
– pH values and temperature,
– chemical and physical properties of water–bearing layer,
– content of calcium ion which limits dissolution of fluorine to 3.1 mg/l concentration,
– depth of source,

Specific geological conditions which result in higher concentration of fluoride in water are related to volcanic activity. Acidic rocks which are poor in calcium and rich in fluoride under high temperature activity release fluoride from the rocks or fluids after eruptive processes and hydration in water bodies.

Volcanic rocks and geothermal fluids can be regarded as key factor for the high concentration on fluoride in water (Lottermoser, B. G., and Cleverley, J. S. 2007; Hem, J. D.,1989; Sharma S. K.2003).

Fluoride is dissolved salt whose major sources in ground waters are apatite, mica and fluorapatite. They are associated with water with high pH values and low calcium concentration (Karthikeyan,.G, A. Shunmugasundarraj, 2008; Alagumuthu G and Rajan M 2008).

RESULTS AND DISCUSSION

Table 1 shows the chemical composition of investigated waters. Dependence between F^-–Cl^-, F^-–Na, F^-–Ca, F^-–Mg, F^-–As, F^-–Al, F^-–Fe, F^-–Cr is shown on Figs. 1–8. Correlation coefficient can be seen from the results given in Table 2

Table 1

Chemical composition of investigated geothermal waters

	Kežovica	Kumanovo	Katlanovo	Konjari	Bansko	Istibanja
As	0.177	0.076	0.004	0.060	0.016	0.187
Al	0.025	0.000	0.008	0.004	0.008	0.025
Sr	0.379	1.08	0.334	0.354	1.10	1.26
Ca	14.6	127.6	54.7	124.6	54.4	9.3
Ba	0.024	0.316	0.541	0.050	0.145	0.086
Mn	0.029	0.004	0.005	0.070	0.004	0.002
Fe	0.037	0.015	0.013	0.013	0.012	0.033
Cr	0.017	0.007	0.007	0.006	0.006	0.005
Mg	0.734	46.2	16.98	24.8	15.6	9.2
Na	524	311	27	70	189	543
F^-	14	0.58	1.5	0.33	1.8	5.4
P	0.024	0.022	0.022	0.761	0.005	0.003
Zn	0.019	0.008	0.596	0.178	0.007	0.005
Pb	0.011	0.003	0.014	0.001	0.001	0.006
Co	0.007	0.007	0.005	0.007	0.006	0.006
K	12.7	16.8	3.6	13.7	10.7	26.5
Cl^-	1368	312	354	1259	232	267
NO_3^-	0.059	0.068	0.029	0.066	0.029	0.016
NH_4^+	0.029	0.044	0.098	0.050	0.058	0.057
Hardness concentracion $CaCO_3$ (mg/l)	39.5	508.3	206.4	413.4	200.0	60.8
Classification	soft water	very hard	hard	very hard	hard	soft water

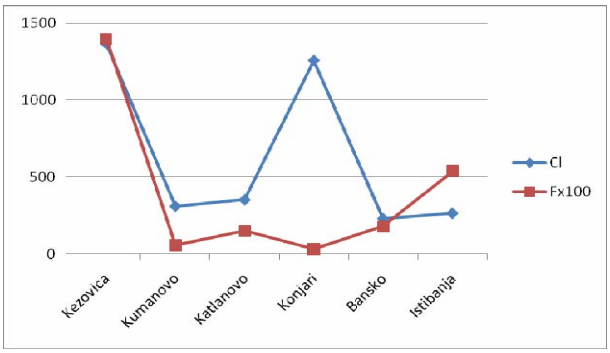

Fig. 1. Dependence between F^- and Cl

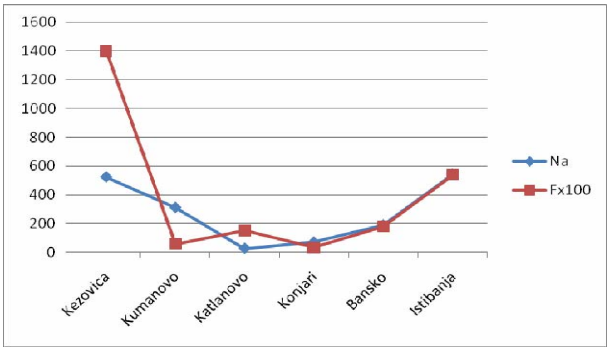

Fig. 2. Dependence between F^- and Na

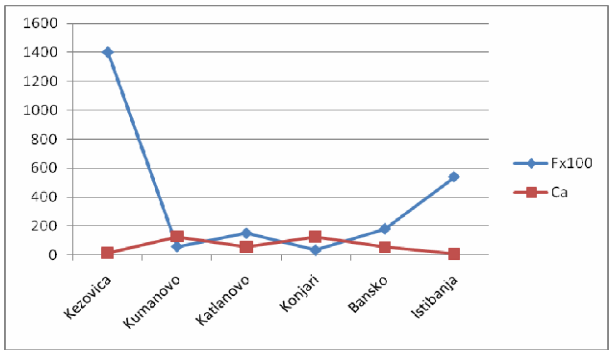

Fig. 3. Dependence between F^- and Ca

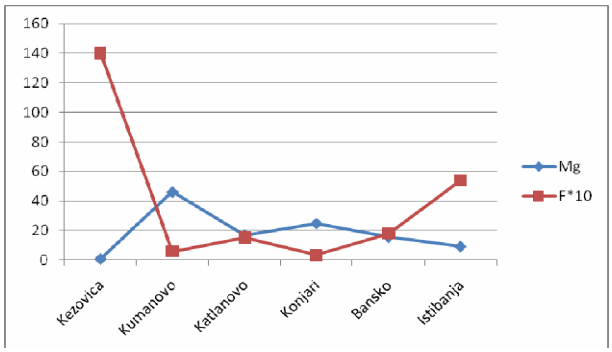

Fig. 4. Dependence between F^- and Mg

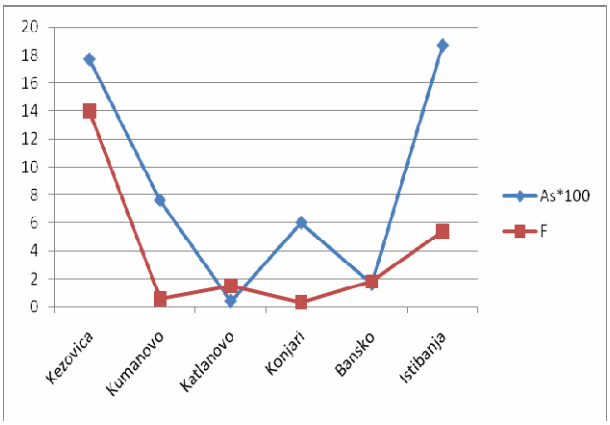

Fig. 5. Dependence between F^- and As

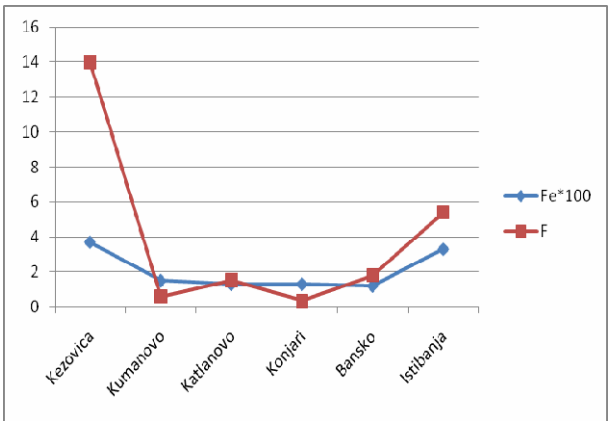

Fig. 7. Dependence between F^- and Fe

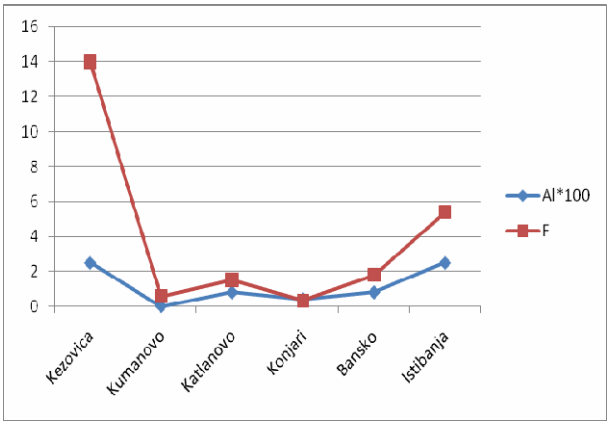

Fig. 6. Dependence between F^- and Al

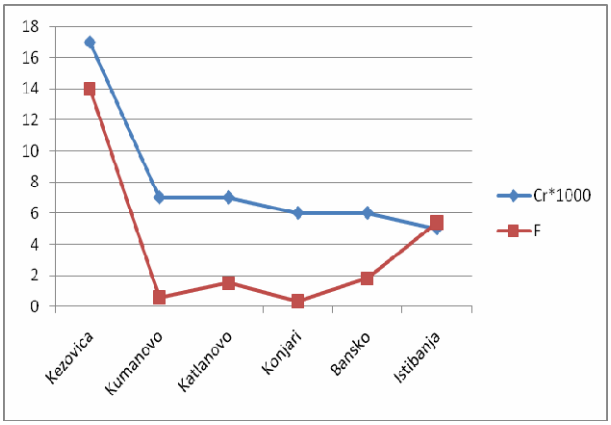

Fig. 8. Dependence between F^- and Cr

Table 2.

Correlation coefficient between F^- and Cl^-, Na, Ca, Mg, Al, As. Fe and Cr

	Cl^-	Na	Ca	Mg	Al	As	Fe	Cr
Correlation coefficient (r)	0.5174	0.7383	–0.7121	–0.7268	0.8400	0.7456	0.8930	0.8801

CONCLUSION

Investigations carried out led to the conclusion as follows.

Fluoride content is higher in Kežovica water and lowest in Konjare water. Dependence between F^-–Cl^-, Na, Al, As, Fe and Cr is proportional. Correlation coefficient for F^- and Cl^- has lower value, 0.5174 and correlation coefficient for F– and Fe has higher value, 0.8930 Non-proportional dependence was established between F^-–Ca and F^- Mg with correlation coefficient, –0.7121 and –0.7268. Kežovica and Istibanja are soft water. Kumanovo and Konjari are very hard water. Kežovica water, except higher concentration on F^- has higher value on Cl^-, Na, Al, Fe and Cr.

	Higher value	Lower value
F^-	Kežovica	Konjare
Cl^-	Kežovica	Bansko
Na	Istibanja, Kežovica	Katlanovo
Ca	Kumanovo	Istibanja
Mg	Kumanovo	Kežovica
Al	Kežovica, Istibanja	Kumanovo
As	Istibanja	Katlanovo
Fe	Kežovica	Bansko
Cr	Kežovica	Istibanja

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Р е з и м е

ЗАВИСНОСТ ПОМЕГУ КОНЦЕНТРАЦИЈАТА НА ФЛУОР И ОСТАНАТИТЕ ЕЛЕМЕНТИ ВО НЕКОИ ГЕОТЕРМАЛНИ ВОДИ ВО РЕПУБЛИКА МАКЕДОНИЈА

Тена Шијакова-Иванова[1], Весна Амбаркова[2], Vassiliki Topitsogloy[3], Весна Панева-Зајкова[1]

[1]Факултет за природни и технички науки, Универзитет Гоце Делчев, ул. Гоце Делчев, 89, МК-2000 Штип, Република Македонија
[2]Стоматолошки факултет, Катедра за превентивна стоматологија, Универзитет Св. Кирил и Методи во Скопје,Република Македонија
[3]Стоматолошки факултет , Аристотел Универзитет , Солун, Грција
[1]Faculty of Natural and Technical Sciences, "Goce Delčev" University, Goce Delčev 89, MK–2000, Štip, Republic of Macedonia
tena.ivanova@ugd.edu.mk

Клучни зборови: флуор; јон анализатор; AES-ICP

Содржината на флуоридните јони е највисока во водата од Кежовица, а најниска во водата од Коњаре. Корелацијата помеѓу содржината на флуоридни јони со содржината на Cl^-, Na, Al, As, Fe и Cr пропорционална. Коефициентот на корелација за F^-–Cl^- има најниска вредност, 0,5174, а за F^-–Fe највисока, 0,8930. Корелацијата помеѓу концентрацијата на F^-–Ca и F^-–Mg е обратно пропорционална со коефициенти на корелација –0,7121 и –0,7268. Водите од Кежовица и Истибања се меки води, а водите од Куманово и Катланово се многу тврди. Во водата од Кежовица се одредени највисоки концетрации не само за флуоридните анјони, туку и за Cl^-, Al, Fe и Cr.