

DETERMINATION OF INORGANIC COMPOUNDS IN DRINKING WATER ON THE BASIS OF HOUSE WATER HEATER SCALE

Part 1. Determination of heavy metals and uranium

*Miloš B. Rajković, Mirjana D. Stojanović,
Gordana K. Pantelić and Dragan V. Tošković*

The analysis of scale originated from drinking water on the house water heater, showed that scale is basically calcium carbonate that crystallizes hexagonally in the form of calcite. Scale taken as a sample from different spots in Belgrade – upper town of Zemun (sample 1) and Pančevo (sample 2) showed different configuration although it came from the same waterworks. That indicates either that the water flowing through waterworks pipes in different parts of the city is not the same or the waterworks net is not the same (age, maintaining, etc.).

All the elements which are dominant in drinking water (Ca, Mg, K, and Na), and which could be found in water by natural processes, are by their content far below the values regulated by law. The analysis also showed the presence of many metals: Ti, Pb, Zn, Cu, Li, Sr, Cd, and Cr in the first sample, which are not found in the scale taken near Pančevo.

The results obtained by calculating the mass concentration in drinking water on the basis of scale content, showed that both waters belonged to the category of low mineral waters. Contents of inorganic substances in these waters (117.85 mg/dm³ for sample 1 or 80.83 mg/dm³ for sample 2) are twice lower than the values predicted by the legislation. Gammaspectrometric analysis indicates the presence of radioactive elements – uranium and strontium which can influence human health.

KEYWORDS: Drinking water; scale, scanning electron microscopy (SEM);
X-ray diffraction analysis; gamma-spectrometry

Dr. Miloš B. Rajković, Associate Professor, Institute of Food Technology and Biochemistry, Faculty of Agriculture, 11080 Belgrade-Zemun, Nemanjina 6, Serbia&Montenegro; E-mail: rajmi@agrifaculty.bg.ac.yu; Dr. Mirjana D. Stojanović, Head of Sistem Quality and Characterization Laboratory, Institute for Technology of Nuclear and Other Mineral Raw Materials (ITNMS), 11000 Belgrade, 86 Franchet d'Esperey, P.O.Box 390, Serbia&Montenegro; Mr. Gordana K. Pantelić, M.Sc., Research Associate, Section Head of Radiology, KCS Institute of Occupational and Radiological Health "Dr Dragomir Karajović", Belgrade, Serbia&Montenegro; Dr. Dragan V. Tošković, Associate Professor, Faculty of Technology, University of Serbian Sarajevo, 76000 Zvornik, Karakaj b.b., Republic of Srpska, Bosnia&Herzegovina

INTRODUCTION

The hygienically correct drinking water is the basic postulate for good health, because it is necessary for living and personal and global hygiene. World Health Organization (WHO) ranks the quality of drinking water in twelve basic indicators of health conditions of a country's population, which confirms its important role in health protection and improvement.



The importance of drinking water is basically in its physiological role in the organism, e.g. in maintaining metabolic processes. Drinking water is of epidemiological and toxicological importance because bacteria, viruses and parasites may develop if drinking water contains contaminants in concentrations higher than allowed.

The water used for drinking, food preparation and for personal and global hygiene, must satisfy the basic health and hygiene requirements: sufficient quantities of safe water, i.e. the water that must not contain toxic and carcinogenic substances as well as pathogenic microorganisms. Drinking water must be without colour, smell and any energetic content. However, each water has its own organoleptic attribute or, as people say, it is drinkable or undrinkable (1).

Physical attributes of drinking water are: temperature, colour, turbidity, odour, conductivity, and so on.

The subject of the analysis in this paper is the scale originating from a house water heater and being a consequence of the sedimentation of inorganic non-volatile substances that are present in the water. As the content of scale is mainly due to the presence of inorganic compounds in water (2), the aim of this paper was to establish in an indirect way, the precise content of scale, and identify inorganic compounds and elements, especially heavy metals, which exist in drinking water. The part of inorganic compounds and elements is compared with maximum allowed concentrations (MAC) of these substances in water, given by the legislation (3,11).

EXPERIMENTAL

Two samples of scale formed by precipitation on water heater surface during a time period of 6 months have been used for this investigation. The scale originated from water present in the water-supply system of the city of Belgrade - Upper Town of Zemun (sample 1) and town of Pančevo-Krnjača (sample 2). Content of total solids, which actually represents the scale, was determined by heating 1.0 dm³ of drinking water to boiling and evaporating to obtain dry residue (4,5).

X-ray diffraction analysis was performed on previously ground scale, and the fraction of fine powder (6.3-2 μm) has been investigated. X-ray analysis was performed on a diffractometer Phillips PW 1009 with CuKα rays $\lambda = 1.54178$, under the operating conditions of the tube $U = 36$ kV, $I = 18$ mA, with goniometer velocity $V_g = 1^\circ 2\theta/\text{min}$ and the conditions $R/C = 8/2$ (6).

Scale was also analysed by scanning electron microscopy SEM, using a JSM-840A, JEOL, Tokyo, Japan, with the possibility of enlargement by 180.000 times and the resolution of 10 nm (7,8).

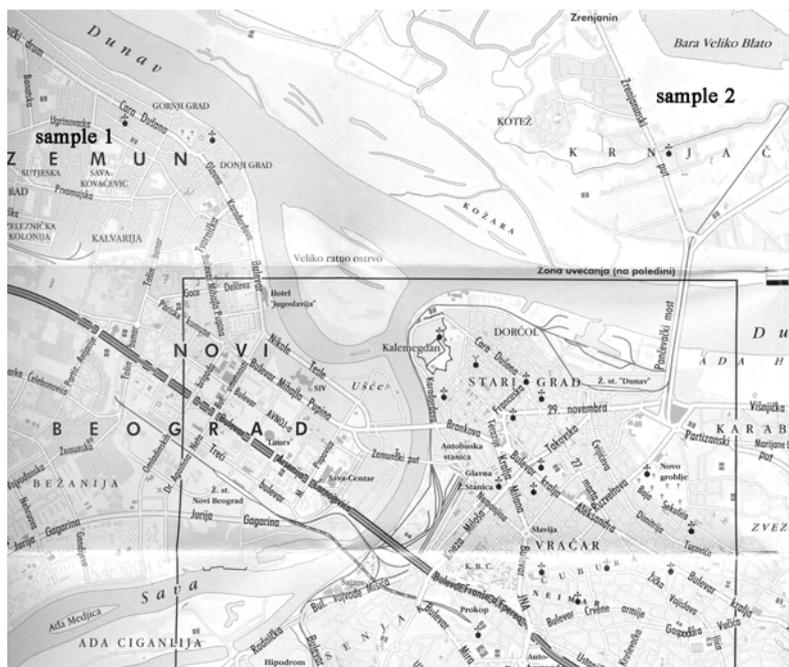


Fig. 1. Sampling spots

Composition of the scale was determined on an AAS Perkin Elmer 703 atomic absorption spectrophotometer, according to the methods DM 10–0/4, 0/6, 0/7, 0/8, 0/9, 0/10, 0/11, 0/12, 0/13 and 0/17 (9).

Quantitative content of uranium was assayed by fluorometric method based on linear dependence of the fluorescence intensity of the uranium solutions on their concentration. Linear dependence exists in very large range of low concentrations (to the power of four). Reduction of the fluorescence intensity is brought to the least possible amount by the technique of "standard addition" after the extraction of uranium with the synergistic mixture TOPO (three-n-octal fosphine oxide) ethyl acetate. Fluorescence intensity is determined by Fluorimeter 26-000 Jarrel Ash Division (Fisher Scientific Company, Waltham, 1978).

Low phonon measurements were carried out using CANBERRA Hp Ge coaxial detector with relative efficiency of 14%, FWHM of 1.7 keV, placed in vertical cryostat and protected with 2 cm of iron and 15 cm of lead. Total measured speed of phonon counting in the energy range of 20-2880 keV was 0.9 pulse/s. The spectrometer was connected to a CANBERRA 8k ADC "MCA 35" multichannel analyser which was connected to a HP Vectra ES/12 computer. Treatment of gamma spectra was performed using "Micro SAMPO" program. Time for sample measurements was about 160 ks, while measurements of phonon spectra were significantly longer and were carried out regularly between sample measurements.

Radiochemical method of separation of ^{90}Sr is based on oxalate displacing calcium from strontium, calcinated to the oxide and using tin as collector for ^{90}Y . The balance is established after 18 days, whereby ^{90}Y was removed by collector $\text{Al}(\text{OH})_3$, which was then ignited to obtain oxide that was measured on the α - β anticoincident counter (10).

RESULTS AND DISCUSSION

The results of the analysis of scale samples are given in Table 1. Chemical substances found in scale and their calculated concentrations in water compared with concentrations of these substances in Instruction of EU and WHO.

Table 1. Results of the analysis of scale samples

Chemical substance	Found in scale (in wt.%) in sample		Calculated mass concentration drinking water (mg/dm ³) in sample		Maximum of allowed concentrations in drinking water (mg/dm ³)		
	1	2	1	2	S&M	EU	WHO
Calcium, as CaO	50.25	48.85	107.50	69.83	100	–	–
Magnesium, as MgO	4.71	4.24	8.50	5.15	30	–	–
Sodium, as Na ₂ O	0.081	0.034	0.18	0.05	20.0	–	–
Potassium, as K ₂ O	0.024	0.012	0.06	0.02	10.0	–	–
Iron, as Fe ₂ O ₃	0.26	4.02	0.54	5.62	0.05	–	–
Manganese, as MnO	0.024	0.031	0.06	0.05	0.02	–	0.5 ^P
Silicon ^I , as SiO ₂	0.24	0.10	0.34	0.09	–	–	–
Aluminium, as Al ₂ O ₃	0.009	< 0.02	0.01	< 0.02	0.05	–	–
Titanium, as TiO ₂	< 0.02	–	0.04	–	–	–	–
Lead, as Pb	0.021	–	0.06	–	0.05	0.01	0.01 ^{II}
Zinc, as Zn	0.11	–	0.33	–	0.1	–	–
Copper, as Cu	0.016	–	0.05	–	0.1	2	2 ^{P,III}
Strontium, as Sr	0.05	–	0.15	–	–	–	–
Lithium, as Li	0.009	–	0.03	–	–	–	–
Uranium ^{IV} , as U	1.38 ppm	1.1 ppm	0.4 µg/dm ³	0.2 µg/dm ³	0.05	–	–
Nickel, as Ni	< 1 ppm	–	0.3 µg/dm ³	–	0.01	0.02	0.02
Cadmium, as Cd	5 ppm	–	1.5 µg/dm ³	–	0.005	0.005	0.003
Chromium, as Cr	7 ppm	–	2.1 µg/dm ³	–	Cr(VI) 0.05 Cr(III) 0.10	0.05	0.05
Loss by volatilization at 1000°C *	43.98	42.67	131.43	85.34			
Total amounts of inorganic substances	99.81	99.98	117.85	80.83	257.71		

Abbreviations used in the Table 1:

1 – sample 1

2 – sample 2

S&M – Serbia and Montenegro

EU – European Union

WHO – World Health Organisation

^p **Temporarily recommended value.** This term is used for water components which had been proved to be dangerous for health, but the available information on their impact on health are limited or uncertainty factor higher than 1000 had been used for calculation of their **tolerable daily intake (TDI)**. Temporarily recommended values are also recommended for: 1. substances for which the calculated recommended value would be below the limit of quantitative determination or below the limit that can be achieved by application of processing procedures, or 2. when there is a possibility that disaffection could contribute to the exceeding of recommended values.

^I Concentration in drinking water is not regulated by law

^{II} It is recognised that all waters can not fulfill recommended conditions immediately. In the meantime, all measures should be taken to diminish exposure to lead.

^{III} Concentration of a substance that is equal or lower than the recommended value based on the influence on health, but which may influence appearance, taste and smell of water.

^{IV} Maximal permitted concentration in bottled drinking water.

On the basis of the obtained results, the waters belongs to the category of weak mineral waters because total content of inorganic substances (117.6 mg/dm^3 and 80.83 mg/dm^3 , respectively) is lower than 500 mg/dm^3 . Also, contents of inorganic substances in these water samples are two and three times lower than the quantities permitted by regulation (257.1 mg/dm^3) (3,4). From that point of view, the water absolutely fulfills the hygienic conditions regulated by laws.

Diffractiongram of the analysed scale sample is presented in Fig. 2.

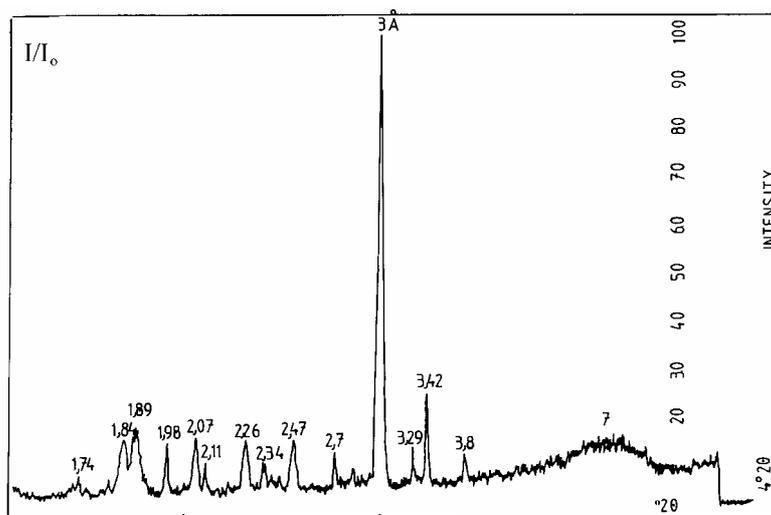


Fig. 2. Characteristic X-ray diffractiongram of the scale (sample 1)

In the obtained diffractogram the position of reflection has been determined and d value of the measured area, i.e. the integral intensities of certain reflections have been calculated with the aid of the program DRX Win 1.4 designed by V.P.Martin (6).

Calcium carbonate (CaCO_3) in the form of *calcite* (crystalizing in a hexagonal form) and *aragonite* (crystalizing in a rhombic form) gave numerous reflections in this diffractogram. Reflections of quartz are sharp and intensive. *Calcite* is detected on the basis of the strongest characteristic reflection at 3 Å and weaker ones at 3.8 Å, 2.47 Å, 2.26 Å, 2.07 Å and 1.89 Å. The presence of *aragonite* has been established on the basis of weaker reflections at 1.74 Å, 1.84 Å, 1.98 Å, 2.11 Å, 2.34 Å, 2.7 Å, 3.29 Å and the most intensive reflection at 3,42 Å.

On the basis of the presented diffractogram, it is not possible to establish the presence of other compounds, although an irregular and widened form of the reflection at 7 Å indicates the presence of other substances, but at very low concentrations, which can not be determined by this method. This extended peak indicates the presence of amorphous substances of organic and inorganic origin, and if inorganic, the most frequent of them is *limonite*.

Gamma-spectrometric analysis of the scale sample is carried out after drying scale sample at 105°C for 24 hours, in order to remove the moisture and reduce measurements to dry substance. The fur was packed into plastic dish and hermetically closed in order to keep developed radon. Measurement was performed after 20 days in order to balance developed radon with radium from which it originated and obtained spectrum is presented in Fig. 3.

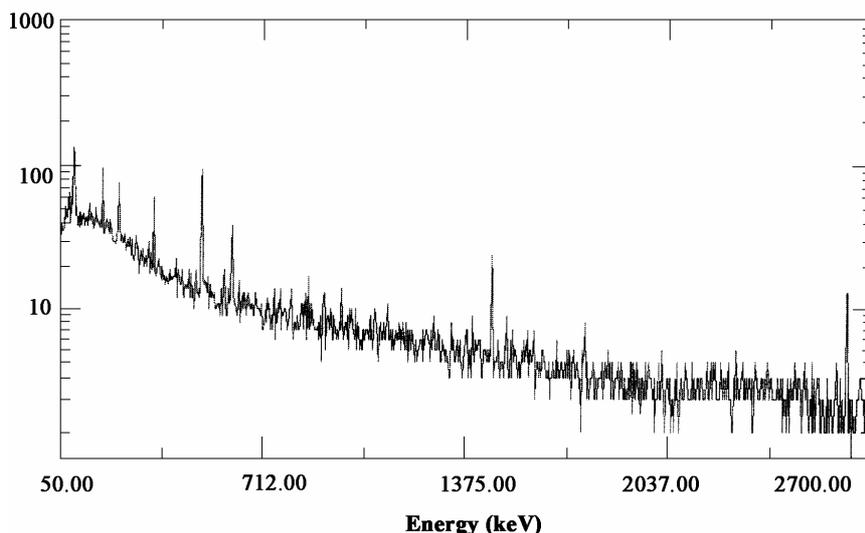


Fig. 3. Gamma-spectrometric spectrum of boiler scale (sample 2)

The results of measurement of gamma-emitter activity concentration in the scale samples (in Bq/kg) are represented in Table 2.

SEM photographs of samples heater scale are presented in Fig. 4 and Fig. 5.



Fig. 4. SEM photograph of sample 1 of heater scale (x500)

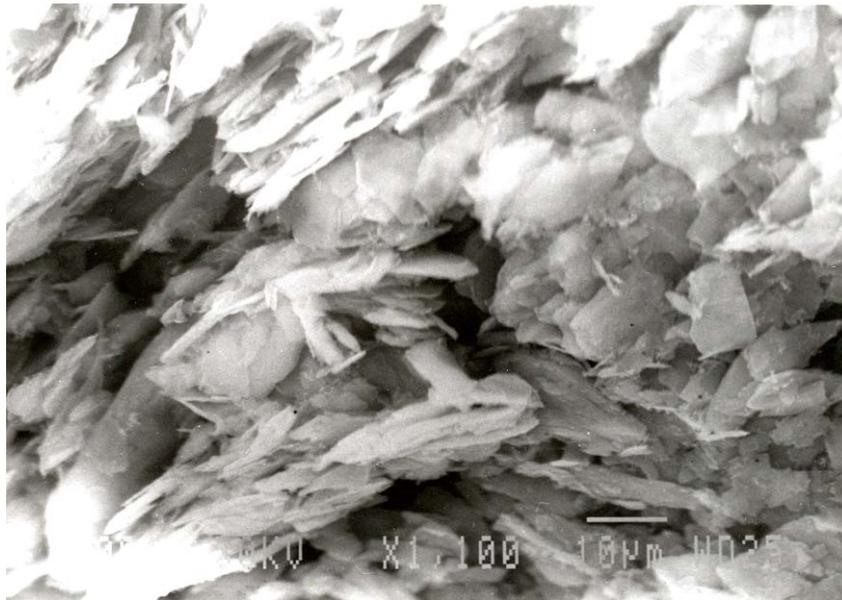


Fig. 5. SEM photograph of sample 2 of heater scale ($\times 1,100$)

Table 2. The results of the measurement of gamma-emitter concentration activity in the scale samples (in Bq/kg)

^{238}U	1	38.6 ± 11.7
	2	< 10
^{235}U	1	–
	2	< 0.3
^{226}Ra	1	1.19 ± 0.11
	2	4.6 ± 1.3
^{232}Th	1	0.91 ± 0.06
	2	1.8 ± 0.5
^{40}K	1	< 4.19
	2	2.06 ± 0.22
^{134}Cs	1	–
	2	< 0.2
^{137}Cs	1	< 0.45
	2	< 0.3

1 – sample 1 ; 2 – sample 2

The obtained results show that the first sample is more than four times more radioactive (as ^{238}U) than the other sample. Also, in the first sample, the measurable concentration of strontium of 0.05 wt.% was determined, while in the second sample the presence of strontium was not determined by AAS. However, the activity of the isotope ^{90}Sr that is 0.72 ± 0.11 Bq/kg was measured by radiochemical separation of strontium.

CONCLUSIONS

The analysis of scale obtained from drinking water in house water heater, at two places in Belgrade waterworks, showed that scale, although it has the same structure and crystallizes in the form of *calcite*, which was proved not only by taking SEM pictures but also by X-ray diffractational analysis, has the different content of chemical substances in different parts of the city.

Sample 1, which was taken from the spot of Zemun Upper Town, showed the presence of many inorganic substances, even strontium in measurable concentration (0.05 wt.%), whose presence was not confirmed by AAS in second sample.

The total amount (in mg/dm^3) of inorganic substances in water from which originated the first sample was by about 30 % higher than in water from which originated the second sample (part of the city Pančevo-Krnjača). In the first sample we found Ti, Pb, Zn, Cu, Li, Ni, Cd, Cr which were not present in the second sample.

In the water from which the first sample was taken we found higher presence of Fe, Cu, Mn, and especially Pb, than the maximum allowed concentrations.

As for the water from which the second sample was taken, the presence of iron in concentration more than 100 times higher than is allowed is really alarming.

These results indicate the damage of waterworks net, even the usage of iron and lead pipes, which shows the age of all waterworks system. The cause of higher presence of these metals in scale is also the house water heater.

In both samples of scale the presence of uranium was confirmed (1.38 and 1.1 ppm, respectively), which contributes to their total radioactivity.

ACKNOWLEDGEMENTS

The work was supported by the Ministry for Science, Technology and Development of the Republic of Serbia (Project 1941).

REFERENCES

1. Rajković, M.B.: Neke neorganske supstance koje se mogu naći u vodi za piće i posledice po zdravlje ljudi. *Hem. Ind. (Beograd)* **57**, 1 (2003) 24–34.
2. Rajković, M.B., I. Sredović i L. Perić: Određivanje kvaliteta vode na osnovu izdvojenog kamenca u bojleru. *EKO-KONFERENCIJA 2002: Zdravstveno bezbedna hrana*, Novi Sad, 25.–28. septembar 2002., Tematski zbornik, 2. Sesija: Zemljište i voda kao osnova poljoprivredne proizvodnje zdravstveno bezbedne hrane, s. 153–157.
3. Pravilnik o higijenskoj ispravnosti vode za piće, *Službeni list SRJ*, **42**, 1998., s. 4-10.
4. Rajković, M.B. and M. Stojanović: Determination of Heavy Metals in Drinking Water, *Международный форум "Аналитика и аналитики"*, Воронеж, 2-6 июня 2003, *КАТАЛОГ рефератов и статей, том 1, 4–С16*, с. 165.
5. Rajković, M.B. i M. Stojanović: Određivanje neorganskih jedinjenja u vodi za piće na osnovu izdvojenog kamenca, *XLI Savetovanje Srpskog hemijskog društva*, Beograd, 23. - 24. januar 2003., *Sekcija za analitičku hemiju, AH 18, Izvodi radova*, s. 32.
6. Martin, V.P.: DRXWin 1.4 a computer program: A graphical and analytical tool for powder XDR patterns, *University of Valence, Faculty of Chemistry, Valenca (1994)*.
7. Rajković, M.B. and M.M. Mitrović: Phosphogypsum Surface Characterisation Using Scanning Electron Microscopy", *PHYSICAL CHEMISTRY 2000, 5th International Conference on Fundamental and Applied Aspects of Physical Chemistry, The Society of Physical Chemists of Serbia, September 27 – 29, 2000, Belgrade, SOLID STATE PHYSICAL CHEMISTRY (H), MATERIAL SCIENCE (G), Proceedings, HG24–P*, pp. 453–455
8. Rajković, M.B. and D. Tošković: Phosphogypsum Surface Characterisation Using Scanning Electron Microscopy. *Acta Periodica Technologica* **34** (2003) 61–70.
9. Rajković, M.B. and M. Stojanović: Determination of Inorganic Compounds in Drinking Water on the Basis Boiler Fur. *Ekologija* **36**. 1 (2001) 71–85.
10. Francois, M. H.: Dosage du Sr-90 et de Y-90 dans les eaux naturelles chargees. *Rapport CEA No.1965; 1961*
11. Pravilnik o izmenama i dopunama Pravilnika o higijenskoj ispravnosti vode za piće, *Službeni list SRJ*, **44**, 1999., s. 19-20

ОДРЕЂИВАЊЕ НЕОРГАНСКИХ ЈЕДИЊЕЊА У ВОДИ ЗА ПИЋЕ НА БАЗИ КАМЕНЦА

Део 1. Одређивање тешких метала и урана

*Милош Б. Рајковић, Мирјана Д. Стојановић,
Гордана К. Пантелић и Драган В. Тошковић*

Испитивање каменца, који је настао из воде за пиће на грејачу кућног бојлера, указало је да је каменац у основи калцијум-карбонат који кристалише хексагонално у облику *калцита*, што је потврђено снимањем на електронском микроскопу и путем рендгенске дифракционе анализе.

Каменац узоркован на различитим местима града Београда – горњи град Земун (узорак 1) и Панчево-Крњача (узорак 2), показао је различит састав иако је настао из исте водоводне мреже. То указује да вода која протиче кроз водоводне цеви различитих делова града или није иста или није иста водоводна мрежа (старост, очуваност и др.).

Сви елементи који су доминантни у води за пиће (Ca, Mg, K, Na), а који могу да се нађу природним процесом у води су по свом садржају далеко испод Правилником дозвољених вредности.

Испитивања су такође указала на присуство многих метала: Ti, Pb, Zn, Cu, Li, Sr, Cd, Cr у првом узорку, којих нема у каменцу насталом у околини Панчева (узорак 2).

Резултати добијени прерачунавањем масене концентрације у води за пиће на основу састава у каменцу показали су да обе воде припадају категорији слабо-минералне воде, јер је укупан садржај соли мањи од 500 mg/dm^3 . Такође, унос неорганских супстанци овом водом ($117,85 \text{ mg/dm}^3$ за узорак 1 одн. $80,83 \text{ mg/dm}^3$ за узорак 2) је двоструко мањи од Правилником прописаних вредности ($271,71 \text{ mg/dm}^3$).

Такође, оба узорка су на основу израчунавања присутних супстанци у води за пиће показала да вода за пиће садржи повишену концентрацију појединих метала, у првом узорку олова, мангана, гвожђа и бакра, док је у другој води око 100 пута виша концентрација гвожђа од дозвољене.

Гамаспектрометријска испитивања указују на присуство радиоактивних елемената – урана и стронцијума, што може имати утицаја на здравље људи.

Received 24 March 2004

Accepted 12 May 2004