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DETERMINATION OF CHANGE IN CONTENT OF HEAVY AND RADIOACTIVE METALS IN DRINKING WATER BY AN INDIRECT ANALYSIS METHOD BASED ON SCALE TESTS

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Abstract

In this paper the content of metal in drinking water was determined in two samples, one from 2008 and other from 2010, by the indirect method based on the analysis of scale, which had originally been suggested by Rajkovic and associates. Received results confirmed that drinking water according to the metal content was of constant level (metals are lower than MAC values), but with increased content of U. By the method of fraction extraction it was proved that increased content of U regarded mainly to natural U, and less to U of anthropogenic origin. The increased content of isotope ^{90}Sr was also noticed, probably as the effect of increased presence of alkaline earth metals. The analysis structure of scale by the usage of SEM determined that the dominant form was calcium carbonate of crystal structure of hexagonal shape which corresponded to calcite. By Röentgen diffraction analysis of dust it was determined the content of calcite which contained CaO; MgO; FeO; MnO and CO_2 and it belongs to medium manganese calcites.

All the analyses done in this paper, confirmed that indirect method of determination of metal content had been reliable and applicable for determination of low concentrations of metals in drinking water.

Keywords: *drinking water, scale, heavy metals, scanning electron microscopy, X-ray diffraction analysis · Gamma-spectrometry*

1. INTRODUCTION

In drinking water there are many non-organic substances which contribute to water hardness and influence on its quality and hygienic correctness [1]. Existent methods for the analysis of content (or traces) of metals (heavy and radioactive) cannot detect the presence of low concentrations of metals in drinking water, so the new method of determination of metal content (heavy and radioactive) was suggested and it proved to be totally applicable [2,3,37].

The gist of the method for the analysis of drinking water quality from the plumbing system is to use scale (dry residue) that deposits on the heater of home boiler during the water heating and it is formed by sedimentation of non-organic non-volatile substances in drinking water**.** As scale content comes from the present non-organic compounds in water, by this method it is possible to determine reliably and indirectly by determination of basic content of scale the structure of scale and metals: heavy metals and radioactive elements (isotopes) which can be find in drinking water.

The aim was to use the original method of indirect determination of elements for estimation of drinking water quality by monitoring the content of metals during the years of usage of drinking water from the same plumbing system of Belgrade.

2. EXPERIMENTAL

2.1. *Study Site Description*

The Scale (dry residue) analysed in this paper origins from the water from plumbing system of Belgrade, and came from plumbing system of New Belgrade (housing blocks near the Sava river) (44º48'06.56" N, 20º24'08.46" E). For the analysis it was used fur formed be sedimentation on the heater of the house boiler, during the period from 2008 (when it was analysed for the first time) till 2012. The content of all solids, which actually represents scale, has been determined by boiling 1.0 dm^3 of drinking water to obtain the corresponding dry residue. The scale sample composition has been identified by the AAS Perkin Elmer 703 atomic absorption spectrophotometer according to standard JUS B.B8.070 [4,5].

2.2. *Determination of Heavy Metals and Uranium*

Share of elements in form of compounds or in basic form was compared in % with maximum allowed concentrations (MAC) of non-organic substances in water which are regulated by Law [6] but also by Law for bottled drinking water and Law for natural disaster [7].

The quantitative content of uranium has been determined by the fluorometric method based on the linear dependence of the fluorescence intensity of uranium solutions on their concentration. The linear dependence occurs within a very large range of low concentrations (to a magnitude of four). The reduction in the fluorescence intensity has been brought to the lowest degree possible by the technique of ”standard addition” after the extraction of uranium by the synergetic mixture of TOPO (tri-*n*-octyl phosphine oxide) and ethyl acetate. The fluorescence intensity has been determined by means of a Jarrel Ash Division 26-000 Fluorimeter (Fisher Scientific Company, Waltham 1978).

2.3. *Application of Fractional Extraction Method for the Determination of Uranium Origin*

After determination of uranium presence in drinking water indirectly by the analysis of scale [5,8], the quantitative determination of uranium bond form was done by the method of fraction extraction [9,10,38].

The fractional extraction is based on the theory that metals form bonds of dissimilar strength with the solid phase [11] and that the bonds can gradually be broken by the action of reagents of different strength [12]: *first fraction*, 0.1 mol/dm^3 solution of $CaCl_2$ (pH value 7.00), is used for the extraction of water-soluble and exchangeably adsorbed forms of metals; *second fraction,* 1 mol/dm^3 solution of CH_3COOH (pH value 5.00), is used for the extraction of specifically adsorbed metals and metals bound to carbonates; *third fraction*, hydroxlamine hydrochloride in a 25 % solution of CH_3COOH (pH value 3.00), is used for the extraction of metals bound to oxides of manganese and iron; *fourth fraction*, 0.02 mol/dm^3 solution of HNO_3 in a 30 % solution of H_2O_2, is used for the extraction of metals bound to an organic substance. Forms of metals structurally bound to silicates (*fifth fraction*) are determined from the difference between the total content of uranium and the uranium content in the first four fractions.

It should be emphasized that the means for a fractional analysis are not standardized, so that it cannot be claimed with absolute certainty that some forms of uranium are really contained in scale. The basic criterion for the evaluation of its validity are statistic correlations.

By the usage of estragens of different pH values, the method of fraction extraction gives information about the degree of solubility and reversibility of uranium bond form showing at the same time the origin of uranium (natural or anthropogenic) in drinking water.

2.4. *The Gamma-spectrometric Analysis of the Scales*

Low phonon measurements have been carried out using the Hp Ge coaxial detector with the relative efficiency of 14 %, FWHM of 1.7 keV, the scale sample being placed in a vertical cryostat and protected by 10 cm thick layer of lead, plexiglass and cadmium. The total measured speed of the phonon count in the energy range of 15-2915 keV has been 0.99 pulse/s. The spectrometer has been connected to a multichannel analyser linked to a computer. The treatment of gamma spectra has been performed using the ”Omnigam” program. Energy calibration, as well as the detector efficiency calibration has been conducted using an Amersham radioactivity standard. The duration period of the sample measurements has been about 60 ks, whereas the measurements of the phonon spectra have lasted 150 ks, being carried out regularly between the sample measurements.

The gamma-spectrometric analysis of the scale sample has been carried out after predrying at a temperature of 105 ºC (for 24 hours) in order to remove free moisture and to reduce the measurements to the dry substance. The scale sample has been packed into a plastic vessel and hermetically closed to retain the developed radon. The measurement was carried out after twenty days to balance the developed radon with radium it originated from [13].

The radiochemical method of ^{90}Sr separation is based on the oxalate reduction of calcium and strontium, on the calcination of oxalate to oxide and on using an aluminium compound as a collector for ^{90}Y. The balance is established 18 days later, whereupon ^{90}Y is separated on the collector $Al(OH)_3$, which is then roasted to oxide that is afterward measured on the α-β anticoincidence counter [14].

2.5. *X-ray diffractional analysis of the Scales*

The X-ray diffraction analysis of the preground scale sample has been performed, and a fraction of fine scale powder (6.3-2 μm) has been studied. The X-ray analysis has been conducted on a PHILLIPS model PW 1009 diffractometer, with CuKα rays λ = 1.54178Å, under the operating conditions of the tube U = 36 kV, I = 18 mA, at a goniometer velocity Vg = 1º2θ/min and under the conditions R/C = 8/2 [15].

3. RESULTS AND DISCUSSION

The results of scale analysis received from water from Belgrade plumbing system are shown in Table 1.

The results received by the calculation of mass concentration in drinking water according to the content of fur showed that analysed water in this part of Belgrade plumbing system belongs to the category *moderately hard* (200-400 mg/dm^3 of $CaCO_3$ in water) and its concentration didn't significantly change during this period of time (about 4 %). Also, intake of non-organic substances by this water (261.80 mg/dm^3 and 251.27 mg/dm^3, respectively) is almost identical as values regulated by Law (271.71 mg/dm^3) [7,8].

All elements dominant in drinking water - *alkali* and *alkaline earth metals elements* - light metals (Na, K, Ca, Mg) (*elements of IA and IIA groups*), and which can be found by natural processes in water are by its content (104.85 and 82.85, respectively) far below from concentrations regulated by Law (200 mg/dm^3).

In *the second group* there are d-elements – heavy *metals* (Cr, Mn, Fe, Ni, Cu, Zn, Cd, Hg), which presence is determined in fur, that is, in water meant for humans but their concentration doesn't surpass values regulated by Law [10].

Concentration of elements of *VIIIb subgroup* (Fe, Co, Ni) in drinking water according to calculated values in fur sample is different: iron is found in concentrations which are 3 to 3.5 times higher than values regulated by Law, while nickel is also found but in concentration which is far below from values regulated by Law (20 μg/dm^3). Cobalt wasn't found.

In *the third group* of elements there are p-elements (Al, Si, Pb), that only confirms the presumption that water from plumbing system originates from artesian well considering increased amount of Al.

It is normal that silica is found in water because of water's flow through silicate rocks. It is natural element which concentration is not regulated by Law. Both samples of scale contain silica.

Aluminium in water from which scale was taken, is present in concentration 2 times (more precisely 2.2) higher than it is allowed by Law in bottled water (**sample 2008**). What is promising is that Al is not present (or just in traces) in water from which fur originates after few years period.

Lead in drinking water originates from lead pipes, PVC pipes that contain lead component or from home taps and pipe fittings. Speed of lead dissolving from lead pipes depends on: concentration of chloride, pH values, oxygen, temperature, hardness and time of water retaining in pipes. Lead in water can come from soldered pipe connections and amount of lead in drinking water can be reduced by the control of corrosion and adjusting of pH values of water in the system.

In Serbia lead pipes are not used in system of water distribution but in both samples lead was found**.** Calculated on content of lead in drinking water, received values of 0.025 mg/dm^3 correspond to values that are allowed for bottled water (0.05 mg/dm^3), but it is 2 times higher than values regulated by Law in drinking water (0.01 mg/dm^3). But it is alarming that concentration of lead in water in this period increased more than twice, so it surpasses values allowed by Law (10 µg/dm^3, and 24.7 µg/dm^3 was found).

In *the fourth group* there is a radioactive element **uranium** (isotops ^{233}U, ^{234}U, ^{235}U, ^{236}U, ^{238}U) which is significantly toxic. Uranium in drinking water comes from natural sources: lithosphere, volcanic rocks, sediments, phosphate rocks and soil [16] or it is of anthropogenic origin: from different industrial branches (mining, smelter, metallurgy, chemical industry etc.), by non-controlled usage of organic and mineral fertilisers and pesticides and from waste mud.

Table 1. Chemical substances inorganic origin found in scale samples and their calculated mass concentration in water

Chemical substance	Scale sample (% by mass)		Calculated mass concentration in drinking water sample (mg/dm^3)		Maximum allowed concentrations in drinking water (mg/dm^3)
	sample 2008	**sample 2012**	**sample 2008**	**sample 2012**	
Calcium, as CaO	48.90 %	46.93 %	104.85 as Ca	82.85 as Ca	200.0
Magnesium, as MgO	5.43 %	5.21 %	9.82 as Mg	7.76 as Mg	50.0
Sodium, as Na_2O	0.034 %	0.033 %	0.076 as Na	0.0605 as Na	150.0
Potassium, as K_2O	0.007 %	0.0067 %	0.018 as K	0.014 as K	12.0
Iron, as Fe_2O_3	0.08 %	0.063 % as Fe or 0.090 % as Fe_2O_3	0.176	0.156	0.3 (0.05 *)
Manganese, as MnO	$2\cdot10^{-3}$ %	$3.3\cdot10^{-3}$ %	4.65 $\mu g/dm^3$ as Mn	6.42 $\mu g/dm^3$ as Mn	0.05 (50 $\mu g/dm^3$)
Silicon, as SiO_2	1.14 %	–	1.60 as Si	–	–
Aluminium, as Al_2O_3	0.07 %	–	0.11	–	0.2 (0.05 *)
Lead, as Pb	0.003 %	0.01 %	9.9 $\mu g/dm^3$	24.7 $\mu g/dm^3$	0.01 (0.05 *)
Zink, as Zn	0.02 %	0.043 %	0.069	0.106	3.0 (0.1 *)
Copper, as Cu	0.14 %	0.103 %	0.402	0.254	2.0 (0.1 *)
Uranium, as U	$2.03\cdot10^{-3}$ %	$3.12\cdot10^{-3}$ %	0.61 $\mu g/dm^3$	0.77 $\mu g/dm^3$	0.05 (50 $\mu g/dm^3$)
Nickel, as Ni	$2\cdot10^{-3}$ %	0.004 %	6 $\mu g/dm^3$	9.88 $\mu g/dm^3$	20 $\mu g/dm^3$
Sulfur, as S	0.14 %	–	0.42	–	–
Cadmium, as Cd	$6\cdot10^{-4}$ %	$6\cdot10^{-4}$ %	1.8 $\mu g/dm^3$	1.8 $\mu g/dm^3$	3 $\mu g/dm^3$
Chromium (total)	$1\cdot10^{-3}$ %	<$2\cdot10^{-4}$ %	3 $\mu g/dm^3$	0.49 $\mu g/dm^3$	50 $\mu g/dm^3$
Dry residue (in g)	0.300	0.247			
Water hardness, $CaCO_3$ (mg/dm^3)	261.80	251.27			
°D	14.67	14.08			
Firing loss	44.03 %	47.60 %			
$\sum$	99.99 %	100.01 %			

* *MAC permitted concentration in bottled drinking water.*

The first alarming data was the increase of uranium in fur, that is, drinking water (2.03 and 3.12 ppm, respectively, that is, for 54 %). Because of that, the control of the origin of uranium in water (fur) was done, weather it was formed in anthropogenic way by contamination or was it of natural origin, by the usage of the method of fraction extraction for determination of different forms of uranium bond. Results are shown in Table 2.

According to the results of fraction extraction, it can be concluded that the content of uranium in fur, and in drinking water, is in *the third fraction* which represents potentially available and mobile fraction of uranium and clearly shows that these compounds have great affinity towards uranium. Values are between (in % from total content of uranium in scale) 53.20 % (**sample 2012**) and 60.59 % (**sample 2008**).

Table 2. The results of examination of uranium origin obtained from drinking water using fractional extraction method

Fraction	Scale sample	**sample 2008**		**sample 2012**	
	Uranium	U, ppm	% from U_{uk}^{*}	U, ppm	% from U_{uk}^{*}
	Total uranium content in the scale sample (U_{uk})	**2,03**	100	**3,12**	100
Fraction I	Water-soluble and measurably adsorbed	< 0,01	< 0,493	< 0,01	< 0,32
Fraction II	Specifically adsorbed and bound to carbonates	0,56	27,58	1,37	43,91
Fraction III	Bound to manganese and iron oxides	1,23	60,59	1,66	53,20
Fraction IV	Bound to organic matter	< 0,01	0,0,49	< 0,01	< 0,32
Fraction V	Structurally bound to silicates	0,24	11,82	0,09	2,88
	Σ	**2,05**	100,98 %	**3,14**	100,64 %

* *Content, in %, individual fractions of total uranium content in the scale sample*

According to the results of fraction extraction, it can be concluded that the content of uranium in fur, and in drinking water represents potentially available and mobile fraction of uranium, which shows its anthropogenic origin [11]. That means that in drinking water there is natural uranium but also uranium that came to environment in anthropogenic way. The uranium that came to environment in Serbia during NATO bombing of SR Yugoslavia during 1999 cannot be excluded.

As the content of iron in drinking water is determined as Fe_2O_3 (of 0.08 % and 0.06 %) and manganese as MnO (from 20 ppm to 33 ppm) (Table 1), that means that content of possibly adsorbed uranium is very small but not negligible. However, as conditions in a boiler are hardly changeable, meaning drastically reduced acidity, uranium in fur stays fixed, and unchanged in water.

It is noticeable that uranium in fraction II (specifically adsorbed and connected with carbonates), which largely depends on pH values of hard substance – sediment, shows significant increase (for about 60 %). Uranium bonded to oxide of manganese and iron (fraction III) shows decrease for 12.20 %. Received data shows that uranium which originates from anthropogenic sources (fraction III) (according [17]) shows tendency of decreasing, and there is increase of uranium which emerges from geochemical sources in less appropriate form (carbonates, oxides, phosphates, sulphides, silicates) [11].

The intake of elements into a human organism by drinking water is calculated according to the data that *cubage of one glass* is 200 cm^3 (0.2 dm^3) and *daily intake* is based on presumption that a man normally drinks 10 glasses of water (2 dm^3 of water). Calculation is based on calculated content of appropriate elements in dry residue. *Monthly intake* is based on 30 days period, and *year intake* is based on 12 months period (365 days).

By drinking water the largest intake is of *alkaline earth metals* (depending on a year of taking sample from 82.56 g (97.54 %) (**sample 2008**) and 65.24 g (99.31 %) (**sample 2012**), but total mass of elements in water is noticeably reduced (from 84.64 g (**sample 2008**) to 65.69 g (**sample 2012**) or for 18.95 g that is, 22.38 %), which undoubtedly tells about the change of water hardness (Figure 1). Indicatively, the amount of *amfoteric metals* is drastically reduced (for example, there is no Al in the second scale sample) for 73.53 %.

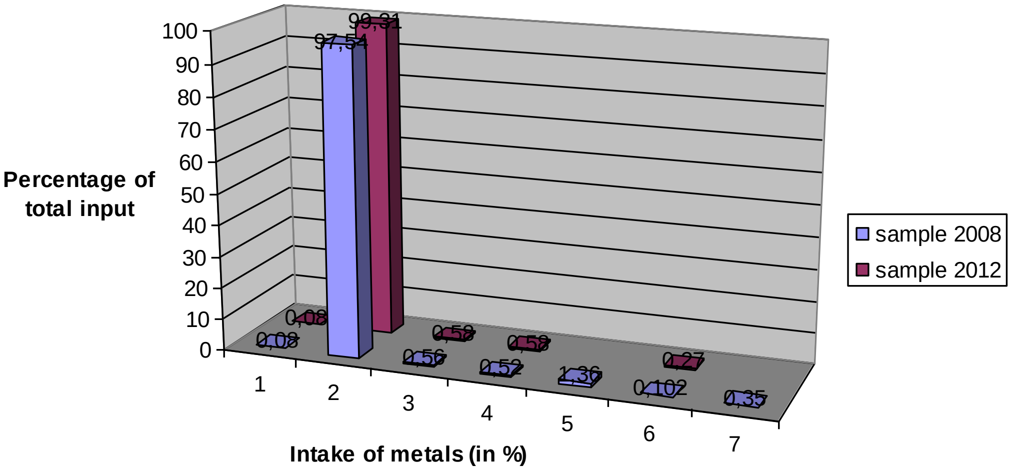


Figure 1. Input elements in the human body consumption of drinking water, where: 1 – alkali(ne) metals, 2 – alkaline earth metals, 3 – d-elements, 4 – heavy metals, 5 – metalloids, 6 – amphoteric metals, 7 – non-metals

The intake of (in %) *alkali* and transient metals is practically unchanged, while some elements like half-metals (Si, As) and non-metals (S) are simply lost. This undoubtedly tells that contamination of water from plumbing system existed in 2008. The intake of *alkaline earth metals is* higher for almost 2 % but the content of uranium is increased (even for 60.96 %).

The gamma-spectrometric analysis of the scale sample has been carried out after predrying at a temperature of 105 ºC (for 24 hours) in order to remove free moisture and to reduce the measurements to the dry substance. The scale sample has been packed into a plastic vessel and hermetically closed to retain the developed radon. Measurement was done after 20 days in order to allow developed radon to come into balance with radium from which it emerges. Received spectres are shown in Figure 2 (**sample 2008**) and Figure 3 (**sample 2012**).

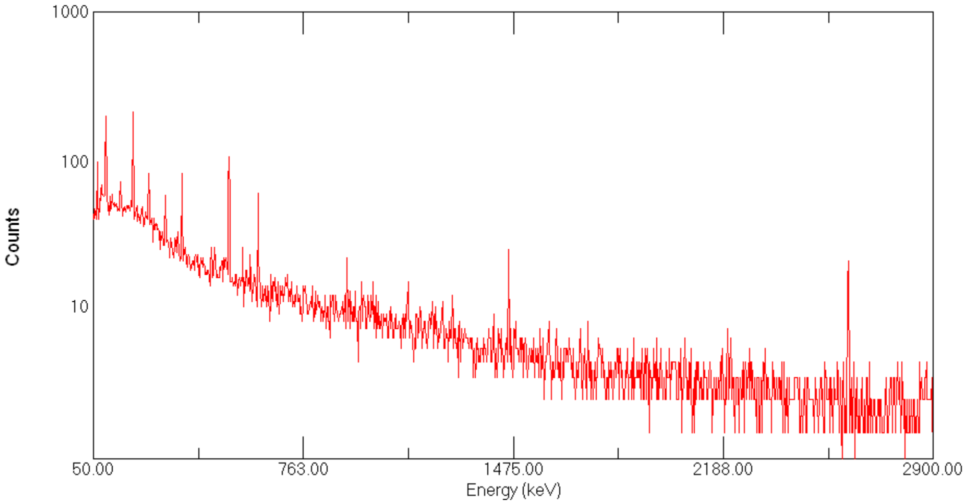


Figure 2. Gamma-spectrometric spectrum of the scale (sample 2008)

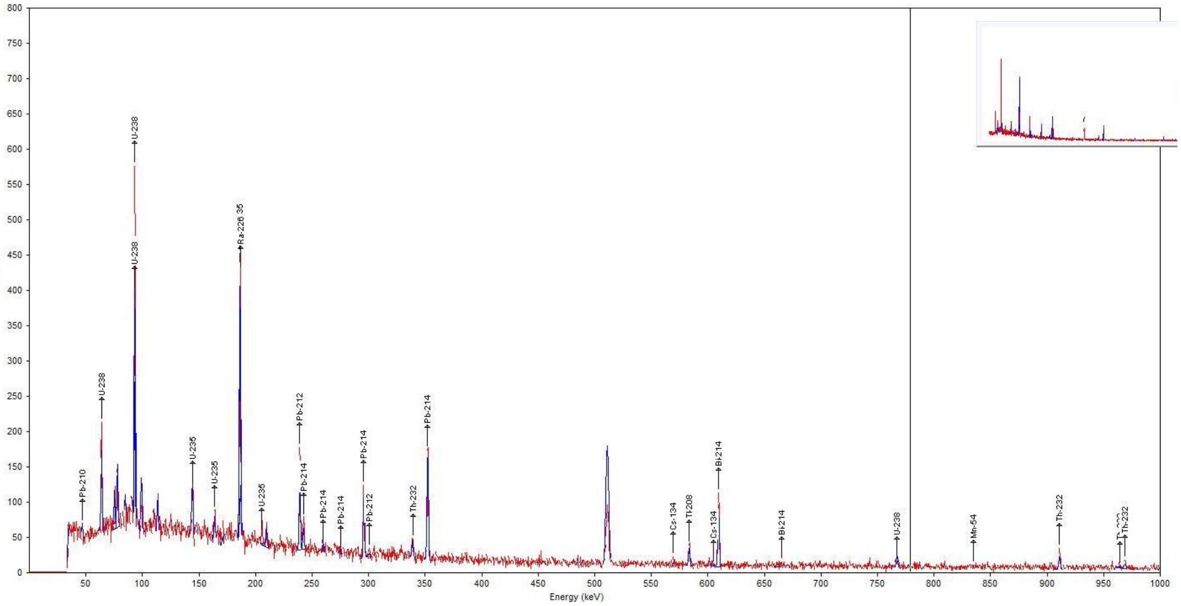


Figure 3. Gamma-spectrometric spectrum of the scale (sample 2012)

Results of measurements of concentration of gamma-emitters activities in scale (in Bq/kg) are shown in Table 3.

Measured activity that comes from isotope ^{90}Sr in samples of fur is shown in Table 4.

The method of measurement and determination of activities of ^{90}Sr. Samples are measured on alpha-beta anti-coincidence proportional gas counters PIC-WPC-9550, Protean, of 0.5 imp/min of basic radiation. Diameter of planchet is 5 cm. The efficiency of the counter is 47 %, and is determined by the standard ^{90}Sr.

The radiochemical method of ^{90}Sr separation is based on the oxalate reduction of calcium and strontium, on the calcination of oxalate to oxide and on using an aluminium compound as a collector for ^{90}Y. The balance is established 18 days later, whereupon ^{90}Y is separated on the collector Al(OH)$_3$, which is then roasted to oxide. The activity of itrium that is in balance with strontium is measured on α,β anti-coincidence counter and the activity of ^{90}Sr is calculated according to the activities of ^{90}Y.

Table 3. Measurement results of gamma-emiter activity concentration in the scale samples (in Bq/kg) [2,13,18]

^{40}K		^{137}Cs		^{134}Cs		^{232}Th		^{226}Ra		^{238}U		^{235}U	
2008	2012	2008	2012	2008	2012	2008	2012	2008	2012	2008	2012	2008	2012
<1,11	<1	<0,15	<1	<0,49	<0,1	1,1±0,5	0,9±0,2	10,2±1,7	1,6±0,2	30,4±5,2	24,5±3,1	1,5±0,5	1,3±0,1

Table 4. ^{90}Sr activity concentration in the scale samples

Sample	^{90}Sr activity concentration in scale sample
sample 2008.	0,322±0,036 Bq/kg
sample 2012.	0,43±0,04 Bq/kg.

All isotopes that are determined in scale (except ^{90}Sr) show significant decreasing, comparing them with a sample from 2008, even the isotope ^{235}U, which is of artificial origin.

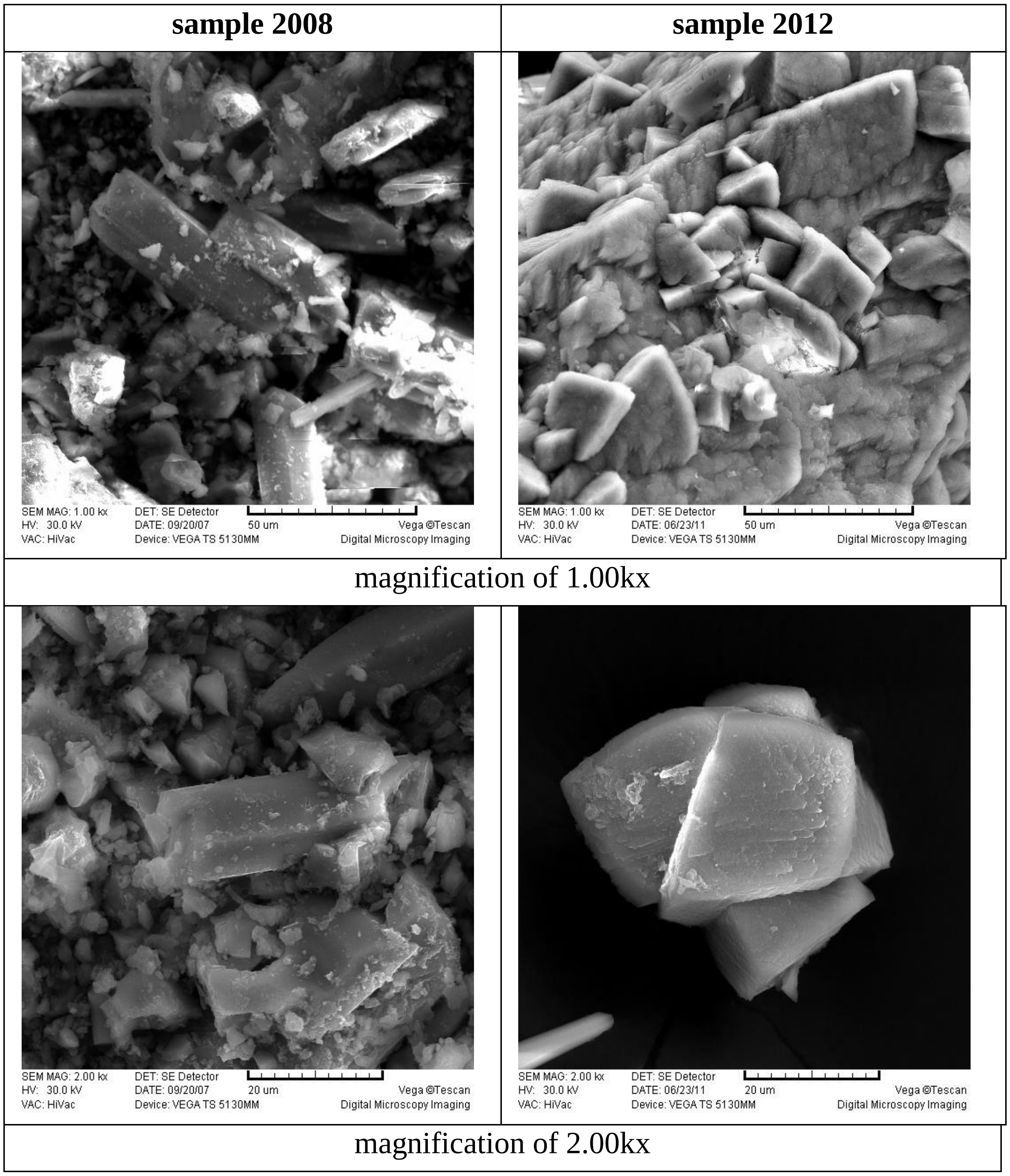
Gamma-spectrometric analysis showed that isotope ^{238}U (from 10 to 38,6 Bq/kg) had the highest contribution while of strontium isotope the presence of isotope ^{90}Sr was noted, which had been slightly increased. The explanation lies in increased amount of (percentage) *alkaline earth metals* (where strontium belongs) for 16.75 % that can increase the isotope ^{90}Sr which contributes to the higher activity.

As the values for activity of gamma-emitters are given in Bq/kg and from 1 dm^3 of water comes 0.3 g (**sample 2008**) and 0.247 g (**sample 2012**), respectively, of scale, it means that over 3 000 dm^3 water is needed (depending on the sample) to notice the calculated activity. In a home boiler of 60-80 dm^3 cubage it is not likely that the mass of scale that would emit the calculated radiance is going to emerge, because, for technical reasons, a boiler would stop to work or the heating would be difficult.

So, radiation from present scale is of small intensity, but in any case it is a measurable value and a clear warning.

For practical evaluation and making decision about eligibility of drinking water, from radiological aspect, for recommended dosage of 0.1 mSv appropriate concentrations of certain radionuclide in drinking water are defined. In case of isotope ^{90}Sr for dosage of 0.1 mSv for one year of drinking water intake, the referent level of concentration is 5 Bq/dm^3.

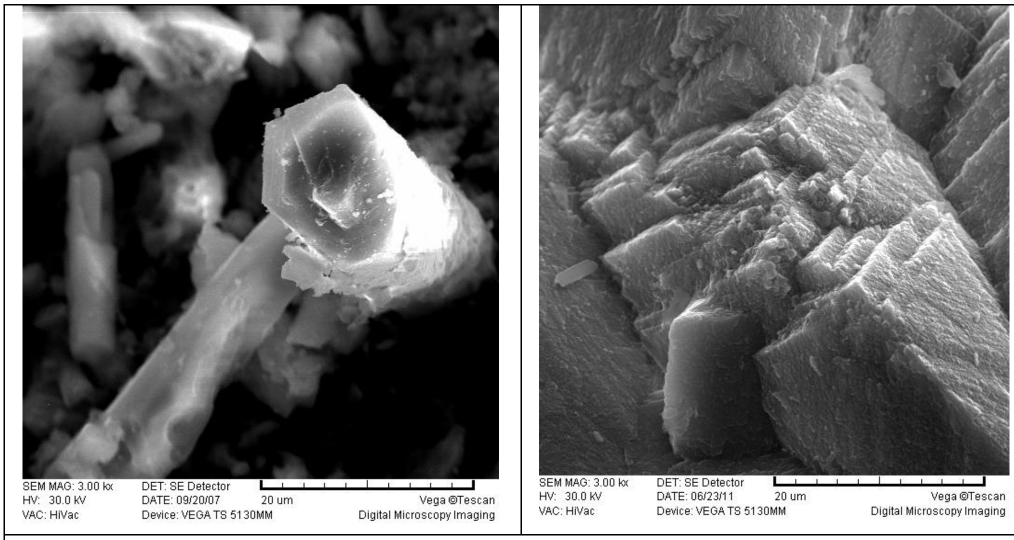
By the usage of scanning electronic microscope (SEM) for the analysis of crystal structure of calcite in scale, the following SEM photographs were taken and qualitative and quantitative analysis (in atomic %) was done, as shown in Figure 4 and in Table 5.



sample 2008 | **sample 2012**

magnification of 1.00kx

magnification of 2.00kx



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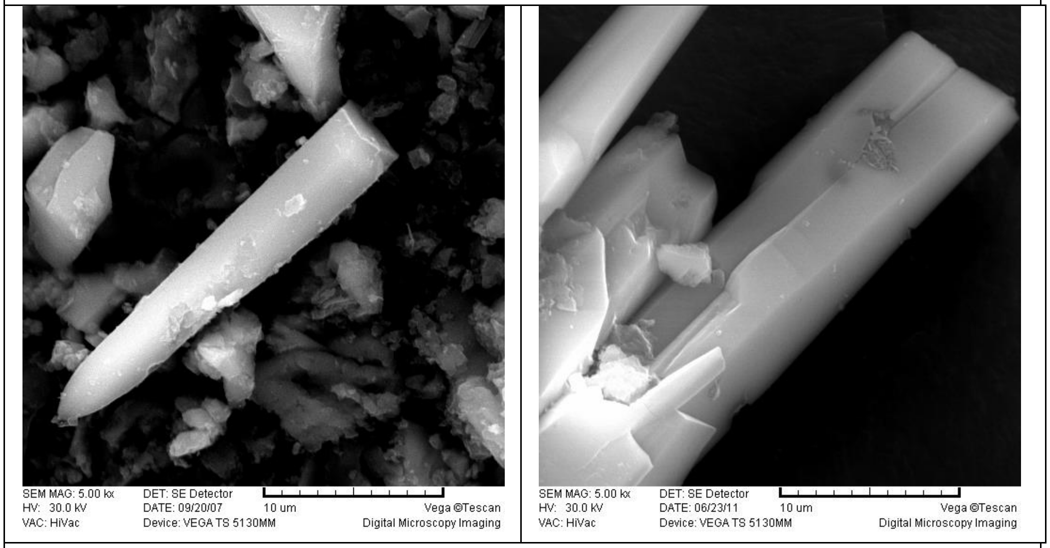
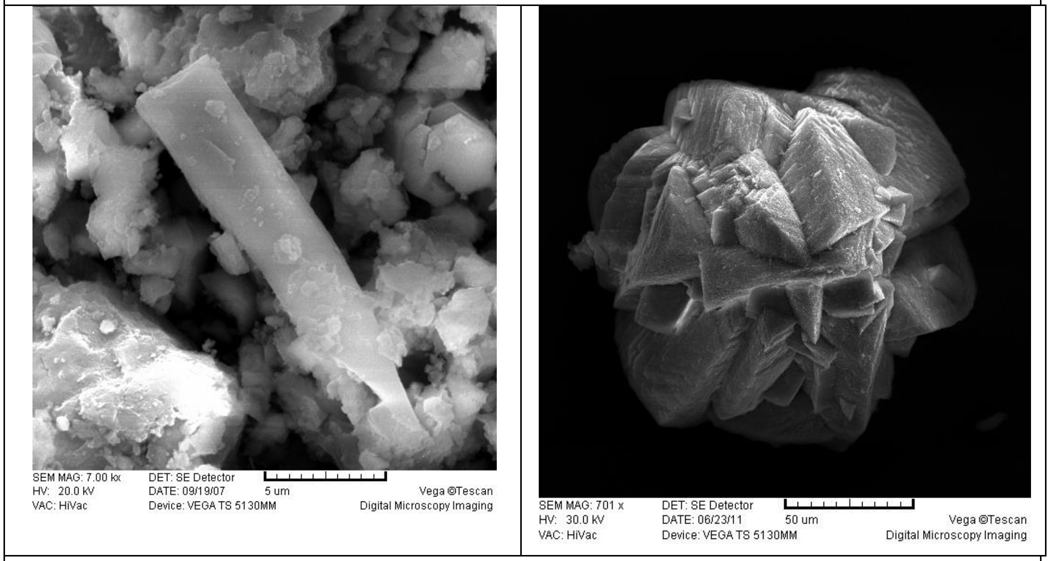


magnification of 5.00kx



magnification of 7.00kx

Figure 4. SEM photograph of the scale samples (magnification from 1000 to 7000 magnification)

Table 5. Qualitative and quantitave analysis of the scale samples (in atomic %)

Sample 2008

Spectrum	In stats.	C	O	Ca	I
Spectrum 1	Yes	17.94	66.53	15.46	0.06
Mean		17.94	66.53	15.46	0.06
Std.deviation		0.00	0.00	0.00	0.00
Max.		17.94	66.53	15.46	0.06
Min.		17.94	66.53	15.46	0.06

Sample 2012

Spectrum	In stats.	C	O	Mg	Si	Ca	Sc	Fe	Cu	Br	Y	Sn	I
Spectrum 1	Yes	14.02	66.55	1.16	0.03	17.78	0.14	0.03	0.06	0.04	0.03	0.04	0.12
Spectrum 2	Yes	13.16	65.36	1.35	0.07	19.61	0.10	0.04	0.09	0.03	0.04	0.05	0.11
Mean		13.59	65.96	1.26	0.05	18.69	0.12	0.03	0.07	0.03	0.03	0.04	0.11
Std. deviation		0.61	0.84	0.13	0.03	1.29	0.03	0.00	0.02	0.00	0.01	0.01	0.01
Max.		14.02	66.55	1.35	0.07	19.61	0.14	0.04	0.09	0.04	0.04	0.05	0.12
Min.		13.16	65.36	1.16	0.03	17.78	0.10	0.03	0.06	0.03	0.03	0.04	0.11

Photographs taken on scanning electronic microscope confirmed that dominant form of calcium carbonate, in scale, has significantly crystal structure of hexagonal form that corresponds to calcite but crystal modification that crystallises as a rhombus and corresponds to aragonite is also present. Aragonite is present in significantly smaller amount than calcite.

The structure of calcite is rhombohedral in which angles are atoms of calcium. Atom of carbon is in the middle of rhombohedral, and atoms of oxygen lay at an 120 ° angle (sp^2-hybridization of carbon atoms) [19,20,21].

The composition of the scale sample, which represents the carbonate mixture composed of Mg calcite and aragonite, has been determined based on the X-ray diffraction of the scale powder applying the qualitative and semiquantitative method (Table 6).

Miller indexes (**h k i l**) have been determined on the basis of the obtained angular values (**θ**) and interplate distances (**d**). Dimensions of elementary cells have been calculated on the basis of the hexagonal and rhombic grating, by means of the LSUCRI program (Table 7)

Based on the qualitative and semiquantitave X-ray analysis, the carbonate mixture has been found to consist of 66.92 % of calcite and 33.07 % of aragonite. Calcite and aragonite are two polymorphic modifications of the $CaCO_3$ composition. Aragonite belongs to the rhombic and calcite to the widespread rhombohedral carbonates.

Table 6. X-ray diffractogram of the scale powder

Sample	d_{calc} (Å)	d_{obs} (Å)	Mg calcite (h k i l)	Aragonite (h k l)
1	4.2117	4.2201		1 1 0
2	3.9877	3.9900		0 2 0
3	3.8154	3.8101	$0\ 1\ \bar{1}\ 2$	
4	3.7531	3.7530		1 0 1
5	3.3967	3.3950		1 1 1
6	3.2806	3.2719		0 2 1
7	2.9987	3.0060	$1\ 0\ \bar{1}\ 4$	
8	2.8002	2.8010	0 0 0 6	
9	2.6964	2.7330		1 2 1
10	2.7009	2.7000		0 1 2
11	2.6585	2.6600		0 3 0
12	2.4798	2.4787		2 0 0
13	2.4725	2.4780	$1\ 1\ \bar{2}\ 0$	
14	2.4124	2.4121		0 3 1
15	2.3720	2.3711		1 1 2
16	2.3431	2.3434		1 3 0
17	2.3297	2.3300		0 2 2
18	2.2765	2.2760		2 0 1
19	2.2619	2.2600	$1\ 1\ \bar{2}\ 3$	
20	2.1891	2.1900		2 1 1
21	2.1084	2.1084		1 2 2
22	2.0749	2.0750	$2\ 0\ \bar{2}\ 2$	
23	1.9770	1.9770		2 2 1
24	1.9938	1.9930		0 4 0
25	1.9505	1.9500		0 3 2

Sample	d_{calc} (Å)	d_{obs} (Å)	Mg calcite (h k i l)	Aragonite (h k l)
1	4.2117	4.2201		1 1 0
2	3.9877	3.9900		0 2 0
26	1.9077	1.9080	$0\ 2\ \bar{2}\ 4$	
27	1.9137	1.9140		0 0 3
28	1.8835	1.8840	$0\ 1\ \bar{1}\ 8$	0 4 1
29	1.8534	1.8540	$1\ 1\ \bar{1}\ 6$	
30	1.8608	1.8610		0 1 3
31	1.8765	1.8765		2 0 2
32	1.8499	1.8499		1 4 0
33	1.8266	1.8270		2 1 2
34	1.8151	1.8150		1 3 2
35	1.7422	1.7420		1 1 3
36	1.7253	1.7260		0 2 3
37	1.6112	1.6100	$2\ 1\ \bar{3}\ 1$	
38	1.4898	1.4900	$1\ 1\ \bar{2}\ 9$	
39	1.4000	1.4000	0 0 0 12	

The interplate distances as of calcite so too of aragonite have revealed minor deviations in relation to the standard values (JCPDS 47-1743; 41-1475) [22,23]. The interplate distance $d_{(10\bar{1}4)}$ of the main calcite reflection has shifted towards higher angular values θ, indicating the partial substitution of Ca^{2+} ion for ions of a smaller ionic radius, among which the commonest are Mg^{2+}, Ni^{2+}, Fe^{2+}, Mn^{2+} and etc. The parameters of the calcite elementary cell are very close to the standard values [24]. Moreover, the decrease in the value of parameters a_o and c_o has confirmed the substitution of Ca^{2+} ion for the ions of the smaller ionic radius as also testified by the interplate distances. The substitution of the Ca^{2+} ion for Mg^{2+}, Fe^{2+} or Mn^{2+} ions has been determined through various diagrams of interdependence between the substance composition and the crystallographic parameters.

Table 7. Parameters of the elementary cell (Å) and the standard values

Parameter	Sample		ASTM Mg calcite 43-0697	ASTM calcite 47-1743	ASTM aragonite 41-1475
	Mg-calcite + aragonite				
a_o	4.945(2)	4.9597(7)	4.942	4.9896	4.962
b_o	-//-	7.975(1)	-//-	-//-	7.968
c_o	16.80(1)	5.7411(7)	16.85	17.0610	5.743
V_o(Å^3)	355.8(2)	227.09(4)	356.53	367.85	227.11
$d_{(10\bar{1}4)}$	3.0060	3.395	3.004	3.0355	3.397
c/a	3.397	1.157	3.409	3.419	1.157

The content of magnesite ($MgCO_3$), siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$) components (mol %) in calcite has been defined by extrapolating the diagram of interdependence that exists between the elementary cell parameters and the composition (Tables 8 and 9).

Table 8. Content of $MgCO_3$ (mol %) in calcite based on the different crystallographic parameters

References	Crystallographic parameters	$MgCO_3$ content (mol %)
[25]	$\Delta 2\theta$	9.20
[26]	$\Delta d_{(104)}$	10.24
[27]	a_o	10.50
[28]	c_o	11.92
[28]	$d_{(104)}$	10.72
[29]	a_o	10.90
[29]	c_o	12.70
[30]	V_o	10.20
[31]	V_o	11.90
[31]	c_o / a_o	12.20
Mean value $MgCO_3$ (mol %)		**11.05**

Table 9. Content of $FeCO_3$ and $MnCO_3$ based on $\Delta 2\theta^o$ i $\Delta d_{(104)}$

Sample	Crystallographic parameters		$FeCO_3$ (mol %)	$MnCO_3$ (mol %)
Δ2θ° [32]	Δ2θº	0.995	1.90	–
$\Delta d_{(104)}$ [27]	$\Delta d_{(104)}$	0.03	–	1.80

A large number of authors [24-36] have studied the dependence of the calcite elementary cell parameters on the substance composition and proved the linear dependence, especially of the interplate distance of the strongest reflection, $d_{(10\bar{1}4)}$, on the substance composition, in certain carbonate systems (pairs). The composition of all minerals, so too of the carbonate ones, depends on a wide range of factors, prominent among them being the concentration of ions, temperature and pressure. Based on the content of the magnesite (11.05 mol %), siderite (1.90 mol %) and rhodochrosite (1.80 mol %) component, the analyzed calcite belongs to the medium magnesian calcites (3 to 17 mol % of $MgCO_3$ component).

The solid solution of magnesite ($MgCO_3$) in calcite is one of the most important ones in nature. The actual stability field of the magnesian calcites is positioned under the T, P, X conditions behind the calcite-dolomite solidus. It practically means that the solubility of $MgCO_3$ in calcite, up to a few molecular percents, is of the metastable nature at ambient temperature. However, those metastable solid solutions are wide-spread at low temperatures too, which additionally arouses considerable interest, as on account of stability so too because of the difference between the ionic radius of Ca and Mg.

The study of Mg calcite, at low temperatures, presents a special field of research in the world. The content of $MgCO_3$ in Mg calcites, precipitated in sea water in the form of skeletons of organisms or in the form of homogenous cement, is mostly associated with the change in temperature and with the concentration of CO_3^{2-} ions in the deposition environment. These relations permit the chemical control of the residue composition, so that the composition of water saturation, depending on the temperature, determines the content of $MgCO_3$ in calcite. With biogenetic phases, some of the essential factors are larger ions, particularly Sr^{2+}, the presence of water and hydrated Mg^{2+} ions.

Table 10. Total content of Mg calcite and aragonite defined through different crystallographic parameters and the number of cations based on 6 atoms of oxygen (O)

Component	100 % of calcite	100 % of aragonite	Number of cations	Mg calcite	Aragonite
$FeCO_3$	1.90	–	Fe^{2+}	0.032	–
$MnCO_3$	1.80	–	Mn^{2+}	0.031	–
$MgCO_3$	11.05	–	Mg^{2+}	0.258	–
$CaCO_3$	85.25	97.86	Ca^{2+}	1.678	1.970
$SrCO_3$	–	2.13	Sr^{2+}	–	0.030
Σ	100.0	99.99		1.999	2.000

On the basis of the above-mentioned factors, the crystallochemical formula of the Mg calcite has been determined as follows: $(Ca_{1.678}\ Mg_{0.258}\ Fe_{0.032}\ Mn_{0.031})_{1.999}\ (CO_3)_{1.999}$ based on 6 atoms of oxygen (6 O) (Table 10).

Another essential aspect in the studied sample is the Mg calcite being in balance with aragonite. This two-phase area, in which the calcite and aragonite type of solid solution (rhombic and rhombohedral) co-exist, is possible in the $CaCO_3$-$SrCO_3$ system. When the pressure increases, the two-phase area becomes smaller so that the calcite type of the solid solution has not been found at the pressure of 25 kbar (2 500 MPa). At the pressure of 25 kbar (2 500 MPa), there occurs a very simple phase relation of the complete solid solution series of the aragonite structure type. With the decrease in pressure, to 15 kbar (1 500 MPa), as well as in temperature, the two-phase area grows larger depending on the substance composition. The calcite and aragonite solid solutions occur in a very limited area and at very low temperatures and pressures, and for these reasons they represent a stimulating field of research.

Table 11. Content of $SrCO_3$, $PbCO_3$ and $BaCO_3$ (mol. %) in aragonite depending on the parameters of the elementary cell

References	Aragonite	
[30]	$SrCO_3$	$CaCO_3$
a_o	1.8	98.2
b_o	2.8	97.2
c_o	1.8	98.2
Mean content of $SrCO_3$	2.13	97.86
[34]	$PbCO_3$	$CaCO_3$
a_o	0	100
b_o	0	100
c_o	0	100
Mean content of $PbCO_3$	0	100
[35]	$BaCO_3$	$CaCO_3$
a_o	0	100
b_o	0	100
c_o	0	100
Mean content of $BaCO_3$	0	100

The interplate distances of the studied aragonite have shifted towards the higher angular values and they show an insignificant reduction as compared to the standard ones. The stated deviation of the interplate distances has caused a minor aberration of the elementary cell parameters from the standard values (ASTM 41-1475) [23]. The values of the two parameters, a_o i c_o, are lower, whereas the values of of the parameter b_o and the elementary cell volume (V_o) reveal a negligible growth (Table 10). Such values of the elementary cell parameters suggest the partial substitution of the Ca^{2+} ion in aragonite for other ions. It is well-known that there are natural aragonites containing ions of greater ionic radius (such as Sr^{2+}, Pb^{2+}, Ba^{2+}) or smaller ionic radius (such as Mg^{2+}, Mn^{2+}, Fe^{2+}, Zn^{2+} etc.) than the Ca^{2+} ion.

On the basis of the different diagrams of dependence that display the linear correlation with the substance composition, the content of other bivalent cations in aragonite has been determined and checked (Table 11).

The linear composition change in the $CaCO_3$-$SrCO_3$ system is known, and on this basis the content of 2.13 mol % of the $SrCO_3$ component has been calculated, which comes to 1.495 % of SrO in 100 % of aragonite. Aragonite is contained in the scale sample in the amount of 32.2 %. The 1.495 % of SrO recalculated for 32.2 % gives 0.481 % of SrO.

The content of the $PbCO_3$ component in the scale sample has been checked through the diagrams of the dependence of the unit cell parameters on the composition. The results suggest that the $PbCO_3$ component is not included in the scale sample since a_o, b_o and c_o are below the linear line that determines the content of $PbCO_3$ in aragonite. It has also been established, on the basis of the elementary cell parameters, that aragonite does not contain the $BaCO_3$ component either [35].

The crystallochemical formula of aragonite: $(Ca_{1.970}\ Sr_{0.030})_{2.000}\ (CO_3)_{2.000}$ has been defined based on the scale composition obtained through the parameters of the unit cell.

Holland [36] have precipitated aragonite and strontianite from aqueous solutions at temperatures between 90 ºC and 100 ºC. The authors have established that the dimensions of the unit cells of the solid solutions of (Ca, Sr) CO_3 increase compared to strontianite but only the parameter a_o alters linearly with the mol % fraction of $SrCO_3$. The parameter c_o is slightly above the boundary that connects the final members of the series, whereas the parameters b_o and V_o occur a little below the line that links the final members of the series.

The effect of the $SrCO_3$ component alters the correlation between the rhombohedral (calcite type) and rhombic (aragonite type) phase, whereat the rhombic solid solution decreases as the temperature grows [33].

Up to 420 ºC there is a complete set of solid solutions between $CaCO_3$-$SrCO_3$. Above 420 ºC the monophase calcite and the monophase aragonite areas occur and between them the two-phase area of the calcite and aragonite type of solid solutions. This two-phase area is formed during the rise of pressure up to 25 kbar (2 500 MPa) while at this pressure the calcite solid solution decreases gradually to its complete disappearance.

The larger Sr^{2+} ion in this kind of a system tends to stabilize the aragonite type phase both at low temperatures (below 420 ºC) and at constant pressure.

The qualitative and semiquantitave composition of the sample has been defined on the basis of the X-ray diffractional analysis of the scale powder. The dimensions of the unit cells of aragonite and Mg calcite have been calculated whereby their chemical composition has been determined, that is, the change in the dimensions of the unit cells, depending on the chemical composition, has been studied.

The sample represents the carbonate mixture consisting of 66.92 % of Mg calcite and 33.07 % of aragonite. The unit cell dimensions of Mg calcite are as folows:

$$a_o = 4.945\ (2)\ \text{Å},\ c_o = 16.80\ (1)\ \text{Å},\ V_o = 355.8\ (3)\ \text{Å}^3$$

and the unit cell dimensions of aragonite are:

$$a_o = 4.9597\ (7)\ \text{Å},\ b_o = 7.975\ (1)\ \text{Å},\ c_o = 5.7411\ (7)\ \text{Å and } V_o = 227.09\ (4)\ \text{Å}^3.$$

On the basis of the obtained crystallographic results, that is, a_o, b_o, c_o and V_o, it has been established that the substitution of the Ca^{2+} ion for ions of Pb^{2+} and Ba^{2+} does not occur in aragonite, but there is the partial substitution of Ca^{2+} ion for Sr^{2+} ion. In aragonite the $CaCO_3$ component has been replaced with 2.13 mol % of the $SrCO_3$ component. Those 2.13 mol % of the $SrCO_3$ component is contained in 100 % of aragonite. Since there is 32.2 % of aragonite present in the sample, it makes 0.481 % of SrO. In view of the content of CaO (54.836 %) and SrO (1.495 %) the crystallochemical formula of aragonite $(Ca_{1.970}Sr_{0.030})_{2.000}(CO_3)_{2.000}$ has been determined.

Mg calcite, which is in balance with aragonite, has shown a rise in the parameter a_o value and the fall in the value of the parameters c_o and V_o in relation to the standard calcite values. The increase in the parameter a_o value and the decrease in the parameter c_o have affected the axial ratio c/a, which is also lower as compared to the standard one. The afore-said crystallographic parameters demonstrate that the considerable substitution of the Ca^{2+} ion for cations of the smaller ionic radius has taken place.

By extrapolating the diagrams of the dependence of the substance composition and the crystallographic parameters on calcite, the calcite composition has been determined to consist of 47.77 % CaO; 5.285 % MgO; 1.178 % FeO; 1.110 % MnO and 44.657 % CO_2. The analysed calcite belongs to the medium magnesian calcites, its crystallochemical formula being:

$$(Ca_{1.678}\,Mg_{0.258}\,Fe_{0.032}\,Mn_{0.031})_{1.999}(CO_3)_{1.999}\ ,$$

determined on the basis of 6 atoms of oxygen (6 O).

The obtained composition reveals that the significant substitution of the Ca^{2+} ion for the ions of Mg^{2+}, Fe^{2+} and Mn^{2+} has taken place in the calcite structure, and that the substitution of the Ca^{2+} ion for ions of Pb^{2+}, Sr^{2+} and Ba^{2+} has not occurred.

On the strength of the crystallographic parameters and the obtained composition, Mg calcite and aragonite have developed under undisturbed conditions of sedimentation, in a semiclosed shallow-water environment at a temperature between 60 ºC and 100 ºC (approximately 80 ºC) and at low pressure. The lower temperature of aragonite formation is affected by solutions containing some sulphate, or small quantities of strontium carbonate or lead carbonate. It is evident that carbonate of Sr has affected the formation of aragonite but not calcite. Likewise, the content of of Mg in calcite points to the content of Mg salts in the solution that have helped the deposition of aragonite from the solution, and the Mg^{2+} ion has replaced the Ca^{2+} ion in the calcite structure.

The pressure being low has been determined through Mg calcite. The increase in pressure considerably above 1 kbar (100 MPa) stimulates the dolomitization of Mg calcite. On the other hand, Mg calcite is in balance with aragonite in the carbonate mixture with no occurrence of dolomitization, which leads to the conclusion that the pressure has been low, ranging about 1 kbar (100 MPa).

4. CONCLUSIONS

The method of determination of metal content in drinking water by indirect method based on the analysis of fur showed full accuracy, reliability and reproducibility of received results.

The results of the analysis confirmed that quality of water, based on content of metals in water, is really constant and that metals are present in concentrations that are under amounts allowed by Law. The increase of uranium in drinking water has been shown, and with fraction extraction results it was proved its of anthropogenic origin.

Gamma-spectrometric analysis showed that isotope ^{238}U (from 10 to 38,6 Bq/kg) had the highest contribution while of strontium isotope the presence of isotope ^{90}Sr was noted, which had been slightly increased. The explanation lies in increased amount of (percentage) *alkaline earth metals* (where strontium belongs) for 16.75 % that can increase the isotope ^{90}Sr which contributes to the higher activity.

By the usage of scanning electronic microscope (SEM) for the analysis of crystal structure of calcite in scale, dominant form of calcium carbonate with crystal structure of hexagonal form that correspond to calcite has been confirmed but crystal modification that crystallises as a rhombus and corresponds to aragonite is also present. Aragonite is present in significantly smaller amount than calcite.

The qualitative and semiquantitave composition of the sample has been defined on the basis of the X-ray diffractional analysis of the scale powder. The dimensions of the unit cells of aragonite and Mg calcite have been calculated whereby their chemical composition has been determined, that is, the change in the dimensions of the unit cells, depending on the chemical composition, has been studied.

The sample represents the carbonate mixture consisting of 66.92 % of Mg calcite and 33.07 % of aragonite. The unit cell dimensions of Mg calcite are as folows:

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and the unit cell dimensions of aragonite are:

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By extrapolating the diagrams of the dependence of the substance composition and the crystallographic parameters on calcite, the calcite composition has been determined to consist of 47.77 % CaO; 5.285 % MgO; 1.178 % FeO; 1.110 % MnO and 44.657 % CO_2. The analysed calcite belongs to the medium magnesian calcites, its crystallochemical formula being:

$$(Ca_{1.678}\,Mg_{0.258}\,Fe_{0.032}\,Mn_{0.031})_{1.999}\,(CO_3)_{1.999}\,,$$

determined on the basis of 6 atoms of oxygen (6 O).

On the strength of the crystallographic parameters and the obtained composition, Mg calcite and aragonite have developed under undisturbed conditions of sedimentation, in a semiclosed shallow-water environment at a temperature between 60 ºC and 100 ºC (approximately 80 ºC) and at low pressure.

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ODREĐIVANJE PROMENE SADRŽAJA TEŠKIH I RADIOAKTIVNIH METALA U VODI ZA PIĆE INDIREKTNOM METODOM BAZIRANOM NA ISPITIVANJU KAMENCA

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Izvod

U radu je praćen sadržaj metala u vodi za piće ispitivanjem dva uzorka vode za piće, jedan iz 2008. i druge iz 2010. godine, indirektnom metodom baziranoj na ispitivanju kamenca (suvog ostatka), koja je originalno predložena od strane Rajkovića i saradnika. Dobijeni rezultati potvrdili su da je voda za piće konstantna po sadržaju metala (metali se nalaze ispod MDK vrednosti), ali sa povećanim sadržajem urana. Metodom frakcione ekstrakcije dokazano je da se povećani sadržaj urana odnosi prevashodno na prirodni uran, a manje na uran antropogenog porekla. Takođe je zapažen i povećan sadržaj izotopa ^{90}*Sr, što je verovatno posledica povećanog prisustva zemnoalkalnih metala. Ispitivanje strukture kamenca upotrebom skenirajućeg elektronskog mikroskopa (SEM) utvrđeno je da je dominantni oblik kalcijum-karbonata kristalne strukture heksagonalnog oblika koja odgovara kalcitu. Rendgenskom difrakcionom analizom praha određen je sastav kalcita koji se sastoji od CaO; MgO; FeO; MnO i* CO_2 *i da pripada srednje magnezijskim kalcitima.*

Sva ispitivanja, sprovedena u radu, potvrdila su da je indirektna metoda određivanja sadržaja metala pouzdana i promenljiva za određivanje niskih koncentracija metala u vodi za piće.

Ključne reči: *voda za piće, kamenac, teški metali, skenirajući elektronski mikroskop, difrakciona analiza, gama spektroskopija*