Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 79 (11) 1395–1404 (2014) UDC 546.3:577.1+541.132+54.05:504.53:628
JSCS–4673 *Original scientific paper*

The migration of some biometal ions in the systems mineral tissue of teeth–soil and teeth–water media

RUŽICA S. NIKOLIĆ[1], NATAŠA V. RADOSAVLJEVIĆ-STEVANOVIĆ[2], TATJANA D. ANĐELKOVIĆ[1#], MAJA N. STANKOVIĆ[1] and NENAD S. KRSTIĆ[1*#]

[1]*Department of Chemistry, Faculty of Sciences and Mathematics, University of Niš, Višegradska 33, 18000 Niš, Serbia and* [2]*The National Crime-Technical Centre, Ministry of Interior of the Republic of Serbia, Kneza Miloša 103, 11000 Belgrade, Serbia*

(Received 7 February, revised 30 May, accepted 30 May 2014)

Abstract: This paper outlines the changes in the mineral tissue of teeth that had been exposed to the influence of the agents of natural media. Such mineral tissue could be used as a potentially important forensic material that is gradually altered under the influence of external media. The biometal content was determined using the ICP-OES technique. According to the quantitative changes of the biometals in teeth tissue after its exposure to different media, the migration of Ca^{2+}, Mg^{2+}, Fe^{2+}, Cu^{2+} and Zn^{2+} in teeth–soil and teeth–water media was observed. The content of Ca^{2+} and Mg^{2+} in the mineral tissue increased, but the Cu^{2+} content decreased. The migration of Fe^{2+} and Zn^{2+} depended on the content and type of the soil media and differed for clay soil, limestone enriched soil and urban area soil. The changes that occurred in the mineral matrix of teeth were detected by the SEM–EDS technique. The intensity of the biometal content and the mineral matrix changes are a potentially significant subject matter for forensic examination, because they indicate the kind of medium to which the material was exposed.

Keywords: biometal ions; migration; teeth; soil; water media.

INTRODUCTION

The hard mineral tissue of bones and teeth represents readily available biopsy material that is relatively easy to analyze and could be used in forensics, especially in examination of bones. It is potentially important and convenient in cases of exposure to the influence of different external media.[1] Tooth enamel consists of 96 % hydroxyapatite (HAp).[2] Through the influence of agents in ambient media, the mineral tissue of teeth changes, and the change is manifested, among other things, in an alteration of the elemental composition of the HAp.[3–5]

* Corresponding author. E-mail: nenad.krstic84@yahoo.com
# Serbian Chemical Society member.
doi: 10.2298/JSC140207058N

In the structure of the HAp, the Ca^{2+} are surrounded by the oxygen from the phosphate and they can, under certain conditions, be replaced in the crystal lattice by other M^{2+} (metal ions) with an appropriate radius.

The efficiency of the substitution depends on the strength of the interaction between the cations and the oxygen found in the immediate environment, as well as on the ionic potential.[6,7] According to data found in the literature, during ionic replacement processes, the Ca^{2+} in synthetic HAp were almost completely replaced by Ba^{2+} and Pb^{2+} and somewhat less effectively by Cd^{2+} and Sr^{2+} from diluted solutions of their salts.[8–10] During contact between teeth and environment media, and in natural HAp tissue, similar processes occur (substitution, diffusion, ionic exchange and others), during which the Ca^{2+} are replaced by the cations of other M^{2+}. In addition, sorption of ions from the ambient environment into the HAp of natural teeth is possible. These processes occur in living human bodies during contact between teeth and food, water and oral fluids.[11] Similar processes occur in bones exposed to the influence of the natural environment, and probably in teeth. Unfortunately, not enough data exists on the changes that occur in teeth.[4]

Soil represents natural ground, a multiphase system with a mineral matter content of approximately 40 % and an organic matter content of approximately 6 %.[12] The organic soil content, in which humic acids are found, influences the possibility of adsorption, desorption, absorption, buffer capacity and exchange of constituent ions of soil with materials from the external environment, both of natural and anthropological origin.[13] Forensic examinations of soil samples are based on a qualitative comparison of undisputed and disputed samples through the application of different methods of analysis.[14–16] It was shown that the soil components interact with metal ions; especially with the ions of heavy metals, and that these interactions depend on the soil pH, buffer capacity, humic matter content, ionic radius and charge, and atmospheric conditions.[17,18]

There are multiple possibilities (adsorption, desorption, diffusion, ionic exchange, precipitation and co-precipitation) in the natural environment for ionic exchange in a system of soil-exposed anthropogenic material. This has already been used in practice for the determination of time of death.[2,19] The intensity of ion migration into or out of mineral tissue could be an indicator of tissue exposure time to the environment, as well as the type of environment. According to data found in the literature, the current studies in forensic practices have focused on the examination of the content of hard mineral bone tissue that had been exposed to soil.[20] No detailed studies were found regarding how the mineral content of hard teeth tissue reacts in the natural environment and in different types of soil and water.

Based on the qualitative and quantitative changes that occurred in the mineral tissue of teeth after it had been exposed to different types of soil and to water, the aim of the study was to obtain potentially useful information for forensic

experts. With the aim of examining the changes in the mineral content of hard teeth tissue, changes in the contents of the biometal ions, Ca^{2+}, Mg^{2+}, Fe^{2+}, Cu^{2+} and Zn^{2+}, in teeth were also studied, as well as the migration trend of these metal ions in a teeth–natural environment system. The calcium ion was chosen as the basic constituent of the HAp, Fe and Mg as metals present in soil in high concentrations, and Zn and Cu as biometals the M^{2+} of which are readily mobile. Data regarding changes in the mineral tissue were also obtained by the characterization of the mineral tissue using inductively coupled plasma-optical emission spectroscopy (ICP-OES) and scanning electron microscopy–energy dispersive spectroscopy (SEM–EDS).

EXPERIMENTAL

Model system. The model system for the study of the interaction between soil and anthropogenic material consisted of human teeth exposed to the influence of different natural environment media (soil and water). The soil media from the natural environment consisted of three different types of soil: urban city soil samples from a park (SM1), soil with a predominant clay content (SM2) and soil samples with a mostly limestone content (SM3) from the city of Niš and its surrounding area.[21,22] The aqueous media from the natural environment consisted of: a commercial bottled water "*Aqua viva*" (WM1) and a solution of a "rainwater model system" (WM2). The anthropogenic material exposed to the influence of the aforementioned media consisted of human teeth extracted due to health and orthodontic reasons in the Dental Hospital of the Medical Faculty of the University of Niš.

The teeth were exposed to the aforementioned media in a mass ratio of 100:1 and left for three months at room temperature (22–25 °C). The migration of biometal ions in the studied model systems was examined by measuring the biometal content using the ICP-OES method at the beginning and at the end of the experiment. The changes in the teeth mineral tissue and its structural characterization were examined by SEM–EDS analyses.

Preparation of the media. Approximately 2 kg of soil was sampled from the selected locations, at 30 cm from the surface.[23] The specimen samples were measured in the form of dried soils samples (SM1, SM2 and SM3), and were later moistened with deionized water in glass beakers, while the subjected anthropogenic material was placed into the beakers. The influence of the aqueous media on human teeth was examined in the same mass ratio and under the same conditions.

Preparation of the human material. The extracted teeth were treated with saline solution, washed with deionized water, dried to a constant mass at 70 °C and then measured. One part of the anthropogenic material was separated as the control sample and the rest was divided into five samples that were exposed to each medium for three months. After this period, one part of the anthropogenic material was used for the determination of the contents of the studied biometal and the other part for the study of changes in the mineral tissue through application of techniques that are usually used for the characterization of inorganic material.

Determination of the biometal contents. The biometal contents in the media and in samples of mineral tissue of teeth were determined using a Spectroflame ICP-OES instrument with an argon plasma. The teeth samples, *i.e.*, the control (untreated) sample and the group of samples that had been exposed to the influence of the various media, were solubilized in the same way and under the same conditions. The precisely measured mass of the dried samples was dissolved twice in 6 mol dm^{-3} HNO_3 acid. The obtained dry residue was treated twice

with the same concentration HCl acid and the final dried residue was dissolved in deionized water to a definite volume.[24,25] The biometal content was determined from the solutions. In the same way, and according to the same procedure, the soil samples were treated and prepared for metal content determination.

Mineralogical examination of the mineral material of teeth. The structural characterization of the mineral matrix of teeth of both the control sample and the group of samples exposed to the influence of external environment media was realized by SEM–EDS analyses. The SEM–EDS examination of *in situ* teeth tissue (covered by a vapor of colloidal gold) was performed using a FEI Quanta 200 microscope.

Statistical interpretation of the results. For the statistical interpretation of results, the Student's *t*-test (Microsoft Office Excel) was applied. All of the results of the chosen measurement of the biometal contents are given as the mean value ±*SD*. Statistically important results are shown as $p < 0.01$, $p < 0.05$ and $p < 0.1$.

RESULTS AND DISCUSSION

The results of the determination of the organic matter (OM) content, given as the content of organic carbon, the pH results and the results of biometal determination in the media to which mineral tissue of teeth had been exposed are given in Table I. The results represent the mean value ± *SD* (n = 5, n – the number of probes).

TABLE I. The pH values and contents of organic matter and biometals in the employed media (mg g^{-1}); SM1 – urban city soil, SM2 – clay enriched soil and SM3 – limestone enriched soil; WM1 – "*Aqua viva*" commercial bottled water and WM2 – rain water model; n.d. – not detected

Parameter	SM1	SM2	SM3	WM1	WM2
pH	7.23±0.74	4.55±0.39	7.06±0.82	7.22±0.68	6.13±0.58
Organic C	12.71±1.50	59.58±6.79	21.45±2.47	–	–
Ca^{2+}	48.23±5.16	0.21±0.04	88.44±8.30	120.00±11.56	1.20±0.15
Mg^{2+}	58.00±6.38	0.54±0.09	8.84±0.90	45.20±5.12	0.43±0.09
Cu^{2+}	$(0.03\pm5.8)\times10^{-3}$	$0.04\pm6.4\times10^{-3}$	0.15±0.03	<0.1	n.d.
Fe^{2+}	$(0.02\pm3.9)\times10^{-3}$	0.26±0.05	24.98±2.95	<0.05	n.d.
Zn^{2+}	$(0.62\pm1.1)\times10^{-3}$	$0.03\pm5.4\times10^{-3}$	0.38±0.07	<0.1	n.d.

These results showed that the soil enriched with clay was the most acidic (pH 4.55) and contained the highest content of organic matter. The limestone--enriched soil used in the present study contained the highest level of calcium and about one hundred times more iron than the other types of soil. The urban soil samples contained the highest levels of magnesium and zinc in comparison to the other soil types. In the analyzed soil samples, the level of copper was the mean value of the metal in the soil samples.[12]

The results of the interaction and the change in the biometal ion content in the system "medium–anthropogenic material" during a three-month period are presented in the Table II. The results represent the mean value ±*SD* (n = 5).

TABLE II. The content of biometals in the teeth samples that had been exposed to the influence of different media; SM1 – urban city soil, SM2 – clay enriched soil and SM3 – limestone enriched soil; WM1 – "*Aqua viva*" commercial bottled water and WM2 – rain water model; *: $p < 0.01$, **: $p < 0.05$, ***: $p < 0.1$

Specimen	Ca^{2+}	Mg^{2+}	Cu^{2+}	Fe^{2+}	Zn^{2+}
	Concentration, mg g^{-1}		Concentration, μg g^{-1}		
Control	293.94±34.47	5.50±1.20	37.93±5.96	36.52±6.05	0.53±0.08
SM1	477.52±19.17*	8.63±1.56*	14.47±3.41*	105.24±10.34*	0.22±0.02*
SM2	327.5±11.55***	8.74±1.09*	31.56±4.41***	21.52±2.55*	0.55±0.02**
SM3	372.00±15.37*	6.58±0.37***	22.85±2.96*	117.80±17.32*	0.368±0.02**
WM1	332.00±15.01***	8.12±0.68*	12.04±2.38*	34.84±3.99	0.36±0.02**
WM2	401.78±11.64*	6.00±0.46***	11.98±2.28*	33.26±3.09	–

The percentage of biometals ion migration *IN* or *OUT* of the mineral tissue of teeth that had been exposed to different soil and aqueous medium was calculated by Eqs. (1) and (2), respectively:

$$IN = \frac{(X - Y)}{Y} \times 100 \quad (1)$$

$$OUT = \frac{(Y - Z)}{Y} \times 100 \quad (2)$$

where X is the increase in the value of the metal content compared to the control, Y is the metal content of untreated teeth tissue and Z is decrease in the value of metal content compared to control. The results of these calculations are shown in Fig. 1.

According to the results, it could be concluded that the calcium and magnesium contents increased during teeth exposure to the influence of all the soils and aqueous media from *ca*. 9 to 60 % (Fig. 1). Thus, Ca^{2+} and Mg^{2+} have the same, statistically important, tendency of migration from the soil ($p < 0.01$) and the aqueous media ($p < 0.1$) into teeth. The reasons for this are probably because the media in these experiments contained high concentrations of these two metals and a large relative quantity of the media was used (mass ratio of the medium:teeth = 100:1). The highest quantity of Ca^{2+} (477.52 mg g^{-1}) was adsorbed from the urban soil samples, where probably the limestone-enriched soil contained calcium in the form of insoluble salts. A number of factors affect the migration of calcium and magnesium ions from the soil: the acidity of the medium, the concentration of the other ions present, the organic material, the mineral matrix of the soil samples, temperature, etc.

Copper is a bioelement present in the body in small quantities of 1.0–2.0 mg dm^{-3} of serum, but after a number of years and in contact with food and oral fluids, it begins to accumulate, among other tissues, in the mineral tissue of the teeth (37.93 μg g^{-1}).[25] When such a mineral biomaterial is exposed to the exter-

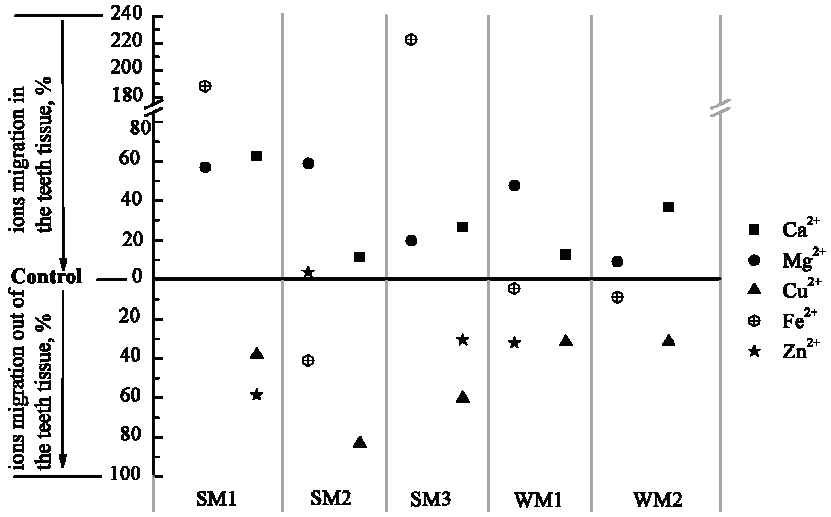


Fig. 1. Percentage of migration of biometal ions: Ca^{2+}, Mg^{2+}, Fe^{2+}, Cu^{2+} and Zn^{2+}, in the systems mineral tissue of teeth–soil and teeth–water media; SM1 – urban city soil, SM2 – clay enriched soil and SM3 – limestone enriched soil; WM1 – "*Aqua viva*" commercial bottled water and WM2 – rain water model.

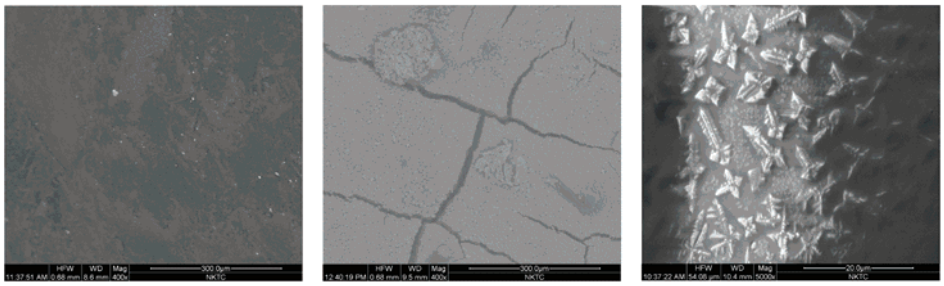
nal environment, statistically significant leaching occurs and the level of Cu^{2+} decreases ($p < 0.01$). Since Cu^{2+} is of small volume, it can easily be assimilated in the structure of HAp, which further contributes to its migration.[26] The results of the measurement of this metal content in the samples of teeth mineral tissue indicated that the copper content decreased, or in other words, it migrated from the teeth to the outer environment regardless to the medium (from *ca*. 30 to 80 %), as shown in Fig. 1. This migration tendency of copper ions occurs with the aim of establishing equilibrium, because of potential interactions and complex reactions of copper ions with the soil components and the possible exchangeable adsorption of this metal.[25]

Iron from a soil with predominantly limestone content, which was analyzed in this study, is relatively available and is adsorbed by biological material in greater amounts. Thus, the content of Fe in the mineral tissue increased in a statistically significant way ($p < 0.01$), up to three times (from 36.52 to 117.80 μg g^{-1}). The content of the clay mineral kaolinite and smectite in addition to feldspar and other minerals in the soil is convenient for the binding of higher charged ions because of the special structure of the aluminum silicates. Thus, it led to a decrease in the iron content in the mineral matrix of the analyzed biomaterial, 41 % for medium SM2, less than 10 % of the aqueous media (Fig. 1), and probably to the formation of a more stable aluminum silicate matrix.[21,22] This type of soil was the one with a higher content of organic matter in comparison to the other types of soil and hence, it potentially has a greater ability for the interaction of

iron ions with O-donor atoms of the organic matter of the soil and for the formation of complexes and sparingly soluble iron compounds.[27] Since the difference in the iron content in the mineral tissue and the aqueous media is the greatest, during the three-month period of exposure to the influence of these media, the content of the iron ions in the mineral tissue decreased because of the diffusion of the metal ions into the surrounding medium. These different migration tendencies of iron ions in the studied model systems, natural medium–teeth, are potentially important for forensic examination and the application of teeth as a forensic material. Research showed that the divalent cation exchange in synthetic HAp depended on the M^{2+}–O interaction (O nearest atoms from the PO_4^{3-} group in HAp) and that the processes of Ca^{2+} replacement by larger cations (Pb^{2+} and Cd^{2+}) in a weakly basic environment is more convenient in terms of energy, whereas the exchange of small ions occurred with a lower tendency in a weakly acidic environment.[7–10]

Zinc is a biometal found in small quantities in the human body, but due to ingestion through food and oral fluids, it starts to accumulate in the mineral tissues. The mean value of this metal in the analyzed biomaterial was 0.53 mg g^{-1}.[25] The study presented in this paper shows that the zinc ions migrate *ca*. 4 % into the mineral content of teeth tissue from the clay mineral enriched soils (kaolinite and smectite near quartz, brookite and feldspar)[21,22] with a higher content of organic matter and lower pH values ($p < 0.05$). In the other studied model systems, the leaching of zinc ions from the mineral content of teeth tissue into the outer medium occurred ($p < 0.01$), as shown in Fig. 1.

The SEM micrographs of the untreated teeth sample and the samples of teeth that had been exposed to the influence of the soil medium SM1 and the aqueous medium WM2 are shown in Fig. 2.



a) b) c)

Fig. 2. SEM micrographs; a) untreated teeth, b) teeth exposed to the urban city soil medium SM1 and c) to the rain water medium WM2.

Based on a comparison of the results of the SEM–EDS analyses of the untreated and the treated samples that had been exposed to different types of soil

media, changes in the content and the surface appearance of the mineral content of the hard dental tissue were noted, while no significant changes were noticed in the samples exposed to water (Fig. 2 and Table III). The EDS spectra indicate local changes in the metals in the studied mineral tissue, which occurred due to adsorption. Al, Mg, Si and traces of Fe could be noticed in the teeth tissue that had been exposed to the urban city soil samples; the adsorption of Mg and Na occurred in the clay enriched medium and the increase in Ca, Si, Mg and Na. Significant changes in the Ca^{2+}/P ratio were noticed for teeth samples that had been exposed to the limestone enriched soil (Table III). The ratio of the Ca^{2+}/P content was altered probably as the result of the adsorption of Ca^{2+} from the surrounding environment or adsorption of an excessive amount of phosphates on the crystal surface or substitution of Ca^{2+} by the ions from the surrounding environment.[28–32] The small diameters of Na^{+}, Mg^{2+} and Al^{3+} enable them to migrate easily into internal dental tissue.[25]

Table III. Dependence of the Ca^{2+}/P ratio in teeth tissue on the investigated soil and water media; SM1 – urban city soil, SM2 – clay enriched soil and SM3 – limestone enriched soil; WM1 – "*aqua viva*" commercial bottled water and WM2 – rain water model

Specimen	Ca^{2+} (wt. %)	P (wt. %)	Ca^{2+}/P, [%]
Control	15.98	8.27	1.93
SM1	26.75	11.56	2.29 (19.68)
SM2	22.29	10.53	2.12 (9.85)
SM3	44.78	9.35	4.79 (147.69)
WM1	20.74	13.13	1.59 (17.61)
WM2	24.30	13.37	1.82 (5.70)

Cracks on the teeth surface were noticed, which originated from the interaction of the teeth with all the surrounding soil environments (Fig. 2).

CONCLUSIONS

This study of the interaction between environmental media and anthropogenic material (teeth) on the model systems of soil and water of different composition showed that after a three-month exposure period, statistically significant changes in the biometals contents in the mineral content of dental tissue occurred due to different physicochemical processes and interactions of the mineral tissue with the surrounding environment. The intensity and direction of the changes in the biometal ions (Ca^{2+}, Mg^{2+}, Cu^{2+}, Fe^{2+} and Zn^{2+}) content could potentially be important in forensic examinations because they could allow focus to be directed on the type of the environmental medium in which the dental material was stored. The SEM–EDS analysis showed differences between the samples exposed to the soil media, on the one hand, and the aqueous medium, on the other. Although the information obtained by the application of the ICP-OES is more reliable, its mutual application with the SEM–EDS technique used in this study

could help end conclusion to be reached and a combination of these methods could allow for a potential differentiation of the environmental medium in which the mineral tissue had been stored.

Acknowledgements. This research was partly realized with the financial help of the Ministry of Education, Science and Technological Development of the Republic of Serbia within the projects III45017 and TR34008. The authors would also like to thank Marta Dimitrijević, MA, for proofreading the text of this paper.

ИЗВОД

МИГРАЦИЈА ПОЈЕДИНИХ ЈОНА БИОМЕТАЛА У СИСТЕМУ МИНЕРАЛНО ТКИВО ЗУБА–ЗЕМЉИШТЕ И МИНЕРАЛНО ТКИВО ЗУБА –ВОДЕНА СРЕДИНА

РУЖИЦА С. НИКОЛИЋ[1], НАТАША В. РАДОСАВЉЕВИЋ-СТЕВАНОВИЋ[2], ТАТЈАНА Д. АНЂЕЛКОВИЋ[1], МАЈА Н. СТАНКОВИЋ[1] и НЕНАД С. КРСТИЋ[1]

[1]*Департман за хемију, Природно-математички факултет, Универзитет у Нишу, Вишеградска 33, 18000 Ниш и* [2]*Национални криминалистичко-технички центар, Министарство унутрашњих послова Републике Србије, Кнеза Милоша 103, 11000 Београд*

У раду су описане промене у минералном ткиву зуба које је било изложено утицају агенаса природних средина. Такође, минерално ткиво може послужити као потенцијално важан форензички материјал који подлеже постепеним променама под утицајем спољашњих средина. Садржај биометала је испитиван применом ICP-OES методе. На основу квантитативних промена садржаја биометала у ткиву зуба након његовог излагања различитим срединама, уочена је миграција јона биометала, Ca^{2+}, Mg^{2+}, Fe^{2+}, Cu^{2+} и Zn^{2+}, у системима зуб–земљиште и зуб–водена средина. Садржај Ca^{2+} и Mg^{2+} у минералном ткиву је повећан, док је садржај Cu^{2+} смањен. Миграција Fe^{2+} и Zn^{2+} зависи од њиховог садржаја и типа земљишта, и различита је за глинено, кречњачко и градско земљиште. Промене у минералној матрици зуба су детектоване SEM–EDS техником. Интензитет промене садржаја биометала и промене у минералној матрици су потенцијално значајни за форензичка испитивања, јер могу указати на тип средине у којој је испитивани материјал био одложен.

(Примљено 7. фебруара, ревидирано 30. маја, прихваћено 30. маја 2014)

REFERENCES

1. B. Nowak, *Analyst* **120** (1995) 747
2. M. Yoshino, T. Kimijuma, S. Miyasaka, H. Sato, S. Seta, *Forensic Sci. Int.* **49** (1991) 143
3. B. M. Kaličanin, R. S. Nikolić, *Connect. Tissue Res.* **51** (2010) 31
4. W. Castro, J. Hoogewerff, C. Latkoczy, J. R. Almirall, *Forensic Sci. Int.* **195** (2010) 17
5. A. Bigi, G. Cojjazi, S. Panzavolta, A. Ripamonti, N. Roveri, M. Romanello, K. N. Suarez, L. Moro, *J. Inorg. Biochem.* **68** (1997) 45
6. B. Wopenkia, J. D. Pasteris, *Mater. Sci. Eng., C* **25** (2005) 131
7. K. Matsunaga, H. Inamori, H. Murata, *Phys. Rev., B* **78** (2008) 094101
8. S. Sugiyama, H. Matsumoto, H. Hayashi, J. B. Moffat, *Colloids Surfaces, A* **169** (2000) 17
9. S. Sugiyama, T. Ichii, H. Matsumoto, H. Hayashi, *Adv. Environ. Res.* **6** (2002) 285
10. A. Yasukawa, T. Yokoyama, K. Kandory, T. Ishikawa, *Colloids Surfaces, A* **317** (2008) 123
11. B. Kaličanin, R. Nikolić, in *Wide Spectra of Quality Control*, I. Akyar, Ed., InTech, Rijeka, 2011, Ch. 12, p. 211

12. L. D. Sparks, *Environmental Soil Chemistry*, 2nd ed., Academic Press, Elsevier, London, 2003
13. M. Jakovljević, M. Pantović, *Chemistry of Soils and Waters*, Naučna knjiga, Belgrade, 1991 (in Serbian)
14. N. Petraco, T. A. Kubic, *J. Forensic Sci*. **45** (2000) 872
15. N. Petraco, T. A. Cubic, N. D. K. Petraco, *Forensic Sci. Int.* **178** (2008) 23
16. W. C. McCrone, *Microscope* **30** (1982) 17
17. A. Dube, R. Zbytniewski, T. Kowalkowski, E. Curkovska, B. Buszewski, *Pol. J. Environ. Stud.* **10** (2001) 1
18. T. D. Anđelković, J. M. Perović, M. M. Purenović, S. D. Blagojević, R. S. Nikolić, D. Anđelković, A. Lj. Bojić, *Anal. Sci.* **22** (2006) 1553
19. A. A. Vass, W. M. Bass, J. Wolt, J. Ammons, *J. Forensic Sci.* **37** (1992) 1236
20. T. Shinomiya, K. Shinomiya, C. Orimoto, T. Minami, Y. Tohno, M. Yamada, *Forensic Sci. Int.* **98** (1998) 1098
21. D. A. Spears, *Int. J. Coal Geol.* **94** (2012) 22
22. W. F. Outerbridge, *Geol. Soc. Am. Bull.* **108** (1996) 120
23. M. Pansu, J. Gautheyrou, *Handbook of Soil Analysis, Mineralogical, Organic and Inorganic Methods*, Springer, Berlin, 2006
24. S. Cazalbou, D. Eichert, C. Crouet, C. Combes, C. Rey, *C. R. Palevol* **3** (2004) 563
25. R. Nikolić, B. Kaličanin, N. Krstić, *Connect. Tissue Res.* **53** (2012) 229
26. A. F. Wells, *Nature* **157** (1946) 192
27. A. Kabata-Pendias, A. B. Mukherjee, *Trace Elements from Soil to Human*, Springer, Berlin, 2007
28. J. Andjić, *Oral Physiology and Biochemistry Fundamentals*, Naučna knjiga, Belgrade, 1990 (in Serbian)
29. C. Drouet, M. T. Carayon, C. Combes, C. Rey, *Mat. Sci. Eng., C* **28** (2008) 1544
30. P. D. Frazier, *Arch. Oral Biol.* **12** (1967) 25
31. W. H. Arnold, P. Gaengler, *Ann. Anat.* **189** (2007) 183
32. S. Kannan, F. Goetz-Neunhoeffer, J. Neubauer, J. M. F. Ferreira, *J. Am. Ceram. Soc.* **91** (2008) 1.